The
Essential Oils

BY

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VOLUME FOUR

INDIVIDUAL ESSENTIAL OILS OF THE PLANT FAMILIES *GRAMINEAE, LAURACEAE, BURSERACEAE, MYRTACEAE, UMBELLIFERAE* AND *GERANIACEAE*

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Dedicated
to Mr. Frederick H. Leonhardt,
President of
Fritzsche Brothers, Inc.,
whose vision and generosity made this
work possible

PREFACE

Following the principle established in Vol. III of this series, the present volume consists of monographs on individual essential oils, arranged according to the botanical family of the plants from which they are derived. The important oils from six families are included. The author has again purposely avoided adherence to any strict taxonomic system in the sequence of these plant families, believing that the order followed here allows for greater flexibility in the practical use of the work by the essential oil producer, chemist and dealer. However, at the end of the final volume of the series there will be a table or key showing the classification of the essential oil plants according to a modern botanical system.

ERNEST GUENTHER

New York, N. Y.
September, 1950

NOTE

All temperatures given in this work are expressed in degrees Centigrade unless otherwise specified in the text.

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The collection of much of the material presented in this volume has been rendered difficult by the same problems of which the author wrote in the Preface to the preceding volume of this series. Many parts of the manuscript have required several rewritings, to keep pace with changing economic and political conditions throughout the world. In this tedious—but essential—task the author has had the generous assistance of a great number of planters, producers, government officials and researchers. To all of these collaborators and friends, the author wishes to express his deepest gratitude, regretting only that it is not feasible here to thank all of them individually. However, to the following the author feels a special indebtedness:

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The Staff of the libraries of the Chemists' Club and of the Bronx Botanical Garden, both in New York, have been unfailingly courteous and helpful with this, as well as with all preceding volumes in this series.

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CHAPTER I

ESSENTIAL OILS OF THE PLANT FAMILY *GRAMINEAE*

OIL OF PALMAROSA AND OIL OF GINGERGRASS

Introduction, Botany and Occurrence.—The grass *Cymbopogon martini* Stapf (syn. *Andropogon martini* Roxb.), in India commonly called "Rusha," "Rosha," or "Rusa" grass, occurs in two varieties: viz., *motia* and *sofia*. On distillation, the leaves and overground parts of the var. *motia* yield the oil of palmarosa which is of better quality and commercially much more important than the oil of gingergrass derived from the var. *sofia*.

Comparing single specimens of dried plants, Stapf[1] was unable to note any morphological difference between the two varieties. According to the observations of Burkill,[2] however, the two varieties do exhibit considerable differences: (1) as regards their field habitat (choice of altitude, soil, locality, growth—see below), and (2) chiefly in regard to the essential oil, which differs substantially in the two plants, the oil derived from the var. *motia* exhibiting a much finer odor than the oil from the var. *sofia*. Burkill also found grasses which were probably hybrids between *motia* and *sofia*.

Both varieties grow wild and abundantly in many parts of India (excepting deserts and the plains of the Punjab) from the Ganges River to the frontier of Afghanistan, and from the subtropical slopes of the Himalaya Mountains south to the 12th degree of latitude. From the commercial point of view the most important regions in which "Rosha" grass is processed for the oil are the Central Provinces, Berar, Khandesh, and Hyderabad (Deccan).

When collecting the grass, the native oil producers usually experience no difficulty in distinguishing between the two varieties, as they seldom grow side by side, but in separate stands at different altitudes and in different environments.

Motia seems to prefer a dry, well-drained soil of basaltic composition, relatively bare and sunny mountain slopes with southern exposure, open forest, or sunny clearings on sparsely wooded land. It thrives in regions with an annual rainfall ranging from 32 to 35 in., but does not withstand stagnant water. *Sofia,* on the other hand, grows best at lower altitudes in moist and poorly drained soil, in valleys, or in dense forests kept humid by rain, dew, and fog. *Motia* usually occurs in scattered patches consisting of stocks 1 or 2 ft. apart, whereas *sofia* grows abundantly and densely, and

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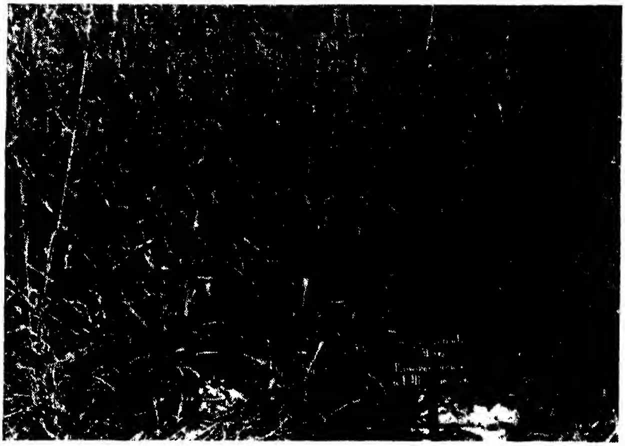
[1] *Ber. Schimmel & Co.,* April (1907), 50.

[2] "First Notes on *Cymbopogon Martini* Stapf," *J. Proc. Asiatic Soc. Bengal* **5,** No. 3 (1909). Cf. *Ber. Schimmel & Co.,* October (1909), 85.



Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 1. Production of palmarosa oil in India. View of palmarosa grass.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 2. Production of gingergrass oil in India. View of gingergrass.

frequently covers large areas. Unlike *motia,* the var. *sofia* is characterized by a large number of radical leaves which form a different angle with the sheath than do the leaves of the var. *motia.*

OIL OF PALMAROSA

(East Indian Geranium Oil)

Essence de Palmarosa *Aceite Esencial Palmarosa (Geranio de Turquia)*
Palmarosaöl *Oleum Palmarosae (Geranii Indicum)*

OIL OF PALMAROSA INDIA

The old term "Indian" or "Turkish" geranium oil, which formerly was occasionally applied to palmarosa oil, dates back to the time when the oil was shipped from Bombay to ports of the Red Sea and transported, partly by land, to Constantinople and Bulgaria, where the oil was often used for the adulteration of rose oil.

In India, where the bulk of commercial palmarosa oil originates, the oil is distilled from *Cymbopogon martini* Stapf var. *motia* (syn. *Andropogon martini* Roxb. var. *motia*) which grass grows wild in several parts of the subcontinent. (Efforts to raise the grass on plantations have been made in the Seychelles Islands and in Java—cf. the monographs on "Oil of Palmarosa Java" and "Oil of Palmarosa Seychelles.")

As was mentioned above, in most producing regions of India, the palmarosa grass and the closely related gingergrass do not grow side by side. However, in a few sections the two varieties occur in neighboring places which, obviously, tempts the native cutters and oil producers to collect the grass from both varieties, and to distill these together. Oils distilled from mixed *motia* and *sofia* grass are, of course, of subnormal quality, but fortunately in most regions the cutters and distillers exercise care in the selection of the distillation material and produce palmarosa oil exclusively.

Producing Regions.—The principal producing regions of palmarosa oil in India, listed according to quality and quantity of the oil, are:

1. Berar and Central Provinces; in the districts of Akola, Elichpur, Amraoti, and Nagpur. Much of the oil comes from the slopes and highlands of the Melghat. Principal marketing center is the town of Elichpur.

The oil produced in the province of Berar has usually been of best quality, possessing a sweet rosy note and a high total alcohol (geraniol) content.

2. Khandesh districts (northeast of Bombay), particularly in the vicinity of Pimpalner, Akrani, and Nandurbar. This type of oil has a somewhat lower total alcohol (geraniol) content, but is still true palmarosa oil.
3. Hyderabad (Deccan), particularly in Zaheerabad and Mahbubnagar. Here the oil is distilled from both the var. *motia* and var. *sofia*, the latter prevailing. The oil originating from Hyderabad is therefore mostly gingergrass oil.
4. Madras, Punjab and Bengal produce almost exclusively gingergrass oil.

The producing areas are partly wilderness and remote from modern civilization. Production of the oil is, therefore, carried out by natives under utterly primitive conditions.

Collection of the Grass and Economic Setup.—As was pointed out above, in India palmarosa is not planted on an organized basis, as it grows wild over large tracts of land. On privately owned land there are no restrictions against cutting and distillation of the grass. However, much of the land is government property, in which case the licenses for cutting and distilling are auctioned off to the highest bidding parties, which also must furnish guarantee that they will actually cut the grass. Palmarosa and gingergrass have a tendency to spread and to invade arable land and pastures, making them unfit for cattle, which cannot feed on these highly aromatic plants. In view of these circumstances the government does not readily grant cutting licenses to outsiders—merchants and oil dealers in Bombay, for example—because such parties cannot always offer sufficient guarantee that the plants will actually be cut.

To overcome government objections the merchants or exporters usually operate through middlemen or village agents known both to the government and to the native distillers. Provided with funds the middlemen in the villages of the producing regions then procure the necessary distilling equipment and hire crews of cutters. Actual distillation is carried out by members of certain native tribes or castes who have practiced this craft for generations. The distillers work for the agent on a sharecropping basis, retaining about one-quarter of the oil produced, while the agent receives three-quarters. The distillers are free to sell their share to whomever they please, but they usually prefer selling to the agent, the price being determined by prevailing market quotations in Bombay. Much oriental shrewdness is displayed in this sort of trading.

The distilled oil then belongs to the agent. As soon as the quantity is sufficiently large to warrant transport, he ships the lot to the exporter in Bombay who in some cases had advanced the necessary funds. While stored in Bombay, the oil often remains the property of the agent in the village; the Bombay exporters or money lenders then purchase the lot only when they receive definite export orders from abroad.

Distillation and Yield of Oil.—Distillation of the grass is carried out between October and December or January, depending upon the rainfall and the development of the plants. The leaves and the upper third of the stems are cut and tied into bundles of ½ lb. each. Systematic experiments by Lall[1] have shown that the leaves of palmarosa grass (*motia*) yield the maximum amount of oil (1.39 per cent[2]) in October, when the plants begin to bloom. After the flowering period the oil content of the plant diminishes steadily, declining to the minimum (0.77 per cent[2]) in the beginning of March. The highest yield of oil is obtained from fully dried grass one week after it has been cut. The top of the grass seems to contain most of the oil, but it is not advisable to cut only the tops for distillation, because the grass will then exhaust itself by too rapid regrowth. In other words, the plant will grow up again within a month but will contain much less essential oil. In actual practice, the natives cut the grass quite close to the ground, in order to gather as much plant material as possible (by weight). Lall's work[3] further indicates that the (lower) stalks of the plant contain only traces of oil; stalks and flowers yield an oil of subnormal quality.

According to Narian and Das Gupta[4] the yield of oil from fresh or carefully dried plant material may amount to 1 per cent; if dried carelessly the yield may be as low as 0.15 per cent. The yield ranges from 1 to 1.25 per cent, if the distillation is carried out with absolutely fresh grass immediately after cutting. The yields from each portion of the plant, when distilled separately, are as follows:

Stalks	0.04 per cent of oil
Leaves	1.32 per cent of oil
Flower Heads	1.71 per cent of oil

Rakshit and Dutt[5] reported these yields of oil:

Whole Plants (before Flowering Tops Appear)	0.13 to 0.21%
Flowering Tops (Separately)	0.70 to 0.98%
Lower Portions	0.39 to 0.61%

Rakshit and Dutt,[6] however, did not indicate the moisture content of the plant material at the time it was distilled; therefore it is not clear whether their yields are based on fresh grass, air-dried grass, or moisture-free grass.

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[1] *Indian J. Agr. Science* **5** (1935), 415. *Bull. Imp. Inst.* **33** (1935), 472.

[2] In the opinion of the author, these figures are extremely high.

[3] *Indian J. Agr. Science* **5** (1935), 415. *Bull. Imp. Inst.* **33** (1935), 472.

[4] *Indian Soap J.* **14** (1948), 260.

[5] *Ibid.* **13**, August (1947), 27.

[6] *Ibid.*

The most reliable figures on yields have been obtained by Subba Rao, George, B. L. Rao, and Desikachar [7] who raised *motia* and *sofia* grass experimentally from seed, and reported:

	Motia (*Manured*)	*Sofia* (*Manured*)
Total Number of Plants	682	1,070
Average Distance Between Plants	6 in.	6 in.
Area of Beds (Sq. Ft.)	424	730
Average Height of Plant	6 to 7 ft.	6 to 6.5 ft.
Proportions of:		
Flowering Tops	17.0%	20.2%
Leaves	23.6%	28.1%
Stems	59.4%	51.7%
Average Moisture Content	62.9%	62.5%
Total Weight of Fresh Grass (in Lb.)	288	1,082
Yield of Grass per Acre (in Lb.)	29,588	64,624
Yield of Oil (from Fresh Grass):		
Whole Plant	0.16%	0.176%
Flowering Tops	0.52%	0.55%
Leaves	0.20%	0.18%
Stalks	0.012%	0.01%
Yield of Oil per Acre (in Lb.)	47.34	113.7

In their experiments Subba Rao and his collaborators cut the grass a week or ten days after flowering; the fresh grass contained 62 to 63 per cent of moisture. Distillation in an aluminum kettle (heated with closed steam coils) was completed in 3 to 4 hr. The best yield of oil from the entire plant is generally obtained one week after flowering. The yield reported by Subba Rao et al. is much higher than that obtained in the primitive stills used by the native producers in the interior of India.

Their method of distillation is perhaps the most primitive employed in essential oil production anywhere. Three or four stills are usually set up along the bank of a river or pond, and imbedded into a rectangular stone hearth, with an open fire underneath. Sometimes a shed of palm leaves protects the distillers from the sun. The stills are either round and made of copper, or cylindrical and constructed of iron. Their capacity is up to 150 gal., or even more. Several hundred bundles of grass are charged into a still and stamped in, to fill the still with as much grass as possible. The still contains some water from previous distillations, which, due to the presence of tannic acid, has become brown. Fresh water is added until it almost covers the plant material. The still is then closed with a wooden plate, and the joints are sealed with mud paste, which hardens with heat. A heavy stone holds the cover in place. An angular (60°) pipe made of bamboo tubes is attached to the still head through a 2 in. hole in the cover.

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[7] *Ibid.* **14**, December (1948), 159.

This pipe is tied to the still head with palm-leaf rope or some other simple material. The long arm of the bamboo pipe, wrapped with cord, reaches into a pot or vessel serving as condenser (and simultaneously as Florentine flask). This receiver, immersed up to its neck in water, is supported by a wooden frame beneath. The top of the receiving vessel, into which the bamboo pipe reaches, is covered with burlap. Wood cut in the nearby forests serves as fuel for the open fire.]

The still content is brought to a boil, and essential oil vapors and distillation water condense in the partly immersed receiving vessel. Distillation lasts from 4 to 5 hr., including the time required (about 1½ hr.) to heat the water in the still to the boiling point. Distillation completed, the oil collected in the receiver is usually skimmed off the distillation water. Frequently, however, oil and water are not separated on the spot; the whole mixture is simply poured into galvanized iron containers of 2 to 4 gal. capacity. These vessels, containing water and oil, are then carried overland to the nearest village, where an expert, or an agent for a Bombay exporter, separates the oil from the water by simple decantation. The oil is finally filtered through cloth into containers or drums. These drums, usually holding 45 gal., serve for storage of the oil until the end of the harvest, or until the filled drums can be shipped to Bombay.

If oil and water are not immediately separated near the stills, the oil stays in contact with water for several days, which obviously does not improve its quality. In general, the oil remains in iron drums for weeks or months, exposed at times to the heat of India's climate. Such exposure, together with the presence of a little water in the oil, is not conducive to good quality.

The yield of oil could undoubtedly be raised substantially if distillation were carried out in more efficient stills. In fact, Pearson[8] proved, by experiments carried out in 1915, that distillation of palmarosa grass in direct steam stills increased the yield of oil 20 to 100 per cent. (According to Trotter,[9] the crude old "country" stills in a few places have been replaced with regular steam stills in which distillation is carried out with steam generated in a separate boiler.)

In general, the quality of the oil suffers from the crude methods of production and from the direct contact of plants with the walls of the vessels heated by open fire, as well as from the inefficent method of condensation. The relatively low ester content of the Indian palmarosa oils, as compared with that of the Java type, is probably the result of these conditions. Since the plant material is immersed in boiling water during the distillation the greater part of the esters will be hydrolyzed (see Vol. I of this work, pp. 112, 120, 142, and 145).

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[8] *Indian Forest Records* **5**, No. 7 (1916). *Indische Mercuur* **39** (1916), 787.

[9] "Manual of Indian Forest Utilization," published by Humphrey Milford, Oxford University Press, London. Cf. *Perfumery Essential Oil Record* **33** (1942), 342.

Shipping of the Oil.—Exporters in Bombay leave the oil in the drums until they receive shipping orders from abroad. The lot is then filtered through paper, or (more often) through cloth, and filled into drums or special containers for export. Years ago these containers consisted of copper, heavily tinned on both sides, and protected on the outside by a net of heavy cord. They were made in Bombay and were quite expensive. More recently the oil has been shipped in ordinary galvanized iron drums.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[10] the properties of Indian palmarosa oil vary within the following limits:

Specific Gravity at 15°	0.887 to 0.900
Optical Rotation	+6° 0′ to −3° 0′ (usually +1° 0′ to −2° 0′)
Refractive Index at 20°	1.472 to 1.477
Acid Number	0.5 to 3.0
Ester Number	12 to 48
Ester Number after Acetylation	226 to 274
Total Alcohol Content, Calculated as Geraniol	74.8 to 94.8%
Solubility	Soluble in 1.5 to 3 and more vol. of 70% alcohol, in very rare cases with opalescence to turbidity. Oils of high geraniol content are soluble in 3 to 5 vol. of 60% alcohol and more

Shipments of Indian palmarosa oil received and examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.887 to 0.895
Optical Rotation	−1° 34′ to +2° 45′
Refractive Index at 20°	1.4730 to 1.4760
Acid Number	0.7 to 1.1
Ester Content, Calculated as Geranyl Acetate	3.3 to 12.6%
Total Alcohol Content, Calculated as Geraniol	84 to 94%
Solubility	Soluble in 3 to 4 vol. and more of 60% alcohol

Narian and Das Gupta[11] reported the following properties of pure palmarosa oil (var. *motia*) from India:

Specific Gravity	0.886 to 0.889
Optical Rotation	−3° 0′ to +5° 0′
Refractive Index	1.4720 to 1.4780
Acid Number	Up to 3
Ester Number	12 to 50
Total Geraniol Content	78 to 94%
Solubility in 70% Alcohol	Soluble in 1 to 3 vol.

[10] "Die Ätherischen Öle," 3d Ed., Vol. II, 294.

[11] *Indian Soap J.* **14** (1948), 260.

According to the same authors,[12] the most characteristic factors in the evaluation of a palmarosa oil (var. *motia*) are its sweet rose-like odor, and solubility in 60 per cent alcohol. If an oil is soluble in 2.2 to 4.2 volumes of 60 per cent alcohol, it is likely that it contains a high percentage of free geraniol.

The characteristic feature of palmarosa oil (var. *motia*) from Hyderabad is that it contains a much higher percentage of esters (11 to almost 15 per cent, calculated as geranyl acetate) than the oils from the Central Provinces (4.33 to 7.14 per cent of esters). Furthermore, the oils from Hyderabad are occasionally insoluble in up to 10 volumes of 60 per cent alcohol.

The Hyderabad oils also differ in themselves to a certain extent, the quality depending upon their origin. A sample of palmarosa oil (var. *motia*)[13] from Hyderabad showed a low geraniol content and was insoluble in 70 per cent alcohol up to 12 volumes. There was no adulteration found in the sample, but the oil contained a relatively high percentage of terpenes. The grass used for distillation of this oil was said to be of inferior quality (probably var. *sofia*—the author).

On the basis of their investigation, Narian and Das Gupta[14] arrived at the conclusion that palmarosa oils from Amraoti (C.P.) and Hyderabad have these properties:

	Amraoti	*Hyderabad*
Specific Gravity	0.887 to 0.892	0.891 to 0.900
Refractive Index at 20°	1.4685 to 1.4729	1.4723 to 1.4763
Acid Number	Up to 1.6	Up to 1.8
Total Free Alcohol Content, Calculated as Geraniol	80%	70%
Solubility in 70% Alcohol	Soluble in 1 to 3 vol.	Soluble in 1 to 3 vol.
Solubility in 60% Alcohol	Soluble in 1 to 4 vol.	Soluble in 1 to 4.5 vol.

Adulteration.—The most common adulterant of palmarosa oil is the inferior gingergrass oil, which may be recognized by an abnormally low total geraniol content in the suspected oil. The total geraniol content can be assayed by the usual method of acetylation, and saponification of the acetylized oil (see Vol. I of this work, p. 271). Oils containing less than 75 per cent of total geraniol should be rejected, the highest qualities of palmarosa oil assaying from 85 to 90 per cent or even more.

Other adulterants used by the native distillers include coconut oil, which can be isolated by freezing (cf. Vol. I of this work, p. 344), and turpentine

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[12] *Ibid.*, 263.

[13] In the author's opinion the oils from Hyderabad are probably not distilled exclusively from the var. *motia*, but from var. *sofia* (gingergrass) or from hybrids of the two varieties. Their properties approach those of gingergrass oil.

[14] *Indian Soap J.* **14** (1948), 263.

oil, the presence of which is indicated by a lowered solubility in 70 per cent alcohol (cf. Vol. I of this work, p. 337). Kerosene and mineral oils are also employed. These can be identified by fractionation and by the so-called oleum test described in Vol. I of this work, p. 332.

Native dealers evaluate an oil simply by shaking it in a small bottle or by hitting the bottle against the palm of the hand. If the air bubbles which then rise to the surface disappear quickly, the oil is assumed to be normal. If they remain a few seconds, and foam forms, the oil is suspect. Exporters in Bombay evaluate palmarosa oil by a simple solubility test, a very good solubility indicating a high geraniol content and hence a good quality.

Total Production and Exports.—The yearly total production of palmarosa oil in India ranges from 20,000 to 40,000 lb. Export figures[15] from Bombay for the years prior to World War II were as follows:

	Pounds
1935	32,083
1936	26,550
1937	35,316
1938	27,380

Of the latter quantity

21,805 lb. went to Europe
5,200 lb. went to America
375 lb. went to Japan

More recent exports[16] of palmarosa oil from India have been as follows (for the fiscal year ending March 31st):

	Gallons
1939–1940	3,568
1940–1941	3,520
1941–1942	7,421
1942–1943	4,345
1943–1944	360
1944–1945	7,061
1945–1946	9,293

OIL OF PALMAROSA SEYCHELLES

For a number of years efforts have been made in the Seychelles Islands to produce a high-grade palmarosa oil. For this purpose *Cymbopogon martini* Stapf var. *motia* was planted exclusively and all gingergrass (var. *sofia*)

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[15] *Ber. Schimmel & Co.* (1939), 60.

[16] "Accounts Relating to the Sea-borne Trade and Navigation of British India," *India Commercial Intelligence Statistics Dept.,* March (1946).

eradicated. According to trade news reports,[17] in the Seychelles palmarosa grows exceptionally well on the sandy coral plateaus. The grass is easily propagated by means of soft cuttings rooted in sand under shade.

The Imperial Institute[18] in London reported properties for two oils from the Seychelles Islands, which resembled those of the Indian oils. The total alcohol content (calculated as geraniol) was 90.1 per cent. The odor of the Seychelles oils was somewhat softer than that of the Indian oils.

OIL OF PALMAROSA JAVA

A few years prior to the outbreak of World War II, Java began to produce oil of palmarosa from *Cymbopogon martini* Stapf var. *motia* (syn. *Andropogon martini* Roxb. var. *motia*), the true palmarosa. Originally the quantities were very small, but in 1937 Java exported 2,755 kg. of oil, chiefly to Holland and England. In 1938, 4,721 kg. were exported.

Java palmarosa oil is distilled exclusively from planted and cultivated grass. Before World War II there were in Java five producers, all European planters, the most important one distilling yearly from 1,000 to 2,000 kg. of oil in Padalarang, near Bandoeng, and another planter somewhat smaller quantities in Modjo-Agoeng near Sourabaya, eastern Java.

The grass, which was originally introduced from India, is planted, by root division, during the rainy season. The segments are set out 80 cm. by 80 cm. apart. When the plants have grown to a height of about 2.25 m. they are ready for cutting. Harvesting can be repeated every four months, but after five years the planting must be renewed. As was said above, in 1939 all palmarosa plantations in Java were in the hands of European producers, the many native and Chinese growers of citronella not yet having started with palmarosa. All palmarosa plantings were, therefore, properly taken care of, carefully weeded out, and in excellent condition. This might be one of the reasons for the good quality of the Java oil.

Distillation was carried out by modern methods. The above mentioned producer in Padalarang, for example, employed direct steam stills of about 5 cu. m. capacity. Distilling one charge of 600 kg. of grass with live steam for 3 hr., he obtained about 1 kg. of oil. The oil yield, therefore, averaged 0.17 per cent.

Distillation with indirect steam and cohobation of the distillation waters also produced a very high grade of palmarosa oil.

Quality of the Java Oil.—It might be interesting in this connection to comment on the quality of the Java oil. Compared with the Indian palmarosa oil, the Java product should be of superior quality because:

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[17] *Perfumery Essential Oil Record* **30** (1939), 42; **31** (1940), 63.

[18] *Bull. Imp. Inst.* **25** (1927), 112.

1. In Java all palmarosa grass originates from well-kept plantations, confined to *Cymbopogon martini* Stapf var. *motia.* In India, on the other hand, the plant material consists of wild growing grass, occasionally mixed with the inferior *sofia* variety (gingergrass).
2. Distillation in Java, as was mentioned above, is carried out in modern steam stills by large-scale producers,[19] whereas in India the grass is distilled by natives in primitive, direct fire stills with insufficient condensation. While the plant material is immersed in boiling water in the Indian stills, hydrolysis of esters takes place which results in a generally low ester content of the Indian oils. Direct steam distillation, as practiced in Java, results in oils with a much higher ester content. Moreover, the Indian oils are frequently improperly stored and may be exposed for weeks or months to the high temperature of central India.
3. In Java every single lot of oil must be analyzed in the Government Analytical Laboratories of Buitenzorg prior to the granting of an export license. Inferior oils are rejected.

In view of all these factors, it would appear that the Java oil should be of excellent quality, unless the plant itself, after its introduction from India, gradually degenerates, under the climatic and soil conditions of Java, or under cultivation.

The difference between the Indian and the Java palmarosa oil is, in point of fact, quite pronounced. Whether this results from the superior methods of production employed in Java, or from mutation of the plant in its new environment, is open to question. When, in 1937, commercial shipments of Java oil reached Europe, the consumers, much to the dismay of the Buitenzorg Experiment Station in Java, rejected the oil as being different from the usual commercial oil from India, and unsuitable for their purposes. Such critical judgment is often encountered in our industry when a new type of oil is introduced to replace an old one, to which the trade has become accustomed through many years of use.

In the author's opinion, the Java oil represents a high grade of palmarosa oil, superior, in fact, to the Indian product, which has a somewhat harsh by-note. Because of its soft, slightly fruity and rose-like character, the Java oil can be used in perfumes and cosmetics, whereas the stronger Indian oil should be employed for the scenting of soaps. The Java product may also serve as a good starting material for the extraction of a very fine geraniol. There is undoubtedly a place for both oils, but each type should be marketed

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[19] At the time of this writing (1949), it is still difficult to judge to what extent conditions have changed during the Japanese occupation and the civil strife in Java after World War II. According to a private communication of Dr. J. A. Nijholt, Buitenzorg (March, 1950), it is probable that no palmarosa oil has been produced in Java since the disruption caused by the war.

under its proper label, as has been customary with several other essential oils—geranium oils from Réunion and Algeria, vetiver oils from Java and Réunion, and patchouly oils from Sumatra and Singapore, for example.

Physicochemical Properties.—According to Koolhaas,[20] the properties of Java palmarosa oil vary within the following limits:

Specific Gravity at 15°	0.886 to 0.899
Optical Rotation	−3° 0′ to +5° 0′
Refractive Index at 20°	1.4720 to 1.4780
Acid Number	0 to 3
Ester Number	12 to 50
Total Geraniol Content	78 to 94%
Aldehyde Content, Calculated as $C_{10}H_{18}O$ (Hydroxylamine Method)	0 to 10%
Solubility in 70% Alcohol	One volume is soluble in 1½ to 10 vol.

Shipments of Java palmarosa oil examined by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°/15°	0.888 to 0.894
Optical Rotation	−0° 6′ to +0° 18′
Refractive Index at 20°	1.4729 to 1.4748
Acid Number	1.4 to 2.8
Ester Content, Calculated as Geranyl Acetate	9.5 to 17.6%
Total Alcohol Content, Calculated as Geraniol	85.7 to 90.2%
Aldehyde Content, Calculated as Citronellal (Hydroxylamine Hydrochloride Method)	1.2 to 10.8%
Solubility at 20°	Occasionally soluble in 3.5 vol. of 60% alcohol. Usually soluble in 2 vol of 70% alcohol, opalescent in 4.5 vol. and more

These limits may be somewhat too narrow; only few commercial lots have been available and more data are required before definite limits can be established.

Adulteration.—The careful examination by the Buitenzorg Government Laboratories to which each shipment of Java palmarosa oil is subjected prevents the exportation of adulterated oils.

CHEMICAL COMPOSITION OF PALMAROSA OIL

The first research on the chemical composition of palmarosa oil derived from true *Cymbopogon martini* Stapf var. *motia* was carried out by Jacobsen[21] who identified an alcohol $C_{10}H_{18}O$ as main constituent and assigned

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[20] Private communication of Dr. D. R. Koolhaas, Buitenzorg, Java (1939).

[21] *Liebigs Ann.* **157** (1871), 232.

to it the name geraniol. Years later Semmler[22] confirmed the validity of the formula $C_{10}H_{18}O$ and found that this important terpene alcohol belongs to the aliphatic series.

More recently van Hulssen, Koolhaas, and Rowaan[23] studied the aldehydes present in palmarosa oil and arrived at the conclusion that the oils distilled in Java contain from 1.3 to 10.2 (on the average 7.0) per cent of aldehydes, whereas the oils produced in India (formerly British East India) contain 5.1 to 9.4 per cent[24] of aldehydes. The aldehydes of the Java oil consist mainly of citral, with occasionally some citronellal. The fresh odor occasionally noted in some lots of palmarosa oil is caused perhaps by low boiling aldehydes. The same authors also confirmed the presence of those constituents which had been identified in earlier investigations of palmarosa oil from India.

The following substances, listed approximately in order of their boiling points, have been observed in palmarosa oils from India and Java:

Formaldehyde. By van Hulssen, Koolhaas and Rowaan.[25]

Isovaleraldehyde. By the same authors.

Methyl Heptenone. Traces of this ketone in the Indian oil were noted by Schimmel & Co.[26] who prepared the semicarbazone m. 135°.

Dipentene. The same workers also found that the Indian oil contains about 1 per cent of dipentene, which was characterized by the preparation of its tetrabromide m. 125°, and nitrolbenzylamine m. 109°–110°.

Citronellal. Identified in a Java type of oil by van Hulssen, Koolhaas and Rowaan.[27] In the opinion of these authors, the presence of citronellal in one of their Java oils is perhaps due to the fact that this particular lot was distilled from a special horticultural variety of *Cymbopogon martini* Stapf var. *motia.*

Citral. Observed by the same workers[28] in palmarosa from Java and India. The aldehydes present in the Java type of oil consist mainly of citral.

Geraniol. When first isolating this main constituent from Indian palmarosa oil, Jacobsen[29] purified it through its calcium chloride addition compound, which procedure later became of great importance for the isolation (and purification) of primary terpene alcohols from complex mixtures.

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[22] *Ber.* **23** (1890), 1098.

[23] *Indische Mercuur* **61** (1938), 489. Cf. *Mededeelingen van het Laborat. voor Scheikundig Onderzoek te Buitenzorg. Handelsmuseum van het Koloniaal Instituut* 1938.

[24] The laboratories of Fritzsche Brothers, Inc., New York, examined a number of pure Indian palmarosa oils which contained very little, if any, aldehydes.

[25] *Indische Mercuur* **61** (1938), 489. Cf. *Mededeelingen van het Laborat. voor Scheikundig Onderzoek te Buitenzorg. Handelsmuseum van het Koloniaal Instituut* 1938.

[26] *Ber. Schimmel & Co.*, April (1905), 39.

[27] *Indische Mercuur* **61** (1938), 489. Cf. *Mededeelingen van het Laborat. voor Scheikundig Onderzoek te Buitenzorg. Handelsmuseum van het Koloniaal Instituut* 1938.

[28] *Ibid.*

[29] *Liebigs Ann.* **157** (1871), 232.

Indian oil of palmarosa contains from 75 to 95 per cent of (free and combined) geraniol. Van Hulssen, Koolhaas, and Rowaan[30] reported a geraniol content (free and combined) of 82–94 per cent, for the Java type of palmarosa oil.

Geranyl Acetate and Geranyl *n*-Caproate. According to Gildemeister and Stephan,[31] about 3 to 15 per cent of the geraniol occurring in Indian palmarosa oil is present in the form of acetic and *n*-caproic esters, the quantities of the two esters being approximately equal. They arrived at this conclusion by analyzing the silver salts of acetic and *n*-caproic acids.

Farnesol. Elze[32] reported on the occurrence of this sesquiterpene alcohol in Indian palmarosa oil.

Years ago Flatau and Labbé[33] claimed that palmarosa oil also contains citronellol and a fatty acid $C_{14}H_{28}O_2$, m. 28°. According to Schimmel & Co.,[34] however, this is not the case; the oil investigated by Flatau and Labbé was probably adulterated with coconut or some other fatty oil.

Investigating a palmarosa oil of Sukhum (U.S.S.R.) origin, Bulanova[35] found that the geraniol content of this type of oil is identical with that of the imported (Indian) type of oil. The Sukhum oil contained:

Geraniol	77.68%
Citronellol	1.18%
Aldehydes and Terpenes	Traces, not studied
Sesquiterpene Alcohols	About 3.9%

As regards the presence of citronellol in palmarosa oil (reported by Flatau and Labbé, and by Bulanova—see above), the chemists of Schimmel & Co. disproved this claim years ago. To eliminate any doubt, the laboratories of Fritzsche Brothers, Inc.,[36] more recently examined genuine East Indian as well as Java palmarosa oils and, using the (modified) method of Tiemann and Schmidt[37] for the separation of citronellol and geraniol, arrived at the conclusion that citronellol is not present, either free or as ester, in East Indian or Java palmarosa oils. Adulteration of palmarosa oil by the addition of "geraniol fractions" (which always contain some citronellol) can thus be detected.

In the course of their investigation the chemists of Fritzsche Brothers, Inc., also confirmed the presence of acetic acid and of *n*-caproic acid in East Indian and Java palmarosa oils.

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[30] *Indische Mercuur* **61** (1938), 489. Cf. *Mededeelingen van het Laborat. voor Scheikundig Onderzoek te Buitenzorg. Handelsmuseum van het Koloniaal Instituut* 1938.

[31] *Arch. Pharm.* **234** (1896), 328.

[32] *Chem. Ztg.* **34** (1910), 857.

[33] *Compt. rend.* **126** (1898), 1725. *Bull. soc. chim.* [3], **19** (1898), 633.

[34] *Ber. Schimmel & Co.,* October (1898), 29.

[35] *Trudy Vsesoyuz. Inst. Efirno-Maslichnoi Prom.* **8** (1940), 183. *Chem. Abstracts* **37** (1943), 3558.

[36] Publication forthcoming.

[37] *Ber.* **29** (1896), 921.

Recently Rakshit and Dutt [38] reported that Indian palmarosa oil contains from 0.04 to 6.0 per cent of phenols. Since this latter percentage seems rather high, the laboratories of Fritzsche Brothers, Inc., New York, examined a few lots of Indian palmarosa oil for the presence of phenols and found that they contained about 0.04 per cent of phenols.

Use.—At one time the oil was used as an adulterant of Bulgarian or Turkish rose oil. Today palmarosa oil is the source of a very high grade of geraniol. The oil is widely employed in cosmetics, particularly in soaps, to which it imparts a pronounced and lasting rose note. Geraniol, the chief constituent of palmarosa oil, being quite alkali resistant, the oil stands up well in soaps.

Another use of palmarosa oil is in the flavoring of tobacco.

OIL OF GINGERGRASS

As was pointed out in the introduction to the monograph on "Oil of Palmarosa," oil of gingergrass is distilled in India from the wild growing grass, *Cymbopogon martini* Stapf var. *sofia* (syn. *Andropogon martini* Roxb. var. *sofia*). Production regions include Hyderabad, parts of Bengal, Punjab, and the presidency of Madras. The oil originating from Madras is derived exclusively from gingergrass, and not partly from palmarosa, as may be the case in the other producing regions.

Harvesting of the plants, distillation and handling of the gingergrass oil take place under conditions almost identical with those described in the monograph on "Oil of Palmarosa."

The bulk of the oil is shipped to ports of the Red Sea, and to the Sudan, for use as a cheap perfume for the native population. In East Africa the oil is also employed, in conjunction with sandalwood oil, as a mosquito repellent that is claimed to be quite effective. Applied alone, the oil dries too rapidly, for which reason it should be incorporated into a base of fatty oils. Gingergrass oil is also said to have some value as a remedy for stiff joints, lumbago, and other ailments.

The export figures for gingergrass oil prior to World War II were as follows: [1]

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[38] *Indian Soap J.* **13**, August (**1947**), **27**.

[1] *Ber. Schimmel & Co.* **(1939), 36.**

	Pounds
1934	63,529
1935	56,290
1936	60,250
1937	26,369
1938	61,445

Of the last quantity, 1,991 lb. were shipped to Europe; 59,454 lb. went to Red Sea ports.

As regards cultivation experiments (yield of plant material, yield of oil from various parts of the plant, etc.) recently carried out with gingergrass in India, see the monograph on "Oil of Palmarosa," section "Distillation and Yield of Oil"—above.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[2] the properties of gingergrass oil vary within the following limits:

Specific Gravity at 15°	0.900 to 0.953
Optical Rotation	+54° 0′ to −30° 0′
Refractive Index at 20°	1.4780 to 1.4930
Acid Number	Up to 6.2
Ester Number	8 to 29; in one case 54.5
Ester Number after Acetylation	120 to 200
Total Alcohol Content, Calculated as Geraniol *	36.3 to 64.7%
Solubility	Mostly soluble in 2 to 3 vol. of 70% alcohol, opalescent to turbid with more alcohol. Soluble in 0.5 to 1.5 vol. of 80% alcohol and more, in rare cases with slight opalescence

* Calculated from the ester number after acetylation.

Data on the physicochemical properties of gingergrass oil reported recently in some Indian publications will not be cited here, as the total geraniol content of the oils described has been calculated erroneously.

Adulteration.—Native producers frequently adulterate gingergrass oil with oils of turpentine or coconut, or with kerosene. These adulterants can be detected by the methods described under "Indian Palmarosa Oil."

Chemical Composition.—The composition of the oil derived from *Cymbopogon martini* Stapf var. *sofia* has been investigated by the chemists of Schimmel & Co.,[3] among them chiefly Walbaum and Hüthig,[4] and Gildemeister and Stephan.[5] The following compounds, listed approximately in order of their boiling points, have been identified:

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[2] "Die Ätherischen Öle," 3d Ed., Vol. II, 300.

[3] *Ber. Schimmel & Co.*, April (1904), 52; October (1904), 41; April (1905), 34; October (1906), 33. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 544.

[4] *J. prakt. Chem.* [2], **71** (1905), 459.

[5] *Arch. Pharm.* **234** (1896), 326.

d-Limonene. Preparation of its α-nitrolpiperidine m. 93°, and α-nitrolbenzylamine m. 93°.

Dipentene. Tetrabromide m. 125°; α-nitrolpiperidine m. 153°.

d-α-Phellandrene. Nitrite m. 120°.

An Aldehyde(?) $C_{10}H_{16}O$. The oil contains small quantities (about 0.2 per cent) of an aldehyde $C_{10}H_{16}O$, b_{754} 221°–224°, b_5 76°–78°, d_{15} 0.9351, $\alpha_D \pm 0°$, n_D^{20} 1.47348, whose odor resembles that of citronellal and heptaldehyde. On reduction, the aldehyde yielded an alcohol $C_{10}H_{18}O$, the phenylurethane of which melted at 100°–101°. Oxidation by air gave an acid $C_{10}H_{16}O_2$, m. 106°–107°, which was observed also in the saponification lyes of the oil. The aldehyde was characterized, but not identified, by these derivatives: oxime m. 115°–116°, semicarbazone m. 169°–170°, semioxamazone m. 244°–245°, phenylhydrazone m. 63°, β-naphthocinchoninic acid m. 261°.

Dihydrocuminyl Alcohol (Perillyl Alcohol). This alcohol has an odor reminiscent of linaloöl and terpineol and yields a naphthylurethane m. 146°–147°. Its identity with perillyl alcohol was established by Semmler and Zaar.[6]

dl-Carvone. Characterized by the preparation of its semicarbazone m. 153°–154°.

Geraniol. Oil of gingergrass contains from 36 to 65 per cent of total alcohols, calculated as geraniol. The alcohols consist chiefly of geraniol, which was identified through its diphenylurethane m. 82°, and by oxidation to citral.

Suggested Additional Literature

F. Bruno, "Acclimatization and Commercial Utilization of *Cymbopogon flexuosus* Stapf, and of *Cymbopogon martini* Stapf var. *motia.*" *Boll. studi inform. R. Giardino Col. Palermo* **13** (1934). *Parfums France* **13** (1935), 33. *Chem. Abstracts* **29** (1935), 3464.

OIL OF LEMONGRASS

Essence de Lemongrass *Aceite Esencial Lemongrass* *Lemongrasöl*
Oleum Andropogonis Citrati

Introduction.—Oil of lemongrass is one of the most important essential oils. Large quantities are used for the extraction of citral, the chief constituent of the oil. Citral is the starting material for the preparation of the important ionones (a series of aromatics with a powerful violet odor).

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[6] *Ber.* **44** (1911), 460.

Because of its high citral content (75–85 per cent) the oil possesses a strong lemon odor, whence the name lemongrass.

The plant grows wild in many tropical and semitropical parts of Asia, Africa, and America. For the extraction of its oil, however, only cultivated lemongrass is now employed, the collection of wild growing plants being too costly.

The trade distinguishes between two principal types of lemongrass oil, viz., the East Indian and the so-called West Indian oil. Both contain from 75 to 85 per cent of aldehydes (chiefly citral),[1] but the oils differ slightly in that the West Indian product is usually less soluble in 70 per cent alcohol than the East Indian. The lower solubility of the West Indian oil, particularly noticeable after storage of the freshly distilled oil, is due to the presence, in the foreruns, of myrcene, an olefinic terpene, which on exposure to air and light readily polymerizes. (Cf. "Physicochemical Properties" and "Chemical Composition.")

The East Indian oil is produced only in a small section of the southwestern part of India, near the Malabar Coast. It is the older of the two types of oil, large quantities having been exported annually for many years. The Indian industry, cultivation as well as distillation, is utterly primitive, and entirely in the hands of natives. Nevertheless, the East Indian oil has always been noted for its good quality, and particularly its high citral content. The high quality of the oil may be attributable to soil conditions, and perhaps also to altitude and climate, because the methods of cultivation and distillation employed in India cannot even be compared with those used for the production of the West Indian type of oil. More probably, however, the good quality of the Indian oil is to be attributed to the plant species from which it derives.

The term "West Indian lemongrass oil" is actually a misnomer. It came into use years ago when small quantities of oil were produced in the West Indian islands, largely on an experimental basis, and were found to differ from the East Indian oil, chiefly in possessing a lower solubility (see above). In order to differentiate this type of oil from the more soluble East Indian oil, the name "West Indian oil" was introduced, and has remained in use, although the oil is now produced in large quantities in several parts of the world: in Guatemala (Central America), Haiti (West Indies), São Paulo (Brazil), the Comoro Islands, Madagascar, and Indo-China. More or less successful experiments in cultivating the plant and distilling the oil have been undertaken in Puerto Rico and Dominica (West Indies), Honduras,

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[1] The aldehydes present in lemongrass oil consist chiefly of citral. Following the usual trade practice we shall, in the following pages, refer to the aldehyde content simply as citral content. In most cases, the aldehyde (citral) content is determined by the bisulfite method. For details see the sections on "Physicochemical Properties" and "Chemical Composition."

Mexico, Paraguay, and even in subtropical countries such as Florida (United States), success or failure depending upon conditions of climate, soil and altitude, and last but not least upon the cost of labor.

For some years prior to World War II Madagascar and the Comoro Islands produced from 50 to 60 metric tons, annually, of lemongrass oil, most of which went to France. A few years before the outbreak of the war Guatemala appeared on the market as a producer, shipping substantial quantities of oil to the United States, but fighting a gradually losing battle against competition from India. Madagascar, the Comoro Islands, French Indo-China, and Guatemala were then the only countries producing the West Indian type of lemongrass oil on a commercial scale. Fortunately for the Western Hemisphere, the Puerto Rico Experiment Station of the United States Department of Agriculture in Mayaguez, Puerto Rico, had been carrying on extensive experiments on the cultivation and distillation of lemongrass. The planting material raised at the Station became of great help to prospective producers in several parts of the Western Hemisphere, when the outbreak of World War II and transport difficulties reduced shipments of the East Indian oil. The ensuing sharp rise in price induced a number of planters in Guatemala, Haiti, and Brazil to grow lemongrass on a large scale, and production of the West Indian type of oil increased rapidly. The grass was grown on extensive plantations and distillation was carried out in efficient, modern equipment. The following figures will convey an idea of the extent of the American lemongrass oil industry by the end of the war: Guatemala produced annually about 120,000 lb., Haiti 50,000 lb., and Brazil 10,000 lb. of oil. The boom lasted until 1948, when the peak price of about $5.00 per pound of oil dropped to less than $1.00. This obviously discouraged many growers, who, on the basis of such low prices, could hardly cover their expenses, the cost of labor having risen sharply during the war. At the time of this writing (1949) the outlook is uncertain. The future of the American lemongrass oil will depend in large part upon competition offered by the East Indian oil. In the author's opinion the American lemongrass industry will be able to withstand competition from India only if it can mechanize part of its operations, particularly the harvesting of the grass, which in over-all calculations involves the greatest item of cost (labor). Very recently, considerable progress has been made in this direction, particularly in Guatemala.

The quality of the West Indian type lemongrass oil was once considered to be inferior to that of the East Indian oil, but the American oil is now readily accepted by the manufacturers of aromatic isolates and synthetic aromatics, provided, of course, that a given lot meets the minimum requirements for citral content (75 per cent). In the war years much experience was gathered in cultivating, harvesting, and distilling the grass, and now, when properly prepared, the American oil is beyond reproach. It can easily replace the Indian oil for the extraction of citral. The fact that the American oil, particularly after storage, exhibits a slightly lower solubility in 70 per cent alcohol than the East Indian oil, does not prevent its use for the scenting of soaps or technical preparations.

Botany.—There was much confusion, years ago, about the taxonomy of the plants which yield the East Indian and the West Indian types of lemongrass oil; however, Stapf [2] ended the long controversy by identifying the plant yielding the East Indian type of oil as *Cymbopogon flexuosus* (D.C.) Stapf, and the plant yielding the West Indian type of oil as *Cymbopogon citratus* (D.C.) Stapf. The two plants have been named variously also *Andropogon nardus* var. *flexuosus* Hack. or *A. flexuosus* Nees *ex* Steud., and *Andropogon nardus* var. *ceriferus* Hack. or *A. citratus* D.C., respectively.

The correctness of Stapf's classification was confirmed experimentally by Jowitt and Pickles,[3] who planted the two species in Ceylon, extracted the oils by distillation, and found that the oil derived from *Cymbopogon flexuosus* Stapf was soluble in 2.2 volumes, and more, of 70 per cent alcohol, whereas the oil derived from *C. citratus* Stapf was not clearly soluble even in 10 volumes of 90 per cent alcohol.

Experiments carried out at the Government Station in Barbados [4] (B. W. I.) with East Indian lemongrass seed imported from the State of Cochin (Malabar Coast) indicated that grass raised from this seed yielded an oil which was readily soluble in alcohol and contained a high percentage of citral.

Hood [5] does not contest the claim of Stapf that there are two distinct species of lemongrass, viz., *C. flexuosus* and *C. citratus,* but assumes the existence of numerous local varieties of *C. citratus.* The Bureau of Plant Industry has, in fact, experimented in the United States with thirteen varieties from eight different localities.

Lemongrass, a stoloniferous plant, is propagated by division of clumps; it does not ordinarily produce seed unless grown in a suitable climate without being cut for several years. For propagation the leaves of a fully matured healthy plant are cut back to about 3 in. One old clump yields as many as 50 new stools. The "bud pieces" or "seed pieces" are then planted in holes 2 to 3 ft. apart. At the Puerto Rico Experiment Station [6] it has been the practice to plant 4 bud pieces to the hill at intervals of 18 in. in rows 32 in. apart.

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[2] *Kew Bull.* (1906), 297.

[3] Cf. *Circ. Agr. J. Roy. Botan. Gardens, Ceylon* **5**, No. 12 (1910), 137. *Bull. Imp. Inst.* **8** (1910), 144.

[4] Cf. *Ber. Schimmel & Co.,* October (1908), 76.

[5] *U. S. Dept. Agr., Bur. Plant Ind. Bull.* No. 442. *Am. J. Pharm.* **89** (1917), 180.

[6] Jones and Arrillaga, "Experiments with Lemongrass in Puerto Rico," *U. S. Dept. Agr., Fed. Expt. Sta., Mayaguez, Puerto Rico* (Publication forthcoming).

Oil of Lemongrass East Indian

Producing Regions.—The East Indian lemongrass oil is produced in Travancore State, in the extreme southwestern part of India. The principal producing regions are confined to a relatively small section of this state and are located for the most part south of the Periyar River which empties into the Indian Ocean a short distance north of Cochin, the old seaport on the famed Malabar Coast. Starting from Cochin and traveling inland, due west, the visitor can reach the lemongrass regions in a day's drive, provided the conditions of the roads permit it. Most of the plantations are located in the foothills of the Ghats, a range of high and wild mountains stretching inland from north to south and paralleling the Malabar Coast.

Local conditions of soil, altitude, and climate in these hills and mountains vary so widely that it is very difficult to classify certain sections according to the quality of the oil and importance of production. In general, the northern sections of the producing regions, from which the bulk of the oil originates, produce a better quality of oil than the southern districts. Main producing centers in this area are the villages of Thoduhpuzha, Vazhakulam, Moovattupuzha, Perambavur, and Alwaye, the latter being an important trading center for the oil. These districts account for about 50 per cent of the total output of oil in southern India. The environs of Kothamangalom (also located in the north) supply about 40 per cent of the total output of Indian lemongrass oil.

Plant Varieties.—There are two types of lemongrass in Travancore State, differing in appearance and readily distinguishable by the color of the stems:

1. The so-called "red grass," locally known as "choomana poolu." The color of the stems is reddish. The leaves of this plant, the true *Cymbopogon flexuosus* Stapf, yield the normal East Indian lemongrass oil, containing 75 per cent or more of aldehydes (chiefly citral) and exhibiting good solubility. The bulk of Indian lemongrass oil is produced from the "red grass."

2. The so-called "white grass," locally known as "wella poolu." The color of the stems is whitish. It has been identified as *Cymbopogon flexuosus* Stapf var. *albescens.*[7] The oil derived from this plant possesses a low aldehyde content and poor solubility; moreover, a planting lasts only a few years. Only small quantities of this type of lemongrass are produced and that chiefly in the southern sections. According to Varier,[8] the oil from the white variety (which could not be identified botanically) contains camphene and dipentene, but no citral. The compound isolated from a sodium bisulfite extraction of the oil was not identified.

[7] *Bull. Imp. Inst.* **12** (1914), 222; **14** (1916), 381.

[8] *J. Indian Chem. Soc. Ind. & News Ed.* **6** (1943), 40, 48.

The oil derived from "white grass" cannot be marketed as normal lemongrass. Indian field brokers and intermediaries, therefore (to the annoyance of the exporters in Cochin), occasionally bulk small quantities of this oil with lots of normal oil, thus lowering the high aldehyde content and normal solubility of the latter. Perhaps the "white grass" is closely related to, if not identical with, the "Inchi grass" discussed below (p. 133).

Soil, Climate, and Altitude.—Lemongrass requires a warm tropical climate, plenty of sunshine, and intermittent, but not excessive, rainfall. It does not thrive in compact soils, which may retain pools of stagnant water. Warmth and sunshine conduce to the development of oil in the plant. In regions of abundant rainfall the plant may be harvested more frequently, during the year, than is possible in dryer regions, but the oil will be of lower citral content. On the higher slopes of the mountains, against which the monsoon clouds discharge their moisture, the grass contains a great deal of water and yields less oil than grass grown on the lower slopes, which are less exposed to the showers.

The quality of the soil exerts a considerable influence upon the yield of grass and oil per acre and upon the quality of the oil. The grass grows best on well-drained sandy loam; it thrives even on light sandy soils, provided they are sufficiently fertile. Plants from such sandy soil yield relatively more oil, and oil of higher citral content, than plants from very fertile soil.

Experimenting with the West Indian type of lemongrass (*Cymbopogon citratus* Stapf) in Florida, Hood[9] found that the moisture content of the soil also influences the citral content of the oil. Dry sandy soil yielded an oil containing 75 per cent of citral, a slightly humid sandy loam an oil containing 68 per cent of citral, and a humid loam an oil containing only 66 per cent of citral.

In southern India the growers obviously cannot use fertile soil for the raising of lemongrass, since such land is expensive and is required for other more vital crops—rice, tapioca, and cashew nuts, for example (the most important food crops). Most of the lemongrass plantings are therefore located on low-priced land on the slopes of hills, up to 2,000 ft. altitude.

Planting and Cultivating.—Until about forty years ago it was chiefly the wild growing grass which served for distillation of Indian lemongrass oil, because at that time buyers abroad did not insist upon a high citral content. Conditions have changed, however. Today it would be much too costly to collect wild growing grass, which is usually scattered over wide areas, and to separate it from other admixed grasses, the presence of which in the distillation material would yield oils of substandard citral content and poor solubility. For these reasons only cultivated lemongrass is at present used for distillation.

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[9] *U. S. Dept. Agr., Bur. Plant Ind. Bull.* No. 442. *Am. J. Pharm.* **89** (1917), 180.

The plantations are scattered widely, and range in size from patch plantings, on jungle clearings, to fields of a hundred or even two hundred acres. The whole industry—cultivation of the grass as well as distillation—is entirely in the hands of natives, utterly primitive, and, as a village industry, forms part of the native's general agricultural activities. There is not a single plantation or distillery owned by white producers. Some of the patch fields and small plantings belong to individual villagers, but most of the land is owned by wealthy Indians, who cultivate it on their own account, with the help of hired labor, but only during periods of attractive prices. Whenever prices are low, they simply rent their land to small peasants on a share-crop basis, or for very small fees—just enough to meet the land tax. The whole economic setup of the industry is such that, in years of very low prices, production diminishes, fewer peasants then being interested in operating the stills. Part of the equipment is left idle until distillation again becomes profitable.

Prior to planting, which in Travancore is by seed, the ground must be prepared, which is usually done toward the end of the dry, hot season (March or April). With the advent of the first, sporadic monsoon showers, the seed is sown by hand. Toward the end of April the showers become more frequent, and the plant develops rapidly. At this point, however, the grass is still too young and too short (being only about 1 ft. tall) to be harvested, as the yield of oil and the citral content would be substandard. While young, the grass must be protected by fences or guards against cattle or goats that may invade the field. The first harvest takes place near the end of May or the beginning of June, when the heavy monsoon rains begin. From then on, the leaves may be cut every 6 to 7 weeks; they grow up rapidly after each cutting.

The time of cutting exerts a considerable influence upon the yield and quality of the oil. Young and tender grass, harvested in the early season (during April, for instance), yields an oil of abnormally low aldehyde content (60 to 70 per cent) and of poor solubility. Later the aldehyde content of the oil increases to 75 per cent and more. A similar increase takes place as regards yield of oil. In general, the yield of oil is lower in the months of heavy rain (June to August) than in the dry months.

In December the monsoon rain ceases, and the dry, hot season begins; it lasts to March or April. During this period the plant develops an inflorescence and the leaves and stems shrivel up; but the root remains alive. With the arrival of the new monsoon rain in March or April the plant develops new life; it flourishes and the cutting can be started anew. Prior to the arrival of the new monsoon showers, the dry grass is usually burnt to fertilize the soil and strengthen the plants. In times of low prices the burning of the grass is sometimes omitted, but this has a detrimental effect upon the later growth of the plant and the yield of oil. Under these circumstances the first cutting in the new monsoon season may be normal, but the second and following cuttings are likely to give an abnormally low yield of grass and oil.

Throughout its life span a plantation should be weeded out, but when prices are low this practice is often neglected, with the result that the planting soon becomes overgrown with weeds.

Cutting is usually done with sickles. Harvesters tie the cut grass into bundles weighing ½ to ¾ lb. These are then gathered into larger bundles, which the harvesters carry on their heads to nearby field stills.

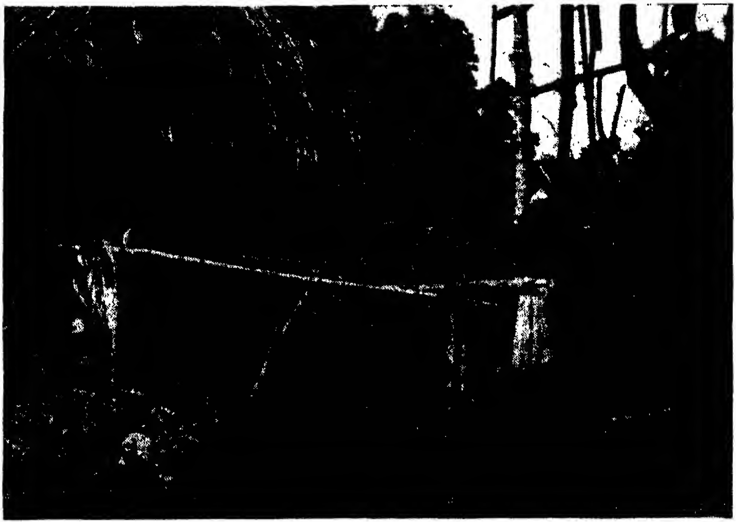
Depending upon soil and climatic conditions, a plantation lasts, on the average, from six to eight years. The yield of oil is small during the first year. It increases with the second, and reaches a maximum in the third and fourth years, after which it declines progressively. If the prices are low, a plantation may be discontinued prematurely, to make room for more lucrative produce—such as rice, tapioca, or ginger. On the average one acre yields 30 to 40 lb. of oil per year with four cuttings. Higher yields may be obtained on fields that are well managed.

Distillation.—Because of the very primitive nature of the Indian lemongrass industry, with its widely scattered plantings in the hills, lack of roads, and difficulties of transportation, there are no centrally located, large-scale distilleries.

The stills, as was noted above, are utterly primitive, made of copper, and not equipped with perforated grids. A wide, protruding palm thatched roof protects the still, the stacked up plant material, and the workers, from exposure to sun and rain. The average retort is 6 ft. high, 3 ft. wide, and has a capacity of about 200 gal. At the side, about 3 ft. above the bottom is a manhole through which the plant material can be charged and discharged. During distillation the manhole is closed with a cover, held fast by means of a mud paste which dries and hardens as the metal walls become hot. The retort, up to the manhole, is imbedded into a hearth made of mud and bricks. It houses the fire beneath the bottom of the retort. About 300 to 500 bundles of freshly cut grass material (weighing approximately 200 to 300 lb.) are packed tightly into the still, up to ¾ of its height. Forty to fifty gallons of fresh water are poured into the still, filling it up to ¼ of its height. Operation in these stills therefore follows the principle of water distillation, a good part of the plant material being immersed in boiling water (cf. Vol. I of this work, pp. 112, 120, and 142). Since most still tops are not removable, all the charging and discharging has to be done through the manhole, a lengthy and tedious task.

The condenser consists of a coil inserted into a large wooden barrel, about 6 ft. high, and usually installed outside of the roof. The barrel is kept filled with cold water drawn from a brook or spring, or, if this is not available, with water drawn by means of a bucket and a high lever from a specially dug well.

A wide, low tin beaker serves as a sort of Florentine flask (oil separator), the accumulating oil being carefully skimmed off with a spoon and poured into bottles. The distillation water is discarded and not returned into the still for use with the next batch of plant material.



Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 3. Lemongrass oil production in Cochin, East India. A typical distillation post in the interior.

Wood, either cut from nearby jungles by the distiller's family or purchased elsewhere, serves as fuel for the fire beneath the still. Since wood is abundantly available in the jungles, the distillers do not use the exhausted grass as fuel. Moreover, the high atmospheric humidity and frequent rain showers prevent drying of the spent leaf material.

Distillation of one charge lasts about 3 hr., yielding ½ to ¾ of a bottle (= ¾ to 1 lb.) of oil. This means approximately 0.2 to 0.3 per cent of oil, calculated upon a charge of 300 lb. of fresh grass material. Exact data are not available, because the plant charge is never weighed, and the yield of oil fluctuates greatly with the season, the condition of the plant material, its moisture content, and the age of the planting.

The distillers and their families work 15 hr. or more a day in the distillery and, by completing five charges, are able to produce 2½ to 3½ bottles of oil per day.

We should not close the section on the distillation of lemongrass without once more emphasizing the fact that in India, the oil is produced by distillation of leaf material while it is partly immersed in boiling water. The West Indian type of lemongrass oil, on the other hand, is obtained by steam distillation with steam supplied from a separate steam generator. In literature the opinion has occasionally been advanced that much of the insolubility of steam distilled lemongrass oil results from the fact that the higher boiling and less soluble fractions are carried over during the process of direct steam distillation, and that many of these would be left behind if the grass were immersed in water during distillation. Experiments undertaken at the Puerto Rico Experiment Station in Mayaguez, United States Department of Agriculture,[10] with a view to comparing yield, solubility, specific gravity, and citral content of the oils obtained by passage of steam through the grass, and by distillation of immersed grass indicate that material immersed in boiling water gave a slightly higher yield of oil (0.385 per cent against 0.375 per cent, calculated upon dried grass), a notably higher specific gravity (0.8945 against 0.8774), and a slightly higher citral content (81.66 per cent against 80.27 per cent) than the leaves distilled with steam. This is rather surprising, as purely theoretical considerations would lead to the conclusion that during distillation with boiling water part of the citral would polymerize.

Courtesy of Fritzsche Brothers, Inc., New York.

Fig. 4. Lemongrass oil production in Cochin, East India. A native distiller scooping the oil from the receiver into a bottle.

In both cases the oils were soluble in 3 volumes of 70 per cent alcohol. These experiments, however, cannot be accepted as fully conclusive, and further study will be required. From the practical point of view, however, the problem is not important, as large-scale distillation of plant material immersed in boiling water would be uneconomical. It is only in the small field stills employed in India, where labor is cheap, that distillation with boiling water can be effected.

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[10] *Rept. Puerto Rico Exp. Sta.* (1939), 34.

As regards drying of the plant material, the Indian producers, as we have seen, use freshly cut leaves for distillation.

Experimenting with the West Indian type of lemongrass in Florida, Hood[11] found that drying of the grass prior to distillation results in only small losses of oil. The yields of oil in his experiments were: 0.37 per cent from fresh grass, 0.31 per cent from sun-dried grass, and 0.32 per cent from artificially dried grass, all yields calculated on the basis of fresh grass. The citral content in the three experiments (determined by the sulfite method) was 77 per cent, 78 per cent, and 79 per cent, respectively. The citral content was thus about equal in the three samples. The solubility of the oils, however, was affected by drying of the leaves: the solubility of oils distilled from dried grass decreased more rapidly on aging than the solubility of oils distilled from fresh material.

Similar experiments carried out by the Puerto Rico Experiment Station, United States Department of Agriculture,[12] led to conclusions significant in field management: it was found that when grass is dried to 45 to 66 per cent of its original weight, it nevertheless yields almost the same amount of oil and content of citral as fresh grass; but the drying results in a great saving of field labor. The procedure would also effect an economy in the fuel required for distillation.

Period of Drying in Sunlight	*Moisture Content of Grass in Per Cent*	*Yield of Oil Calculated on Weight of Fresh Grass, in Per Cent*	*Specific Gravity of Oil*	*Citral Content of Oil in Per Cent*
Distilled Immediately...	80.27	0.348	0.8945	77.50
One Day's Drying......	79.69	0.345	0.8900	76.60
Two Days' Drying.....	77.82	0.287	0.8924	73.00
Three Days' Drying....	71.22	0.244	0.9001	73.04
Four Days' Drying.....	66.50	0.344	0.8970	77.84
Five Days' Drying.....	43.50	0.336	0.8954	79.00

As was to be expected, exposure to sunlight progressively reduced the yield of oil for the first three days on the basis of both the fresh and the treated leaves. However, on the fourth day there was a surprising increase in yield of oil, which was still further increased on the basis of the treated grass on the fifth day.

Handling and Marketing of the Oil.—As has already been mentioned, the distillers in India collect the crude oil in bottles. At the time of collection it still contains small quantities of water and copper salts and has a turbid appearance. Like so much of the native produce of the Orient, the oil has

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[11] *U. S. Dept. Agr., Bur. Plant Ind. Bull.* No. 442. *Am. J. Pharm.* **89** (1917), 180.

[12] *Rept. Puerto Rico Exp. Sta.* (1939), 32.

to pass through the hands of several field brokers, intermediaries, and dealers (all natives), before it reaches the "Go-downs" (warehouses) of the exporters in the port of Cochin.

The distiller is often "financed" by a field broker, whose "capital" consists of a few hundred rupees, and who regularly visits the distillation posts to collect the oil in cans and carry it back to the village where he has his "office." Or the distiller himself brings the oil to the nearest village and sells it to any of the numerous small shops which purchase lemongrass oil and other agricultural crops, often on a sort of barter basis. The field brokers and shop owners then filter the oil through paper into tin cans (old gasoline cans). These men, in turn, are financed by larger dealers, most of them located in the village of Alwaye, the principal trading center of lemongrass oil in the producing regions. Some of these brokers and merchants are relatively wealthy and act as purchasing agents for exporters in Cochin, enjoying their confidence and buying all kinds of native produce for them (lemongrass oil, ginger, etc.). Whenever the exporters in Cochin receive shipping orders from abroad, they either draw from stocks in their own warehouses or call upon their purchasing agents in the larger villages for additional supplies.

Every exporter has a simple "laboratory," where incoming cans of oil are tested for solubility in 70 per cent alcohol and for citral content (by the bisulfite method). Poor oils are rejected, whereas oils on the borderline are bulked with larger lots of good quality. Standard lots of oil, containing at least 75 per cent of citral, are thus made up and shipped abroad in galvanized iron drums.

From experience the exporters—many of them branches of European import and export houses—know that on aging lemongrass oil gradually loses some of its citral content, the loss being about ½ per cent per month. Since the shipping contracts are entered on the basis of a minimum content of 75 per cent of citral (bisulfite method), the exporters standardize their lots in Cochin to a minimum of 77 per cent of citral, which would allow for the loss of some citral during the transport abroad.

Thus each lot of oil shipped abroad consists of bulkings of many small lots. For this reason, oils of high citral content are locally much in demand and at a premium; they are required to counterbalance lots of lower citral content.

In times of high prices, the native dealers in the villages occasionally adulterate their oil lots by the addition of fatty oils or kerosene; but such additions lower the citral content of the oil and its solubility, and the exporters in Cochin will probably reject such lots. A form of adulteration more difficult to detect by the simple tests available to the exporters, consists in the addition of methylated spirits. In times of low prices adulteration of lemongrass oil hardly pays, and is not frequently encountered.

The best time for purchasing lemongrass oil in Cochin, for shipment, is at the end of the main producing season (November to January). Great quantities of oil are then available, usually at low prices, unless the oil is held by some of the wealthy Indian dealers for the purpose of speculation. Immediately after the producing season, the oil has the highest content of citral, which is another reason why the oil should be shipped at this period. Buyers abroad should insist upon oils of most recent harvest.

Exports of Oil.—In the five years preceding World War II, India exported the following quantities of lemongrass oil:

	Hundredweight
1934	6,062
1935	7,067
1936	6,956
1937	7,146
1938	7,694

During and right after the war the figures fluctuated considerably, as can be seen from these statistics: [13]

Fiscal Year (Ending March 31st)	*Quantity of Oil in Gallons*
1939–1940	100,135
1940–1941	83,535
1941–1942	122,924
1942–1943	59,452
1943–1944	54,306
1944–1945	121,629
1945–1946	150,790

According to Volkart Brothers, Inc.,[14] New York, the exports of East Indian lemongrass oil (in long tons) for the last few years have been as follows:

1942–1943	114
1943–1944	382
1944–1945	566
1945–1946	505
1946–1947	465
1947–1948	232

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[13] "Accounts Relating to the Sea-borne Trade and Navigation of British India," *India Commercial Intelligence Statistics Dept.*, March (1946).

[14] Courtesy Mr. E. H. Sennhauser, Secretary.

During the 1947–1948 season, the United States took 85 tons or 38.33 per cent, and the United Kingdom 52 tons or 23.64 per cent of the total exports.

Physiochemical Properties.—Oil of lemongrass is a mobile, yellow to reddish-brown oil with a powerful lemon-like odor.

The quality of the oil is determined by its content of aldehydes (chiefly citral, and usually expressed as citral), which varies from 70 to 85 per cent (assayed by the bisulfite method). Commercial contracts are entered on the basis of a minimum citral content of 75 per cent (bisulfite method). When using the neutral sulfite method, the values, according to Schimmel & Co.,[15] will be 2 to 5.5 per cent lower. This difference may be explained by the fact that the bisulfite method determines not only the citral but also the small quantities of other aldehydes present in the oil, and a part of the methyl heptenone. Both, the bisulfite and the neutral sulfite method, give the percentage of citral by volume, whereas the hydroxylamine method gives it by weight. (For details the reader is referred to Vol. I of this work, pp. 279, 283, 285.)

The British Aromatic Compound Manufacturers' Association [16] proposed replacing the bisulfite method, used for many years for the assay of lemongrass oil, with the more exact hydroxylamine hydrochloride method.

Analysis of 24 samples of lemongrass oil by the hydroxylamine hydrochloride method showed 74 to 75.8 per cent (*by weight*), an average of 74.84 per cent of citral, whereas examination of 17 samples by the bisulfite method showed 73.5 to 81 per cent (*by volume*), an average of 75.66 per cent of citral.

Determinations made by members of the Sub-Committee lead to the conclusion that the maximum variation with the hydroxylamine hydrochloride method should not exceed ±1 per cent.

The hydroxylamine hydrochloride method is undoubtedly the more exact assay, especially in the hands of a skilled analyst; but in the shipping ports of India and other producing countries the necessary laboratory equipment and skill may not always be available.

The export contracts of lemongrass oil should always specify the method by which the citral content of the oil has been assayed.

As has been pointed out above, the content of citral decreases gradually on storage and aging of the oil. This decrease is usually accompanied by an increase in the specific gravity of the oil.[17] For example, an oil with a

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[15] *Ber. Schimmel & Co.,* October (1908), 76.

[16] *Perfumery Essential Oil Record* **39** (1948), 255.

[17] Cf. *Ber. Schimmel & Co.,* October (1909), 65; April (1913), 67. Umney and Bunker, *Perfumery Essential Oil Record* **4** (1913), 38. Parry, *ibid.,* 40; **7** (1916), 95.

citral content of 78 per cent and a specific gravity of 0.889, after two years of storage, exhibited a citral content of only 60 per cent and a specific gravity of 0.895. In a sample, which contained moisture, the citral content decreased from 79 to 68 per cent within three months, whereas another sample, which had been carefully dried, under the same conditions, exhibited a decrease, in citral content, from 79 to 74 per cent only.

It is therefore important, in the storage of lemongrass oil, to exclude air and light, and to dry the oil before it is filled into the storage tanks. Incidentally the oil should not be handled (filtered, etc.) too often in open air, as this may affect the citral content.

Experimenting with the West Indian type of lemongrass oil, the Puerto Rico Experiment Station, United States Department of Agriculture,[18] found that samples of lemongrass oil exposed to air *and* light suffered the most physical and chemical changes. Their solubility was lowered considerably, the citral content decreased (from 86.07 to 78.81 per cent, after eleven months), and the specific gravity increased (from 0.8971 to 0.9055, after eleven months). The freshly distilled oils were soluble in 3 volumes of 70 per cent alcohol; after eleven months they were soluble in 3.7 volumes of 80 per cent alcohol. At the end of the experiments (eleven months) the oil was viscous and resinous.

Other oil samples exposed to air, but not light, did not deteriorate so much, at least as regards citral content and solubility, which would indicate that light is a detrimental factor. Curiously, the specific gravity of these samples, on standing, increased to a much greater extent (from 0.8719 to 0.9364, after eleven months) than the samples exposed to periodic daylight (see above).

Samples protected from both air and sunlight changed little, their properties remaining practically stable.

Gildemeister and Hoffmann[19] reported the following properties of East Indian lemongrass oil:

Specific Gravity at 15°	0.899 to 0.905, exceptionally as low as 0.895 and as high as 0.911 in otherwise good oils
Optical Rotation	+1° 25′ to −5° 0′
Refractive Index at 20°	1.483 to 1.488
Aldehyde Content:	
Bisulfite Method	70 to 85%
Neutral Sulfite Method	65 to 80%
Solubility	Soluble in 1.5 to 3 vol. of 70% alcohol; occasionally with opalescence or turbidity, due to separation of paraffins

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[18] *Rept. Puerto Rico Exp. Sta.* (1939), 35.

[19] "Die Ätherischen Öle," 3d Ed., Vol. II, 310.

Shipments of genuine East Indian lemongrass oil received and analyzed by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.899 to 0.911; usually 0.900 to 0.906
Optical Rotation	−1° 10′ to −3° 10′
Refractive Index at 20°	1.4855 to 1.4899
Aldehyde Content (Bisulfite Method)	71.8 to 79.1%
Solubility at 20°	Usually soluble in 2 to 2.5 vol. of 70% alcohol; occasionally opalescent or slightly cloudy with more. A few lots were not clearly soluble in 70% alcohol, up to 10 vol.

Chemical Composition.—The main constituent of lemongrass oil was first identified by Bertram[20] and named citral because of its strong lemon odor. The configuration of this aliphatic terpene aldehyde has been the subject of much controversy. For details the reader is referred to the monograph on "Citral" in Volume II of this work, p. 326.

The following substances (listed approximately in order of their boiling points) have been identified in the East Indian type of lemongrass oil derived from *Cymbopogon flexuosus* Stapf (cf. "Chemical Composition of Oil of Lemongrass West Indian").

Myrcene(?). Literature does not offer much evidence that this aliphatic terpene actually occurs also in the East Indian type of lemongrass oil. It is quite an important constituent of the West Indian oil; in fact, the latter oil differs from the former mainly in its content of myrcene. In any case, the East Indian oil appears to contain much less myrcene than the West Indian oil does.

Methyl Heptenone. Identified by Barbier and Bouveault,[21] and by Schimmel & Co.[22]

Limonene(?) and Dipentene. The presence of dipentene and perhaps limonene in lemongrass oil has been reported by Stiehl.[23]

A Terpene(?). Barbier and Bouveault[24] noted still another terpene b. 175°, α_D $-5° 48'$ in some lots of lemongrass oil. It yielded a liquid bromide, which on standing separated small quantities of a solid substance m. 85°. The presence of this terpene in some oils perhaps can be explained by adulteration of the lots in question.

Methyl Heptenol. Isolated by Elze[25] who oxidized the alcohol (b_{759} 178°–180°, d_{15} 0.8579, α_D $-2°$) to methyl heptenone and prepared the semicarbazone m. 135°–136° of this ketone.

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[20] *Ber. Schimmel & Co.*, October (1888), 17. Cf. Tiemann, *Ber.* **32** (1899), 115, 117; **33** (1900), 877.

[21] *Compt. rend.* **118** (1894), 983.

[22] *Ber. Schimmel & Co.*, October (1894), 32. Cf. Tiemann and Semmler, *Ber.* **28** (1895), 2126, footnote.

[23] *J. prakt. Chem.* [2], **58** (1898), 51; **59** (1899), 497.

[24] *Compt. rend.* **118** (1894), 983.

[25] *Riechstoff Ind.* **4** (1929), 23.

Linaloöl(?). Schimmel & Co.[26] reported that linaloöl is probably present in the fraction b. 198°–200°.

Citronellal(?). Doebner[27] expressed the opinion that the oil contains citronellal. It is known that citronellal occurs in East Indian lemongrass oil in quantities of 1 per cent only; in some lots of oil this aldehyde seems to be absent.

n-Decylaldehyde. According to Schimmel & Co.,[28] oil of lemongrass contains small quantities of *n*-decanal, which yielded a semicarbazone m. 102° and could be oxidized to *n*-capric acid.

An Aldehyde(?) $C_{10}H_{16}O$. Schimmel & Co.[29] also noted traces of an aldehyde $C_{10}H_{16}O$, b_6 68°, d_{15} 0.9081, α_D +0° 50′, n_D^{20} 1.45641, which gave a semicarbazone m. 188°–189°, and which was isomeric with citral.

Citral *a* and *b*. The main constituent of East Indian lemongrass oil. Good quality lemongrass oil contains a minimum of 75 per cent of citral (bisulfite method).

Nerol. Elze[30] identified nerol by the preparation of its diphenylurethane m. 52°, and its tetrabromide m. 118°.

Geraniol. This terpene alcohol is contained, free and as ester, in the higher boiling fractions of the oil. Tiemann and Semmler[31] isolated geraniol through its calcium chloride compound and identified the regenerated alcohol by preparation of its diphenylurethane m. 82°.

Farnesol. Elze[32] characterized this sesquiterpene alcohol in the fraction b_5 140°–145° by oxidizing it to farnesal and by preparing the semicarbazone m. 134° of farnesal.

Undoubtedly, East Indian lemongrass oil contains quite a number of still other constituents which are present in small quantities and in traces. Therefore, they can be isolated and identified only when large quantities of the oil are processed.

Use.—Because of its powerful lemon-like odor, oil of lemongrass is used widely for the scenting of soaps, detergents, and all kinds of technical products. The bulk of the oil, however, is employed for the isolation of citral, which, as such, is used in flavors, cosmetics, and perfumes, or is converted into ionones, a group of very important synthetic aromatics possessing a strong and lasting violet odor.

As the starting material for the preparation of the ionones, oil of lemongrass has become one of the most important and indispensable essential oils in the course of the past fifty years. This applies to the East Indian,

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[26] *Ber. Schimmel & Co.*, October (1894), 32; April (1899), 73.
[27] *Ber.* **31** (1898), 1891.
[28] *Ber. Schimmel & Co.*, October (1905), 42.
[29] *Ibid.*, 43.
[30] *Riechstoff Ind.* **4** (1929), 23.
[31] *Ber.* **26** (1893), 2721. Cf. Elze, *Riechstoff Ind.* **4** (1929), 23.
[32] *Riechstoff Ind.* **4** (1929), 23.

as well as to the West Indian, type of lemongrass oil. Large quantities of β-ionone are now employed for the manufacture of synthetic vitamin A.

OIL OF LEMONGRASS WEST INDIAN

As was pointed out in the introduction to the monograph on "Lemongrass Oil," the West Indian type of oil has attained great importance since the outbreak of World War II, when the East Indian oil was no longer readily available, due to shipping difficulties. Extended plantations of the so-called West Indian type of lemongrass, *Cymbopogon citratus* (D.C.) Stapf, were started in several parts of the Western Hemisphere, and large quantities of oil have since been produced. The quality of the oil is now excellent, except perhaps in respect to solubility in 70 per cent alcohol, a factor of little importance.

Lemongrass Oil from Madagascar and the Comoro Islands

The Madagascar and the Comoro Islands have been supplying lemongrass oil, West Indian type, regularly for quite some years. Even before World War II, 50 to 60 metric tons were produced annually on these East African islands and exported (chiefly to France). The oil has been of good quality.

The principal producing regions are located on Madagascar proper, in the most northern part, opposite the small island of Nossi-Bé. The Comoro Islands (located between Madagascar and Zanzibar) also supply substantial quantities of the oil.

The plant was introduced to Madagascar and the Comoro Islands long ago, probably from the French West Indies at the time that France started to colonize those parts of the world. The lemongrass does not seem to occur wild in Madagascar and on the Comoro Islands. Only cultivated plants are used for distillation. The plantations, owned chiefly by large-scale European (French) planters, are extensive, well kept, and play an important secondary role in the operation of agricultural enterprises on the island. Since natural pastures for the grazing of cattle are few in Madagascar and on the Comoros, the cattle have to be fed, in part, with lemongrass, after the oil has been removed by distillation, and after the residual plant material has been sweetened by the addition of a little molasses from sugar cane. Thus, the essential oil, which must first be extracted to make the grass palatable to cattle, becomes almost a by-product.

The grass requires much sunshine, occasional rainfall, a warm tropical climate, and some atmospheric humidity, even during the dry season. Excessive rainfall is detrimental to the quality of the oil, as during periods of heavy rains the citral content will be about 5 per cent lower than during the dry season. The grass flourishes best on a well-drained, sandy, or sandy-loamy soil.

Prior to planting, the soil must be loosened by thorough plowing. Planting usually takes place from December to January (the rainy season). The plants are reproduced by root division (segments), and not by seed, since *Cymbopogon citratus* very rarely develops flowers and seed. Holes about 10 in. deep are dug into the ground with a crowbar, and the root segments are planted 1.5 or 2 ft. apart, in rows about 3 ft. apart. The holes are tightly filled with earth to facilitate development of a good root system. Depending upon climatic and soil conditions, the young plants require from four to six months to develop sufficiently to be cut for the first time. After the first harvest, the grass grows rapidly, and, depending upon the rainfall, can be cut every three or four months. In other words, three or four annual harvests are possible. The cutting is done by hand (machetes), with the help of hired native labor. In the Comoro Islands the cut leaf material is sometimes left lying in the fields for three or four days before being transported to the distilleries. In Madagascar the leaves are usually distilled right after cutting. No strict rules hold, however, in this respect, all depending upon the daily exigencies.

A planting should last at least four years. If it is started on fertile ground, and properly cared for, its life span may be nine years. Lemongrass is quite a soil-exhausting plant, and requires potash and phosphate fertilizers. After lemongrass, leguminous plants such as peas should be planted to enrich the soil again. After six months, the leguminosae may be plowed under.

The grass is distilled either by direct steam distillation or by "steam *and* water" distillation. The direct steam stills have a capacity of about 3,000 liters, a charge consisting of about 800 to 1,000 kg. of plant material. The pressure in the steam generator is about 7 kg. Distillation of one charge lasts about 1 hr. During the height of the season up to fourteen charges are distilled daily in each still. The distilleries, located on Madagascar proper, and on Nossi-Bé, usually contain three to five stills each.

The "steam *and* water" stills also have a capacity of about 3,000 liters. The plant material is supported by a perforated grid, beneath which water is brought to a boil by a steam jacket. In the steam jacket the steam pressure is 3 to 3.5 kg. Distillation of one charge lasts for several hours, because the steam pressure is much lower than in direct steam stills.

Exhausted, sun-dried grass is used as fuel, coal being too expensive in Madagascar and the Comoro Islands.

The yield of oil varies from 0.2 to 0.4 per cent, and depends upon season and condition of the plant material. It is relatively higher during the dry season.

One hectare of lemongrass yields from 50 to 80 kg. of oil per annum, the yield depending, of course, upon the age of the plantation. (This represents a yield of approximately 44 to 71 lb. of oil per acre and per year.)

In comparison with these figures, the Puerto Rico Experiment Station, U. S. Department of Agriculture,[33] obtained experimental yields of lemongrass oil ranging from 67.65 lb. to 98.18 lb. per cutting and per acre, four cuttings being made in one year. The total yield of oil per year and per acre in 1938 was 312.05 lb.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 5. Production of lemongrass oil in Madagascar. View of a distillery on one of the plantations.

The quality of the oil produced in Madagascar and on the Comoro Islands is good, the physicochemical properties being normal for the West Indian type of lemongrass oil.

Chemical Composition.—The fact that citral is the main constituent of West Indian (as well as of East Indian) lemongrass oil has been known for a long time. Years ago, Umney and Bennett[34] observed, however, that on fractional distillation the two types of oil behave differently. The East Indian oil starts boiling only above 210°, whereas, at that temperature, 23 per cent of the West Indian oil has already distilled over. Comparative distillation tests at reduced pressure, and separation of each oil into five equal fractions, showed that the physicochemical properties of the corre-

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[33] *Rept. Puerto Rico Exp. Sta.* (1939), 30.

[34] *Chemist Druggist* **70** (1907), 138. Cf. DeJong, *Teysmannia* (1907), No. 8. Watts and Tempany, *West Indian Bull.* **9** (1908), 265. *Ber. Schimmel & Co.*, April (1909), 58; October (1908), 75.

sponding fractions of the two oils displayed considerable differences: the West Indian type yielded optically inactive fractions only, whereas the fractions of the East Indian oil had rotations ranging from −12° to −2°. As far as the specific gravity is concerned, the first fraction of the West Indian oil (20 per cent of the total) assayed 0.821, whereas that of the East Indian type was 0.882. This indicates the presence of an olefinic terpene (myrcene!) in the West Indian oil. As a matter of fact, the two types of oil differ principally in the occurrence of substantial quantities of myrcene in the West Indian oil. The presence of myrcene in this oil also influences its solubility in dilute alcohol. Freshly distilled West Indian oils are soluble in 70 per cent alcohol but lose their solubility on aging, which fact is probably caused by diene-condensation and polymerization of myrcene.

According to Naves and Auriol,[35] both types of lemongrass oil contain from 75 to 85 per cent of citral, but the West Indian oil also contains some other aldehydes (aside from citral) which are difficult to remove from the citral and may cause trouble in the technical separation and purification of citral.

The most complete investigation of the West Indian type of lemongrass oil (origin: equatorial Africa and Comoro Islands), derived from *Cymbopogon citratus* Stapf, is that of Naves,[36] who noted the presence of the following compounds:

Isovaleraldehyde. In the fraction b. 90°–110°. Oxidation with silver oxide in an alkaline medium gave a valeric acid, the silver salt of which contained 51.31 per cent of silver.

Furfural. This content of silver indicated the presence (in much smaller quantity) of furfural. Confirmed by color reaction.

Myrcene. The largest constituent (next to citral) of the West Indian type of lemongrass oil is myrcene, which comprises 12–19 per cent of the oil produced in the Comoro Islands, and 18–20 per cent of the oil distilled in equatorial Africa. The isolated myrcene, rectified repeatedly over metallic sodium, had these properties: b. 168°–169°, b_{12} 53°–55°, d_{15} 0.7943, α_D ±0°, n_D^{15} 1.4698. Hydrogenation with sodium and alcohol gave dihydromyrcene which yielded a tetrabromide m. 93°–94°. (Incidentally the West Indian type of lemongrass oil is the best raw material for the isolation of myrcene.)

Dipentene. Aside from some slightly laevorotatory monocyclic terpenes, the terpene fraction of the oil, b_{12} 55°–58°, contained traces of dipentene which was identified through its tetrabromide m. 124°.

Methyl Heptenone. Isolated from the fraction b_{12} 55°–65°, by means of the solid bisulfite compound, and identified through its semicarbazone m. 136°–137°. The total oil contains 0.2–0.3 per cent of methyl heptenone.

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[35] *XVII Congrès de Chimie Industrielle, Paris* (1937), 83.

[36] *Parfums France* **9** (1931), 60.

An Aldehyde(?) $C_{10}H_{16}O$. On treating the fraction b_{12} 78°–88° with a 35 per cent solution of bisulfite, Naves obtained a mixture (yield 0.05 per cent of the total oil) rich in aldehydes, the most typical fraction of which had these properties: b_{10} 78°–80°, d_{15} 0.9068, n_D^{21} 1.4631; semicarbazone m. 191°–192°. This aldehyde exhibited a disagreeable, camphor-like odor. It is, perhaps, identical with the aldehyde $C_{10}H_{16}O$ which Schimmel & Co.[37] had noted in East Indian lemongrass oil, and which gave a semicarbazone m. 188°–189°.

Citronellal. Observed by Naves[38] in the fraction b_{12} 88°–93°. Separation of citronellal by means of the solid bisulfite compound was unsatisfactory and gave an impure product, probably contaminated with the aforementioned aldehyde $C_{10}H_{16}O$. By repeated fractionation accompanied by heavy losses, Naves obtained a substance b_{10} 88°–89°, d_{15} 0.859, α_D $-0°23'$, n_D^{15} 1.4504. The content of citronellal in West Indian lemongrass oil hardly exceeds 0.1 per cent.

n-Decylaldehyde. Separated from the fraction b_{12} 93°–100° by means of the solid bisulfite compound, and identified by preparation of the semicarbazone m. 101°–102°. The content of *n*-decylaldehyde in West Indian lemongrass oil is less than 0.1 per cent; in some lots of oil the aldehyde seems to be absent.

An Aldehyde or Ketone(?). From the mother liquors of extraction, Naves regenerated a mixture of substances (with an odor of acetophenone) n_D^{15} 1.5110, giving Tollens aldehyde reaction. A semicarbazone melted at 229°–231°. The oil examined contained only minute traces of this aldehyde or ketone.

Citral *a* and *b*. The chief constituent of West Indian lemongrass oil is present in the fraction b_{12} 104°–106° as a mixture of the *a* and *b* isomers. The respective semicarbazones melted at 162°–164°, and at about 132° (not clearly).

According to Naves,[39] the West Indian type of lemongrass oil contains 65–86 per cent of citral (determined by the sodium bisulfite method).

Farnesal. Using the bisulfite method, Naves isolated very small quantities of farnesal from the high boiling fractions b_5 130°–180° of the oil, 120 kg. of oil giving only 12 g. of farnesal $b_{2.5-3.0}$ 135°–140°, d_{17} 0.896, α_D $\pm 0°$, n_D^{17} 1.4988; semicarbazones m. 133°–134°, and m. 134°–135°.

α,β-Dihydropseudoionone. From the odor of the first fraction of farnesal, Naves suspected the presence of α,β-dihydropseudoionone, whose occurrence along with farnesal may be anticipated by reason of their genetic relations, which are analogous to those of methyl heptenone and citral. After destruction of the aldehydes by silver oxide, Naves obtained a semicarbazone from the neutral fraction which, on mixing with the semicarbazone m. 94° of α,β-dihydropseudoionone (obtained by splitting of the farnesal isolated from the oil), melted at 91°–92°.

Esters: (Iso?) Valerates, Caprylates, Caprates, Citronellates, Geranates, and Nerates. The esters present in the West Indian type of lemongrass oil are contained in the fractions distilling after citral. They consist chiefly of (iso?) valerates, caprylates, caprates, citronellates, and geranates.

Citronellic acid could not be obtained in pure form but was evidenced by the properties of the fraction b_3 115°–125°, d_{15} 0.9453, n_D^{20} 1.4610. The higher fractions (93 g. from 125 kg. of oil) contained some geranic acid $C_{10}H_{16}O_2$, b_3 127°,

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[37] *Ber. Schimmel & Co.*, October (1905), 42, 43.

[38] *Parfums France* **9** (1931), 60.

[39] *Ibid.*, 71.

d_{15} 0.9730–0.9690, α_D ±0°, n_D^{20} 1.4836–1.4809, and undoubtedly was accompanied by its isomer, viz., neric acid. On reduction with sodium and alcohol, geranic acid gave (75 per cent yield) citronellic acid b_6 133°–135°, d_{15} 0.9291, α_D ±0°, n_D^{15} 1.4553, whereas on treatment with 75 per cent sulfuric acid at room temperature it cyclized to isogeranic acid m. 105°.

Alcohols. The alcohol fraction b_{12} 60°–98° of West Indian lemongrass oil is rich in tertiary alcohols, as evidenced by the difference in the percentage of free alcohols found by acetylation and by cold formylation (63.2 and 93.4 per cent, respectively).

Methyl Heptenol. Naves isolated methyl heptenol b. 176° (corr.), b_{12} 76°–78°, d_{15} 0.8581, α_D −1° 15′, n_D^{20} 1.4506 by means of its boric ester, and identified it through its allophanate m. 98°–99°.

l-Linaloöl. B_{10} 80°–82°, d_{15} 0.873, α_D −6° 30′, n_D^{20} 1.4620; identified through its phenylurethane m. 63°–64°.

α-Terpineol. B_{12} 96°–98°, d_{15} 0.9323, α_D −0° 36′, n_D^{20} 1.4884; identified through its phenylurethane m. 111°–112°.

Isopulegol. The impure α-terpineol was accompanied by some isopulegol which, on chromic oxidation, gave isopulegone, the semicarbazone of which melted at 172°.

The minimum content of these secondary and tertiary alcohols in the oils examined by Naves was 0.5 per cent, one-tenth of which was α-terpineol.

Geraniol. After the oil had been freed from aldehydes and saponified, the fraction b_{12} 98°–118° represented 0.5 to 0.9 per cent of the total oil, and contained 70 to 75 per cent of primary alcohols. From this fraction Naves isolated geraniol b_{12} 114°–115°, d_{15} 0.8833, α_D ±0°, n_D^{15} 1.4784 by means of its calcium chloride addition product, and identified it through its silver phthalate m. 132°–133°.

Nerol. The alcohols which did not react with calcium chloride contained some nerol which was characterized through its tetrabromide m. 117°–118°, and its diphenylurethane m. 52°.

Citronellol. Whether the oil contains citronellol remains an open question. The properties b_{12} 114°–116°, d_{15} 0.8813, α_D −0° 21′, n_D^{20} 1.4795 of the mixture (resulting from the phthalic treatment of the total fraction) exclude the possibility that an appreciable quantity of citronellol is present.

Farnesol. The fraction b_5 140°–146°, d_{15} 0.892, α_D −0° 12′, n_D^{15} 1.4897, on oxidation in the usual way, gave farnesal (semicarbazone m. 134°–135°) which indicates that the parent alcohol in question was farnesol.

A Bicyclic Sesquiterpene(?). The sesquiterpene fraction amounted to 1 per cent of the total oil. The sesquiterpenes consisted chiefly of a bicyclic sesquiterpene b_8 124°–126°, d_{15} 0.9166, α_D −9° 10′, n_D^{15} 1.5034, which was accompanied by monocyclic sesquiterpenes b_8 128°–132°, d_{15} 0.8984, α_D ±0°, n_D^{15} 1.4978. No crystalline chlorides or bromides could be obtained.

α-Camphorene and Other Diterpenes(?). The diterpene fraction of the oil investigated by Naves was comparatively large, amounting to 2–3 per cent of the total oil. It appeared to contain some optically inactive α-camphorene, along with one or more other inactive diterpenes, possibly bicyclo- or tricyclocamphorenes. For details the reader is referred to the original literature.

In the water oil (obtained by redistillation of the distillation waters) Naves observed *diacetyl, acetone, eugenol,* and other *phenols* (?).

To summarize, the West Indian type of lemongrass oil has the following composition:

Terpenes..... Myrcene (12–20%)
    Dipentene (traces only)

Alcohols
(1–1.5%)... Methyl Heptenol
    Linaloöl
    α-Terpineol
    Geraniol
    Nerol
    Citronellol(?)
    Isopulegol
    Farnesol

These alcohols occur in the oil free or esterified with
    Isovaleric Acid
    Caprylic Acid
    Capric Acid
    Citronellic Acid(?)
    Geranic Acid, and
    Neric Acid(?)

Aldehydes.... Citral *a* and *b* (65–86% by the Bisulfite Method) and other aldehydes (less than 0.1%):
    Furfural
    Isovaleraldehyde
    Decylaldehyde
    Citronellal
    An aldehyde $C_{10}H_{16}O$; semicarbazone m. 191°–192°
    An aldehyde or ketone; semicarbazone m. 229°–231°
    Farnesal

Ketones..... Diacetyl } in the forerun
    Acetone }
    Methyl Heptenone (0.2–0.3%)
    Furthermore, traces of:
        A ketone or aldehyde; semicarbazone m. 229°–231° (see above)
        α,β-Dihydropseudoionone

Sesquiterpenes...	Mostly bicyclic (ca. 1%)
Diterpenes... (2–3%)	α-Camphorene A bicyclocamphorene(?)

Recently Naves[40] reported that the oil of lemongrass distilled from *Cymbopogon flexuosus* Stapf in Guatemala contains about 0.7 per cent of a *diterpene ketone* $C_{20}H_{30}O$ which combines with the P reagent of Girard and Sandulesco under the usual conditions.

Purified by distillation the ketone exhibited these characteristics:

$b_{1.7}$	157°–158°	α_D	Inactive
d_4^{20}	0.9496	n_D^{20}	1.52060

The ketone could be oximized only with difficulty, even on boiling; it reacted very slowly with sodium bisulfite. Naves did not succeed in obtaining a semicarbazone. A dinitro-2,4-phenylhydrazone m. 128°–128.5° gave no satisfactory analysis.

As can readily be seen, the lemongrass oils are of a qualitatively complex composition. According to Naves,[41] this explains the noted differences in the olfactory value of the citrals isolated from the oils, even when purified up to a 100 per cent aldehyde content. It is somewhat difficult to free the citral entirely from other aldehydes and ketones which accompany it.

It has occasionally been asserted that the West Indian type of lemongrass oil is qualitatively inferior to the East Indian type, due to its poorer solubility. This is no criterion, however, owing to the ease with which myrcene and its condensation products may be eliminated. Lately large quantities of the West Indian type of lemongrass oil possessing a high content of citral have been produced in Central America and in some of the West Indian Islands, particularly Haiti. During World War II the American manufacturers of natural isolates and synthetics were dependent almost entirely upon the West Indian type of oil, and much progress both in the production of the oil and in the methods of isolating the citral has been made. With proper precautions in the process of extraction the citral derived from the West Indian lemongrass oil is equally as good as that from the East Indian.

Lemongrass Oil from Guatemala

Development.—The origin and development of the lemongrass oil industry in Guatemala closely parallel those of the citronella industry in the same country (cf. the monograph on "Citronella Oil from Guatemala"). Both

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[40] *Perfumery Essential Oil Record* **39** (1948), 346.

[41] *Parfums France* **9** (1931), 71.

plants were introduced in Los Cerritos by Mr. Julio Samayoa during World War I on an experimental basis. These plantations, later taken over by Mr. René Keilhauer, were subsequently greatly enlarged by his son, Mr. Minor Keilhauer. The industry reached its peak of production during World War II, when shipping difficulties prevented imports of the East Indian oil to the United States and other countries of the Western Hemisphere. At that time, America had to rely almost entirely upon the lemongrass oil produced in Guatemala (and Haiti).

The following production figures[42] will give an idea of the remarkable development of the Guatemala lemongrass industry:

	Pounds
1938	29,500
1939	63,915
1940	116,229
1941	139,751
1942	164,423
1943	190,542
1944	184,908
1945	109,265
1946	109,423
1947	129,977
1948	142,000
1949	135,000

In the course of World War II many new producers entered the field, as the then prevailing high price of oil (up to $5.00 per lb.) permitted good profits. Since then, however, prices have declined as a result of the reappearance of the East Indian product on the market. The bulk of the Guatemala oil is produced today by three large-scale operators, located in Los Cerritos, Retalhuleu, and San Felipe. A number of the smaller growers will probably lose interest in lemongrass, when prices no longer cover operating expenses.

Producing Regions.—In Guatemala, lemongrass oil is produced near the Pacific Coast, in the Departments of Retalhuleu, Suchitepequez, and Escuintla. The total acreage planted with lemongrass in Guatemala at the beginning of 1950 was 1,200 hectares.

Climate, Soil, and Altitude.—Lemongrass grows well at altitudes ranging from 400 to 2,000 ft. above sea level. The plant requires a tropical climate, abundant sunshine, and occasional heavy rains. It is not so much affected by climatic conditions as the citronella plant. Growing in much poorer soil, it can be planted in many places where citronella would not thrive. In general, lemongrass is a hardier plant than citronella and more resistant to

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[42] The author is greatly indebted to Mr. Carlos Schaeuffler of Retalhuleu, one of the largest essential oil producers in Guatemala, for much of the data contained in this monograph.

drought. In Guatemala the lemongrass fields are not irrigated, and no fertilizers are used.

Planting, Cultivating, and Harvesting.—In Guatemala the lemongrass plant (which is of the West Indian type—*Cymbopogon citratus* [D.C.] Stapf) never flowers; propagation, therefore, has to be effected by root division. The stool of a full grown plant yields ten segments. For replanting, each segment is cut to a length of about 2 ft. At the beginning of the rainy season (in May), the segments are set out 3 ft. apart, in rows also 3 ft. apart. Three to four segments are planted into each hole, which should be about 6 in. deep. Deeper planting is dangerous because the plants may develop root rot during the rainy season.

The leaves can be cut for the first time eight months after planting, and then every three months, which permits four annual harvests. Except for weeding and cleaning of the fields, not much cultivation is necessary. The plants are cut by hand with machetes—a practice involving a great deal of labor and constituting the largest item in the total cost of the oil. After four years, the productivity of a lemongrass field declines to such a point that the planting should be renewed.

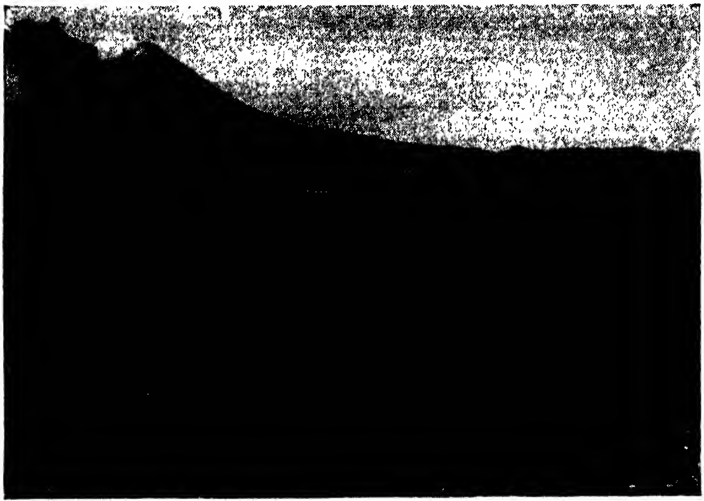
Recently, mechanized methods of farming have been introduced on certain large estates devoted to the cultivation of lemongrass and citronella. Distilling equipment also has been modernized.

Distillation and Yield of Oil.—In Guatemala, lemongrass is usually distilled while still fresh and green. The leaves are cut in the morning, then bundled and hauled to the distilleries to be distilled in the afternoon. As a result, some of the cut grass is half dried, but nevertheless still green.

Prior to distillation, the leaves should be reduced to short lengths in specially constructed, heavy-duty ensilage cutters. This facilitates charging of the stills.

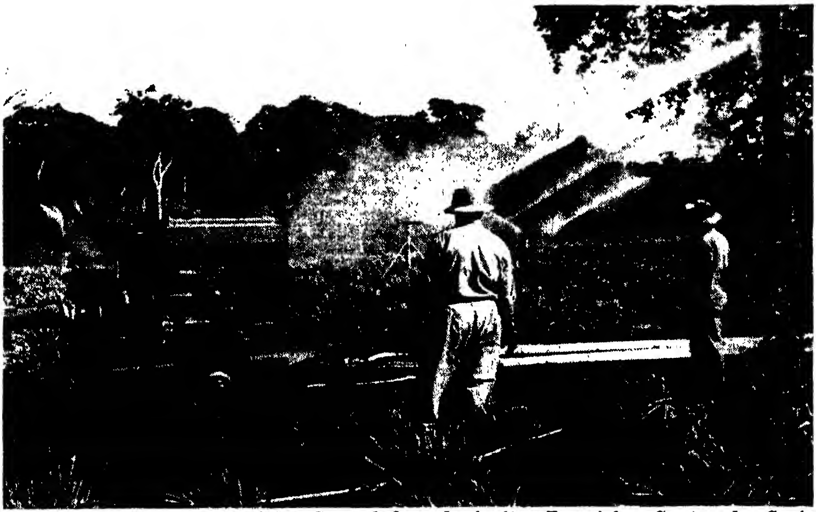
The stills are of the same type as those employed for the processing of citronella (cf. the monograph on "Citronella Oil from Guatemala"). Distillation time is somewhat shorter than in the case of citronella. Prolonged distillation yields oils of low citral content; short distillation gives oils high in citral. During the rainy season the citral content of the oil is generally lower than during the dry season.

According to information given the author by the Oficina Controladora de Aceites Esenciales, Guatemala, C. A., in commercial production, the yield of oil per acre per year declines with the age of a field. Figures furnished by the Oficina in 1950 indicate that, with 3 or 4 cuttings per year, annual yield of oil per acre (in large-scale production) was 96 lb. in the first year, 74 lb. in the second, 66 lb. in the third, and 48 lb. in the fourth. Average yield of oil per acre per year was thus 71 lb.



Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 6. Production of lemongrass oil in Guatemala. View of a large plantation.



Courtesy of Oficina Controladora de Aceites Esenciales, Guatemala, C. A.

FIG. 7. Production of lemongrass oil in Guatemala. View of the modern overhead irrigation system with rotating sprayers, being introduced at present on many plantations of Guatemala's Pacific Coast.

In experiments conducted by Loustalot and Pol,[43] East Indian lemongrass outyielded the West Indian in terms of fresh grass produced, but the yield of *oil* per acre was greater in West Indian grass cut at maximum and low height because the percentage of oil was higher. East Indian grass cut at medium height yielded more oil than West Indian grass cut at the same time, because the percentage of oil was about the same and the East Indian variety yielded more grass. The average annual yield of oil per acre from plots of West Indian grass cut ten, seventeen, and nineteen times over a three year period was 131.0 lb., 132.3 lb., and 110.5 lb., respectively. The average annual yield of oil per acre from East Indian grass harvested at a height of 2.5 ft. was at least 100 lb. more than when the grass was cut at maximum or at low height. The percentage of oil was consistently higher in the West Indian grass, but there was no marked or consistent difference in citral content between the two varieties or among the three harvest treatments.

Use of Residual Leaf Material.—Recently one of the largest lemongrass oil producers in Guatemala erected a factory for the purpose of converting the spent leaf material (after distillation) into paper. Obviously, this will mean a substantial economy in the production cost of the oil and enable the producer to compete more easily with the low-priced East Indian oil.

Physicochemical Properties.—The Guatemala lemongrass oil has usually been of excellent quality, a result of the efficient method of distillation generally employed in that country. The properties fall within the limits of the West Indian type of lemongrass oil.

Numerous shipments imported and analyzed by Fritzsche Brothers, Inc., New York, had properties ranging within these limits:

Specific Gravity at 15°/15°	0.876 to 0.888
Optical Rotation	−0° 4′ to −1° 8′
Refractive Index at 20°	1.4830 to 1.4877
Aldehyde Content (Bisulfite Method)	75% to 81.5%
Solubility	Hazy to cloudy in 1 vol. and more of 80% alcohol, followed by separation of polymyrcene

Samples of oils containing less than 75 per cent of aldehydes (citral) have been examined. However, all contracts today are written on a minimum citral content (bisulfite method) of 75 per cent. This applies to the average citral content of all drums included in the shipment. A discount is allowed on any shipment with an average citral content of less than 75 per cent.

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[43] *Agron. J.* **41** (1949), 375. *Chem. Abstracts* **43** (1949), 8448.

Export.—Guatemala lemongrass oil is now exported through the Oficina Controladora de Aceites Esenciales, Guatemala City, an association founded in May 1948 and acting as consolidated shipping agency. It handles all essential oils produced in Guatemala. (For details see the monograph on "Citronella Oil from Guatemala").

Lemongrass Oil from Haiti [44]

As in most tropical countries where French is spoken, in Haiti lemongrass is commonly called "citronelle." Nothing is known about the introduction of the plant to the island. Before 1937 no plantations existed, and lemongrass was simply one of the scattered aromatic plants that thrived in the gardens of peasants and were used chiefly for the making of infusions supposed to cure tropical fevers. However, since 1937 (particularly during World War II), regular plantations of lemongrass have been started. These now cover more than 2,000 acres. The tendency is toward a further increase, despite the substantial decline in the price of the oil since the end of the war.

In Haiti oil of lemongrass, like sisal, cannot be produced by small growers and peasants. Only large-scale planting, intelligent field management, proper fertilization, and mechanized agricultural methods enable the producers to withstand heavy price fluctuations on the world market and to compete with the oil from East India. Consequently, lemongrass has never been grown outside of the plantations owned by large producers.

All existing fields are located near the distilleries. Plantations have been established and are in actual production at Ducis, Maniche, Fonds des Nègres, Hinche, and St. Michel de l'Attalaye. Experiments with plant selection, fertilization, mechanical cultivation and harvesting by means of specially constructed harvesting machines are being conducted. Although labor in Haiti is (seemingly) cheap, the cost of production is nevertheless high; and at a price of $1.00 per pound of oil, c.i.f. New York (1948), the distillers can hardly compete with the East Indian oil, unless they resort to modern field management and mechanized agriculture.

In Haiti the lemongrass plant yields a normal oil, provided it is grown in good soil, up to 1,500 ft. altitude. At high elevations (which usually receive more rainfall than the low altitudes) the factor of sunlight has to be considered, as this influences the citral content of the oil. At high altitudes the plants should be set out in rows 42 in. apart in one direction, and 36 in. apart in the other. The orientation should be east-west, to obtain a maximum of sunshine.

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[44] The author is greatly obliged to Senator Louis Dejoie, Port-au-Prince, Haiti, for much of the data contained in the monograph on Haitian lemongrass oil.

The grass is ready for cutting when two-thirds of the leaves have fully matured, i.e., when the tips have begun to dry out. A newly established plantation can usually be harvested for the first time eight months after planting. If the field is irrigated subsequent cuttings may take place every three or four months. In general, an irrigated plantation permits three harvests per year, whereas a nonirrigated field gives only two crops per year. The yield of grass per acre depends upon the fertility of the soil (particularly its nitrogen and potassium content), the number of weedings, the amount of rainfall, and the height to which the plants were cut during the preceding harvest. The percentage of citral in the oil is influenced by the amount of sunshine and the degree of plant maturity. Young plants or young shoots should never be distilled; they may yield more oil than older plants, but the oil will be deficient in citral.

Lemongrass represents one of the most soil-exhausting grasses known; it requires intelligent management to maintain a field in good production more than four years. Aside from nitrogen, potassium is the most important growth element.

After cutting, the grass is left in the fields for one day to reduce the moisture content. Drying for one day does not reduce the yield of oil, yet greatly facilitates loading of the trucks and packing of the grass (leaves) into the stills.

Prior to distillation the grass is chopped up in an ensilage cutter and then tramped into the retorts to prevent steam channeling. In Haiti distillation is conducted in one of the most modern tropical essential oil distilleries, with direct steam of constant pressure of 40 lb. per sq. in. (measured in the steam boiler). Water condensed within the retort is drawn off and eliminated after completion of each batch, which to distill requires about 3 hr. One metric ton of grass yields about 1 gal. of oil, a yield of about 0.35 per cent. One particular distillery equipped with 16 stills of 2.5 metric tons capacity each, and using a steam boiler of 300 h.p. capacity, can produce 5 drums of oil per 24 hr. Fifteen trucks are required to haul the cut grass from the fields and to carry the exhausted grass back to the fields for fertilizing purposes. On an average, the grass from 700 acres can be processed in a month. If not used for petitgrain, vetiver, or citronella, the distillery is then shut down until the next lemongrass crop is ready.

After completion of one charge, the exhausted grass is removed from the retort by hand, or by means of an electrically driven hoist, and dumped into trucks that haul it back to the fields or to the compost pit. When spread over the fields, the exhausted grass, together with fertilizers, will help substantially in checking weed growth and in returning to the soil the food elements absorbed by the living plants. Having been sterilized in the course of distillation, the exhausted grass, unfortunately, requires at least six months for decomposition, and the subsequent crop does not get the benefit of all the plant food that the decaying grass contains. Therefore, in the first ensuing crop, the exhausted grass acts only as a mulch, the role of which in the tropics is well known and appreciated, particularly during periods of low rainfall.

Total Production.—The following statistics give a good indication of the development of Haiti's lemongrass oil industry from 1941 to 1949 inclusive:

Fiscal Year	*Quantity of Oil in Kilograms*
1941–1942	2,093
1942–1943	6,303
1943–1944	2,968
1944–1945	4,743
1945–1946	8,071
1946–1947	23,903
1947–1948	33,422
1948–1949	24,175

Production could be increased substantially should demand and prices warrant it, and one day Haiti may easily rank among the largest lemongrass oil producing countries of the world.

Physicochemical Properties.—The Haitian lemongrass oil has properties characteristic of the West Indian type. The bulk of the oil, on analysis, exhibits a citral content higher than 76.5 per cent.

Numerous lots imported and examined by Fritzsche Brothers, Inc., New York, have had properties varying within these limits:

Specific Gravity at 15°/15°	0.883 to 0.898
Optical Rotation	−0° 8′ to −0° 27′
Refractive Index at 20°	1.4842 to 1.4888
Aldehyde Content (Bisulfite Method)	73.5 to 81.5%
Solubility	Cloudy up to 10 vol. of 80% alcohol, followed by separation of polymyrcene

Regarding the aldehyde (citral) content of commercial shipments, see also the monograph on "Lemongrass Oil from Guatemala."

Lemongrass Oil from Honduras

During World War II efforts were made to produce oil of lemongrass in the lowlands of Honduras (C. A.), near the Atlantic seashore. Almost 50,000 lb. of oil were in fact produced from 1942 to 1947. The reappearance of the East Indian oil on the North American market then caused such a sharp fall in prices that most of the lemongrass acreage in Honduras was converted to the growing of other, more profitable crops. Moreover, when five years old, the grass had declined to a point where harvesting became almost uneconomical. This was accompanied by a decline of the citral content of the oil from the required 75 to 70 per cent.

The whole venture in Honduras cannot be considered too successful, perhaps for the reason that the grass was planted in unsuitable soil. Throughout the years of actual production and experiments, which were carried out carefully and systematically, the yield of oil per acre was low, ranging from 12 to 72 lb. per cutting in extreme cases, and from 30 to 50 lb. in most cases. The yield of oil per acre and per year was 86 to 172 lb. with three annual cuttings, and on the average about 140 lb. The grass was cut only three times a year, because the slight increase in oil obtained by harvesting every two or three months was not sufficient to counterbalance the additional cost of harvesting.

The yield of oil per acre gradually increased as the grass became better established, but it was low whenever the grass was cut during heavy rains.

It was found that the grass should be left in the fields to dry for 3 to 5 days prior to distillation, the length of drying time depending upon weather conditions.

Before being distilled, the grass was run through twin power cutters, and mechanically conveyed into the stills. Distillation of one batch required 2 hr. and 45 min. for complete exhaustion of the grass at 5 lb. steam pressure. The cutting of the grass and the charging of the still required an additional half hour.

The yield of oil varied from 0.23 to 0.58 per cent.

The citral content of the oil ranged from 70 to 82 per cent.

Shipments of lemongrass oil from Honduras, received and examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°..	0.877 to 0.885
Optical Rotation...........	−0° 8′ to −0° 21′
Refractive Index at 20°.....	1.4831 to 1.4858
Aldehyde Content (Bisulfite Method)................	75 to 82.5%
Solubility..................	Cloudy in 1 vol. and more of 80% alcohol

As regards the citral content of commercial shipments, see the monograph on "Lemongrass Oil from Guatemala—Physicochemical Properties."

Before concluding this section it should be mentioned that a sort of dermatitis appeared on the hands of laborers who handled wet lemongrass. Gloves were tried for protection, but decomposed after a few hours' use. Eventually a cold cream proved very effective in curing existing skin eruptions and in preventing further outbreaks.

Lemongrass Oil from Puerto Rico

In 1935 the Experiment Station of the U. S. Department of Agriculture in Mayaguez, Puerto Rico, began an extensive investigation of certain aromatic plants, among them lemongrass. Many factors important in the successful production of lemongrass oil have been thoroughly studied—for example, the influence of climate, soil, light, propagation, harvesting methods, damage by insects and diseases, and methods of distillation. The results of this work have been published by Jones and Arrillaga.[45] Space permits citation of only a few points as summarized by these authors:

Courtesy of United States Department of Agriculture, Experiment Station, Mayaguez, Puerto Rico.

FIG. 8. Division of a lemongrass stool into pieces for propagation. Left, whole stool after the removal of leaves. Center, part of the stool in the process of being divided. Right, one of the many "seed pieces" obtained.

1. The grass should be propagated by division of stools and planted 4 to a hill every 2 ft., in rows 3 ft. apart. Planting is best done during the rainy season.
2. Lemongrass thrives in a well-drained soil; it can be grown on hillsides as a soil-conserving grass.
3. Lemongrass responds to fertilization with compost, manure, nitrogen, and potash.
4. The plant should not be shaded.
5. Lemongrass is best cut about four times a year at a height of 2½ to 3½ ft.
6. The grass (leaves) can be harvested at the rate of 20 to 50 tons per acre per year.
7. Prior to steam distillation the fresh leaves should be chopped.

In the author's opinion, those suggestions of Jones and Arrillaga which concern distillation with high-pressure steam, particularly, cannot be applied to industrial production without having first been tried out on a large scale. The cost of specially constructed stills, and other economic factors, will have to be considered. It should be kept in mind that the findings of Jones and Arrillaga, most interesting and detailed though they are, have

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[45] "Experiments with Lemongrass in Puerto Rico," *Fed. Expt. Sta., U. S. Dept. Agr., Mayaguez, Puerto Rico* (Publication forthcoming).

been the result of work on a small experimental scale, carried out chiefly in pilot stills.

Puerto Rico has not yet produced commercial quantities of lemongrass oil. Nevertheless, the Agricultural Experiment Station in Mayaguez has rendered a service of incalculable value to the whole essential oil industry of America, by freely distributing planting material to Central and South American countries during World War II. This enabled several countries to develop into large producers of lemongrass and citronella oil at a time when the Western Hemisphere was almost entirely cut off from its former supplies in Asia.

A small shipment of lemongrass oil produced experimentally by the Agricultural Experiment Station in Mayaguez and examined by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°/15°	0.902
Optical Rotation	−0° 12′
Refractive Index at 20°	1.4880
Aldehyde Content (Bisulfite Method)	74.8%
Solubility	Soluble in 0.5 to 1 vol. of 80% alcohol, cloudy with more

The oil was of excellent quality; it had no odor of methyl heptenone.

Lemongrass Oil from Florida

The first experiments toward the production of lemongrass oil in the United States (in the Everglades of Florida) were made by Hood.[46] Almost twenty-five years later the United States Sugar Corporation started production on a commercial scale near Clewiston, Florida. The venture flourished for a short time because, during the early years of World War II, prices of the oil reached about $4.00 lb. Moreover, the East Indian product was not easily available, and production in Guatemala and Haiti was still limited. The American oil, therefore, found a ready market.

The lemongrass industry of Florida was based upon the principle of utilizing the spent (distilled) grass as cattle feed. The spent grass was chopped, dehydrated in an Arnold dehydrator, and then sweetened with cane molasses supplemented with a small quantity of protein concentrate, such as soybean or peanut meal. This feed permitted producers to "finish" large numbers of range steers to a high degree, without the use of any grain whatsoever. In the whole program the essential oil was, therefore, merely a by-product. To off-set the high cost of labor, Florida's lemongrass industry had to be established from the beginning on a highly mechanized basis. The

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[46] *U. S. Dept. Agr., Bull.* No. 442 (1917), 1.

reader interested in details will find valuable information in several papers by Dr. B. A. Bourne,[47] who directed the whole project. The venture was not successful, however, for the simple reason that, in the course of a few years, the cost of production more than doubled through increased costs of labor and materials. These increases were not adequately compensated for in the sales price of the oil. On the contrary, after World War II, the price of lemongrass oil declined to about $1.00 lb., and production in Florida was abandoned.

Nevertheless, it may be of interest to report the yields of oil obtained in the low organic, sandy soil on which the grass was grown in Clewiston. According to Bourne,[48] the following yields, obtained under curtailed cropping, are representative of average yields from one annual harvest, under conditions prevailing near Clewiston:

Cropping Period	*Acres Harvested*	*Average Yield per Acre* *Tons of Grass*	*Average Yield per Acre* *Pounds of Oil*	*Pounds of Oil per Ton of Grass*
July 1, 1942, to June 1943	1908.1	5.18	29.017	5.603
July 1, 1943, to June 7, 1944	1138.8	6.59	30.107	4.570

A sample of Florida lemongrass oil examined by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°/15°	0.887
Optical Rotation	Inactive
Refractive Index at 20°	1.4871
Aldehyde Content, Calculated as Citral (Hydroxylamine Hydrochloride Method)	72.6%
Solubility	Incompletely soluble in 70%, 80% and 90% alcohol

Lemongrass Oil from Brazil[49]

During World War II, Brazil became a producer of substantial quantities of lemongrass oil, West Indian type, most of which has been absorbed in Brazil itself, Argentina, and neighboring South American countries. Substantial quantities have also been exported to the United States and to Great Britain. Chief producer of the oil is the Companhia Agricola Fazendas Paulistas, a large estate located near Mattão, State of São Paulo, and cover-

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[47] *Drug Cosmetic Ind.* **49**, September (1941), 262, 271. *Chemurgic Digest* **4**, No. 8 (April 1945), 148. Cf. Bourne and Nielsen, *Florida Cattleman Dairy J.* **7**, No. 12 (1943), 15.

[48] *Ibid.*

[49] The author is greatly indebted to Mr. Charles Henderson, of Cochabamba, Bolivia, for much of the information contained in this monograph.

ing more than 130,000 acres, most of which is devoted to the growing of coffee, cotton, and to the raising of cattle. This estate (British controlled) is one of the largest single coffee-producing enterprises in the world.

Experimental work on the production of essential oils was started in 1937 and has been conducted scientifically and systematically. At the time of the author's visit to the estate, a few years ago, several hundred acres were under lemongrass cultivation. This acreage has since been increased. The future development will depend obviously upon the demand, and particularly upon the price that oil of lemongrass brings on the world market. Potential production of the oil in the State of São Paulo is large.

Most of the plantations are located within a few miles of the centrally located, high-capacity modern distillery. The pH of the soil averages about 5.5. The soil is of light sandy consistency, subject to much leaching. Provided rain falls at reasonable intervals, acidity in the soil does not seem to affect either the yield or the citral content of the oil.

New plantings are started as early in the rainy season (November to February) as possible, in order to take advantage of the cool weather. Experiments indicate that plants spaced 50 cm. apart, in rows 50 cm. apart, develop more satisfactorily than plants spaced 50 cm. x 100 cm. Planting is done by men, women, and children (who must be older than 14 years, as the law does not permit employing younger children). Clumps of planting material are hauled to the site, and the tops of the grass are cut off to within 6 in. of the root. The latter is divided, and the lower brown sheath ripped off to uncover young roots. Holes 4 to 5 in. deep are punched into the ground with a crowbar or mattock, along marked lines. Baskets of prepared roots are carried along the line, and one or two roots placed into each hole. Men then tramp each root firmly into the ground.

The young plants develop rapidly and may be cut for the first time some three months after planting. Although an early first harvest gives a very low yield of grass per acre, it seems to produce a more rapid growth as well as an increase in the number of new shoots. On older fields three harvests can be obtained per year. During the season of growth (November to April) the grass may be cut within 45 days of the previous harvest. During the dry season the grass tends to dry up; but even grass (leaves) cut in this condition appears to give a good quality of oil, with a high citral content.

The grass is generally harvested when the tips of the leaves turn brown. Care has to be taken to cut the leaves before the tops have withered too much, as such material yields an oil of brownish color (but normal citral content). The leaves are cut with small sickle knives similar to those used for the harvesting of rice. Men and women work in separate groups because the men can collect twice the quantity of grass per day. However, the same price per weight of harvested grass is paid to men and women. When working on a good stand of grass, a skilled man can gather as much as 2 metric tons of fresh leaves in a day's work. The price contract includes loading up the carts, each of which holds about 2 metric tons of grass.

Depending upon the fertility of the soil and the fertilizer used (if any), the amount of fresh leaves per running meter in the rows varies from 1½ to 5 kg. The latter quantity, however, is obtained only after very heavy fertilization, which, in view of the relatively low price of lemongrass oil, would not appear to be profitable. It has been found that best results are obtained with dressings of cottonseed meal and potash.

On reaching the distillery, the cart or lorry is passed over a weighbridge, tared, and the total daily cut credited to the harvesters. The grass is then charged into the stills by means of pitchforks, and trampled down uniformly on wire trays that are inserted as the retort fills up. Direct steam, generated in a separate steam boiler, is gradually injected into the retort during loading, to facilitate closer packing. With the proper steam pressure the plant material is exhausted in about 1½ hr. During this period, a second still is charged so that there will be no delay other than that caused by the changing of the still head from one retort to the other. The condenser valve is then switched over, and the second still brought into action, while the first is discharged and recharged with another batch of leaf material. The use of two retorts per condenser gives, in effect, continuous distillation.

The yield of oil obtained from the first harvest of a newly established plantation may be as low as 0.1 per cent. Subsequent cuttings yield from 0.20 to 0.25 per cent of oil, the percentage being calculated upon fresh grass material. As a rule, only freshly cut grass is distilled, but it may happen that during the height of the harvest the capacity of the stills does not suffice for immediate distillation of all the cut leaf material. In such an event, some of the harvested grass is left lying in the fields (where it partly dries) until the material can be hauled to the distillery.

After separation from the oil receiver the oil is delivered by the foreman of each shift to the laboratory for filtration and drying. Samples are taken from each batch until all the grass material of one field has been distilled, when the citral content of the combined batches is assayed. Bright dry oil is stored in carboys until ready for shipment.

The citral content of the oil ranges from 75 to 77 per cent (sodium bisulfite method) in oil distilled from the first harvest of a newly established plantation; subsequent cuttings yield oils assaying from 82 to 85 per cent in freshly distilled oils. The citral content varies somewhat with the season in which the grass is cut. Contrary to the general observations in other parts of the world, the citral content does not appear to drop to any appreciable extent on storage (even after six to eight months), *provided the oil has been completely dried* and stored in well-filled carboys.

A sample of Brazilian lemongrass oil produced on the above-named estate and examined by the author had these properties:

Specific Gravity at 15°	0.882
Optical Rotation	−0° 13′
Refractive Index at 20°	1.4845
Acid Number	1.2
Aldehyde Content, Calculated as Citral:	
Bisulfite Method	78.3%
Neutral Sulfite Method	74.4%
Hydroxylamine Hydrochloride Method	76.5%
Solubility	Cloudy in 1 to 10 vol. of 80% alcohol
Color	Yellow

Two shipments of Brazilian lemongrass oil received and examined by Fritzsche Brothers, Inc., New York, had the following properties:

	I	*II*
Specific Gravity at 15°/15°	0.888	0.887
Optical Rotation	−0° 10′	−0° 8′
Refractive Index at 20°	1.4863	1.4872
Aldehyde Content (Bisulfite Method)	75.5%	74.8%
Solubility in 80% Alcohol	Cloudy in 10 vol.	Cloudy in 1 vol.

In the course of the last few years the above-mentioned estate in Mattão, State of São Paulo, produced the following quantities of lemongrass oil: [50]

	Kilograms
1946	4,696
1947	3,259
1948	3,440

Lemongrass Oil from Paraguay

During the years of World War II, Paraguay started to produce limited quantities of lemongrass oil. Two samples examined by Fritzsche Brothers, Inc., New York, had these properties:

	I	*II*
Specific Gravity at 15°/15°	0.891	0.901
Optical Rotation	−0° 24′	−2° 32′
Refractive Index at 20°	1.4863	1.4857
Aldehyde Content (Bisulfite Method)	80.6%	77.0%
Solubility	Soluble in 1 vol. of 80% alcohol; opalescent in 2 and more volumes	Soluble in 0.5 vol. of 80% alcohol; very slightly opalescent in 4 and more volumes

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[50] Courtesy of Mr. Dan Haggard, General Manager, Companhia Agricola Fazendas Paulistas, Fazendas do Cambuhy, Mattão.

Lemongrass oil is now being regularly produced in Paraguay by colonies of Mennonites.

Lemongrass Oil from Various Parts of Africa

Numerous efforts have been made to produce the West Indian type of lemongrass oil (*Cymbopogon citratus* Stapf) in various parts of Africa on an experimental basis. Some of these have actually led to the production of substantial quantities of oil. Tanganyika, for example, exported 10 tons of oil in 1937. Production in a given section, however, varies from year to year, depending upon prices and general market conditions, so that no exact figures can be given.

According to Coomber and Cosgrove,[51] the citral content of lemongrass oil depends upon several factors, chiefly conditions of soil and climate, the time and number of yearly harvests, and the method of distillation. Grass cut six times a year will yield an oil with a somewhat lower citral content than oil from grass harvested only four times per year. The reason is simply that the plants probably are not fully matured when cut too frequently, and that the soil will soon be exhausted by six harvests every year. The method of distillation, too, must be rigidly controlled; higher pressures of steam (about 20 lb. per sq. in.) increase the yield of oil but decrease its citral content in comparison with distillation carried out with steam at lower pressures of about 10 lb. per sq. in. Another point is that the grass should be cut after a spell of dry weather.

Tanganyika (East Africa) for years has been producing substantial quantities of lemongrass oil. Shipments received and examined by Fritzsche Brothers, Inc., New York, had physicochemical properties varying within these limits:

Specific Gravity at 15°/15°	0.884 to 0.887
Optical Rotation	−0° 32′ to −0° 34′
Refractive Index at 20°	1.4860 to 1.4865
Aldehyde Content (Bisulfite Method)	74.0 to 78.2%
Solubility	Turbid in 10 vol. of 80% alcohol

The oils have been of very good quality.

An oil from Tanganyika investigated at the Imperial Institute in London[52] had these properties:

Specific Gravity at 15.5°/15.5°	0.8846
Optical Rotation	−0° 21′

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[51] *Perfumery Essential Oil Record* **39** (1948), 351.

[52] *Bull. Imp. Inst.* **32** (1934), 216.

Refractive Index at 20°	1.4860
Citral Content (Bisulfite Method)	81%
Solubility	Soluble in 1 vol. of 80% alcohol; turbid on further dilution

As regards solubility, the oil had the characteristics of a typical "West Indian" oil, but the content of citral approximated that of East Indian oils.

Two oils from Uganda examined in the same institute[53] had the following properties:

	I	*II*
Specific Gravity at 15.5°/15.5°	0.9178	0.8846
Optical Rotation	α_D^{20} +1° 26′	α_D^{22} −0° 13′
Refractive Index at 20°	1.4913	1.4859
Citral Content:		
Sulfite Method	72%	74.5%
Bisulfite Method		77%
Solubility in 80% Alcohol		Insoluble even in 12 vol.

The Imperial Institute[54] also analyzed an oil from the Seychelles Islands:

Specific Gravity at 15.5°/15.5°	0.9026
Optical Rotation at 19°	−0° 9′
Refractive Index at 20°	1.4884
Aldehyde Content (Bisulfite Method)	86.5%
Solubility at 15.5° in 80% Alcohol	Soluble in 0.7 vol.

Steam distilling the upper parts of lemongrass plants in Barabum, Belgian Congo, Wilbaux[55] obtained 0.507 per cent of an oil with these properties:

Specific Gravity at 15°	0.885
Refractive Index at 20°	1.4856
Citral Content (Bisulfite Method)	61%
Solubility	Soluble in 2.5 vol. of 70% alcohol

Joly[56] examined thirty-one samples of lemongrass oil distilled from plants eighteen months to two years old, grown in Upper French Ubangi, and found them to exhibit a specific gravity (d_{15}) ranging from 0.8875 to 0.8960, and a citral content ranging from 71 per cent to 75 per cent.

Five samples of oil distilled from plants which were either too young or too old had the following properties:

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[53] *Ibid.*, 218.

[54] *Ibid.*, 514.

[55] *Bull. agr. Congo Belge* (1936), 295. Through *Deut. Parfümerieztg.* **23** (1937), 182.

[56] *Parfumerie moderne* **31** (1937), 27.

Specific Gravity at 15°	0.8856 to 0.8942
Optical Rotation	−0° 10′ to +0° 5′
Refractive Index at 20°	1.4867
Aldehyde Content (Bisulfite Method)	54 to 69%
Solubility	Soluble in 0.8 vol. of 80% alcohol; soluble in 0.1 to 0.3 vol. of 95% alcohol

Two samples of oil distilled under most favorable conditions had aldehyde contents of 78 and 90 per cent.

Lemongrass Oil from the Belgian Congo

According to information furnished by various government agencies,[57] *Cymbopogon citratus* Stapf grows semiwild in all parts of the Belgian Congo. It is often erroneously called "citronella." The plant prefers a low altitude and a hot, but relatively dry, climate. Prolonged rains are harmful to lemongrass as they cause attacks by rust. The grass will grow in light soil, but commercial cultivation is profitable only in fairly fertile ground.

According to Goussens,[58] production of lemongrass oil on a commercial scale in the Belgian Congo was started in 1945 near Obokote, Ituri, 314 km. south of Stanleyville, at an altitude of about 600 m. The soil there is ancient alluvium of the lower Lualabian bed, and secondary laterite. Another area of production is located in Kama, Territory of Pangi-Maniema.

For the planting of lemongrass the ground should first be plowed 25 to 30 cm. deep. Rootstocks (which have never been segmented before) are then divided, a two-year-old stock yielding about 200 root segments. A nursery comprising 100 square meters will yield sufficient root segments to plant one hectare, calculating two root segments per planting hole. Depending upon the fertility of the soil and the manure applied, 15,000 to 20,000 segments are planted per hectare. In certain cases as many as 40,000 tufts can be planted per hectare. Planting the lemongrass between rows of coffee trees, 6 to 8 m. apart, has been tried.

The leaves (grass) are harvested with sickles. The plants can be cut for the first time six to nine months after planting, and from then on every three to four months. The number of cuttings per year, of course, depends upon the fertility of the soil and the distribution of the rainfall. In general, the grass can be harvested four times per year. A planting lasts about four

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[57] Ministère des Colonies, Bruxelles. Office des Produits Agricoles de Costermansville. Institut National pour l'Etude Agronomique du Congo Belge, Yangambi. All through the courtesy of Mr. Gerard J. Danco, New York.

[58] Private communication of Mr. E. Goussens, "Plantocitra," Obokote, Belgian Congo, through the courtesy of Mr. Gerard J. Danco, New York.

years, after which the crop has to be rotated. The following yields of green (fresh) leaf material per hectare are quoted from official bulletins:

1. With a soil of medium fertility, five harvests in three years gave 122 metric tons of plant material.
2. With a soil of low fertility, five harvests in three years gave 57 tons.
3. With a soil of medium fertility, enriched with mineral fertilizers, eight harvests in three years gave 248 tons.
4. With a soil of medium fertility, enriched with 60 tons of horse dung or 80 tons of compost, eleven harvests in three years gave 324 tons.

One experienced, large-scale producer[59] in Obokote reported an average yield of 40 metric tons of leaf material (bundled and dried in the field for two days) per hectare per year.

A medium-sized distillery comprises three stills of 2,500 liters capacity each. A still of this size can be charged with 500 kg. of whole leaves (grass), or with 750 kg. of chopped material. It is advisable to cut up the leaves prior to charging. Distillation of one batch with direct steam (3 kg. pressure per sq. cm. in the steam boiler) lasts 1 hr. The above-mentioned producer in Obokote uses stills of the tilting type (see Vol. I of this work, pp. 127 and 130) provided with water seals (hydraulic joints). Each still holds 3,900 liters. In this case distillation of one charge lasts 4 hr. During the peak of the harvest the stills are operated day and night.

The yield of oil varies greatly with the season. It is about 0.2 per cent (from chopped leaf material) in the rainy season, and 0.35 per cent in the dry season, the average yield per year being 0.2 to 0.25 per cent. Yields as high as 0.6 per cent have been reported in exceptional cases. During the rainy season the yield of oil is poor because the grass contains much moisture. Moreover, the citral content of the oil is low. On the average, one hectare yields about 40 kg. of oil per year.

In order to supply buyers abroad with lemongrass oil of high quality and of guaranteed citral content, the above-mentioned producer in Obokote submits the crude oil to rectification. A certain amount of terpenes is thus distilled off and removed. Every lot of oil is carefully analyzed, so that shipments will meet specifications of the contract. Thus, oils containing from 75 to 99.5 per cent of aldehydes (chiefly citral) are exported.

By 1949 total production of rectified lemongrass oil in Obokote amounted to about 12 metric tons per year, but an expansion to about 20 tons was planned at the time of this writing. No substantial quantities of oil were being produced elsewhere in the Belgian Congo.

[59] *Ibid.*

In general, the lemongrass oil industry of the Belgian Congo has suffered from the scarcity of skilled labor and from the indolence of the natives. The oil is merely a by-product in the agriculture of the Congo, and only a well-managed enterprise can produce it economically. The future will depend upon the price of the oil on the world market. If demand should warrant it, the plantings could be increased largely. Moreover, the government agricultural and economic services in the Belgian Congo are anxious to open new sources of revenue, and would encourage additional plantings.[60]

The quality of the lemongrass oil produced in Obokote has been very good. Every shipment is analyzed in the laboratory of the "Office des Produits Agricoles de Costermansville."

Two typical (official) analytical bulletins quote the following figures:

Standard Quality

Optical Rotation	+0° 30′
Refractive Index at 25°	1.4857
Citral Content (Bisulfite Method)	77%

Terpeneless Oil

Optical Rotation	+0° 15′
Refractive Index at 25°	1.4860
Citral Content (Bisulfite Method)	99 to 99.5%

Shipments of lemongrass oil from the Congo, received and examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.880 to 0.884
Optical Rotation	−0° 13′ to −0° 17′
Refractive Index at 20°	1.4840 to 1.4850
Aldehyde Content (Bisulfite Method)	76.2 to 83.5%
Solubility	Cloudy up to 10 vol. of 80% alcohol

Lemongrass Oil from Indo-China

According to Naves and Auriol,[61] the West Indian type of lemongrass, *Cymbopogon citratus* Stapf, is cultivated also in Indo-China for the distillation of the oil, about 20 metric tons of which were produced annually before World War II. The grass is planted 50 to 60 cm. apart, in rows also 50 to 60 cm. apart, one hectare thus containing 25,000 to 30,000 plants. The planting is done by men, women, and children, the children dividing the

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[60] Cf. *U. S. Dept. Commerce, Washington, D. C., Bur. Foreign Domestic Commerce,* "International Reference Service," Vol. 7, Pt. 3 (1949), No. 16—"The Belgian Congo as a Source of Crude Drugs and Essential Oils."

[61] *XVII Congrès de Chimie Industrielle, Paris* (1937).

stools, the women preparing the segments, and the men doing the actual planting. Three or four months after planting the grass can be cut for the first time; from then on it can be harvested three or four times per year. After three or four years the planting has to be renewed.

At the Experiment Station of Ong-Yêm the following yields were obtained on steam distillation of the fresh grass: 0.60 per cent of oil from the upper parts of the grass, and 0.125 per cent from the lower parts of the grass.

The yield of oil varied with the season and the age of the plants, young grass giving the highest yield. It was lower in plants which had not been cut for a long time. One hectare of lemongrass yielded 20 to 30 metric tons of fresh grass per year. In Indo-China only fresh grass is used for distillation, field drying resulting in some loss of oil.

Distillation is carried out in stills 1.5 m. wide and 1.75 m. high, holding 3 cu. m., or 650 to 750 kg., of fresh grass. Distillation of one charge lasts about 3 hr. In a distillery located in Dôn-Thuân the average yield of oil was 0.23 to 0.35 per cent during the rainy season, and 0.45 to 0.55 per cent during the dry season. Lemongrass cultivated in Xacat on red soil yielded 0.30 to 0.35 per cent of oil, whereas grass cultivated in Ong-Yêm on gray soil gave 0.23 to 0.27 per cent of oil, corresponding to 43 to 46 kg. of oil per hectare and per year. Calculated on the basis of dry grass the oil yield was 0.8 to 0.9 per cent.

The oil derived from young plants contained less citral than that distilled from older plants.

Naves and Auriol [62] reported these properties for lemongrass oil from Indo-China:

	Oil from One-Year-Old Plants	*Oil from Older Plantings*
Specific Gravity at 15°/15°	0.878–0.894	0.882–0.902
Optical Rotation	About 0°	About 0°
Citral Content	70 to 82%	78 to 87%
Solubility of Freshly Distilled Oils	Soluble in 1 to 7 vol. of 70% alcohol	
Solubility of Oils after Storage	Soluble in 10 vol. of 95% alcohol	

Lemongrass Oil from the Caucasus

Investigating an oil of lemongrass derived from *Cymbopogon citratus* and produced in Suchum (U.S.S.R.), Rutovski, and Vinogradova [63] found that the oil contained:

Myrcene	ca. 8.5%
Decylaldehyde	ca. 2%

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[62] *Ibid.*

[63] *Riechstoff Ind.* **5** (1930), 15.

Citral *a* and *b*	ca. 55%
Geraniol	ca. 3%
Nerol	ca. 1.5%, partly as isovalerate
A Phenol	ca. 0.1%, with an odor of cresol
and	
Methyl Heptyl Ketone	ca. 0.5%, which was identified by the preparation of its semicarbazone m. 117°–118°

The same authors did not observe any methyl heptenone, limonene, or citronellal in the oil which they investigated.

According to Rutovski and Vinogradova,[64] the oils of lemongrass distilled from *Cymbopogon citratus* (yield 0.2 to 0.62 per cent) in the Caucasian Mountains generally have these properties:

Specific Gravity at 20°/20°	0.8676 to 0.9215
Optical Rotation	−2° 12′ to +12° 45′, usually inactive
Refractive Index at 20°	1.4812 to 1.4892
Acid Number	11.04 to 14.4
Ester Number	19.1 to 39.6
Ester Number after Acetylation	176.10 to 244.38
Aldehyde Content (Bisulfite Method)	51.6 to 65.0%
Solubility	Not always clearly soluble in 80% alcohol

OIL OF CITRONELLA

Essence de Citronelle *Aceite Esencial Citronela* *Citronellöl*
Oleum Citronellae

Introduction.—There are two types of citronella oil: the Ceylon type and the Java type. The former is produced almost exclusively on the island of Ceylon; the latter chiefly on the islands of Java and Formosa, lately also in Central America (Guatemala and Honduras), and on the island of Haiti.

Citronella oil came into prominence rather slowly during the second half of the last century, at which time it was produced only in Ceylon. In fact, until about 1900 the market depended almost entirely upon the Ceylon oil. Today, however, the Java type of oil is of far greater importance. Prior to World War II export figures of the Ceylon oil averaged 600 metric tons per year, while Java exported about 2,000 metric tons. World War II, the

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[64] *Ibid.*

occupation of Java by Japanese forces, and the civil war in the interior of Java after the capitulation of Japan, brought about profound changes in the production of the Javanese oil and the quantity diminished greatly. Guatemala and Honduras began to produce substantial quantities of the Java type of citronella oil, which during and after World War II found an eager market in the United States and in allied countries. At the time of this writing (1949) detailed and reliable information regarding the condition of the citronella plantations in Java is still meager. It is known, however, that in general the citronella area has been reduced to less than 8,000 hectares, because during the Japanese occupation of Java there was no great demand for the oil, and the natives suspended citronella cultivation in favor of rice, tapioca, peanuts, and other food products. Moreover, old citronella fields were neglected, some are at present partly overgrown with weeds, and the yield of oil has declined from the former 0.6–0.7 per cent to 0.4–0.6 per cent. Laborers abandoned the citronella plantings and started working in other enterprises that offered higher wages. As a result of these developments, in 1948 the production of Java citronella oil was only one-eighth of the prewar level. Nevertheless, it may be assumed with some certainty that with the arrival of more normal conditions Java will again assume a leading role in the production of citronella oil. In this respect the island is favored by several advantages: relatively low-priced native labor, a native patch-crop industry against which it is difficult to compete, the "know-how" of the native growers and distillers, and the existence of a great many distilleries, of small, medium, and large size. Ample planting material is readily available, and new fields can be in full production within one or two years, should demand for the oil and good prices encourage such expansion.

So far as the difference between the Ceylon type and the Java type of citronella oil is concerned, it should be mentioned here briefly [1] that the Java oil is much more valuable and useful, as it contains about 85 per cent of total geraniol (including at least 35 per cent of citronellal), whereas the Ceylon oil contains only 55 to 65 per cent of total geraniol (including 7 to 15 per cent of citronellal).

The Java oil serves as starting material for the extraction of several very important isolates (geraniol, citronellal) which can be converted into some of the most widely used aromatics (citronellol, hydroxycitronellal, synthetic menthol, esters of geraniol and citronellol, etc.). With an average annual production, in normal times, of about 2,000 metric tons (in Java alone), oil of citronella, Java type, is therefore one of the most important essential oils. The Ceylon oil, on the other hand, is used mainly for the scenting of low-priced technical preparations such as sprays, detergents, polishes. As a

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[1] For details see the sections on "Physicochemical Properties" and "Chemical Composition" of the two oils.

matter of fact, there is no reason why the Ceylon oil, still employed in some long established formulas, could not be replaced by the superior Java oil with its similar but stronger odor. Then, too, the Ceylon oil is often adulterated with 5 to 7 per cent of kerosene, whereas the shipments of Java oil—in normal times—are carefully checked in the analytical laboratories of the Government Station in Buitenzorg. No substandard lots are permitted to reach the overseas markets.

Botany.—The parent plant of all cultivated types of citronella is probably *Cymbopogon confertiflorus* Stapf, the so-called "mana" grass which occurs wild in Ceylon.

Citronella, a stoloniferous plant, is cultivated in at least two closely related types, which can be distinguished (a) morphologically, by the shape and length of their leaves, and (b) physiologically, by the composition of their respective essential oils:

1. *Cymbopogon nardus* Rendle, *lenabatu* (*Andropogon nardus ceylon* de Jong), the so-called "lenabatu" from which the bulk of the Ceylon oil and a very small proportion of the Java oil are derived.
2. *Cymbopogon winterianus* Jowitt, *mahapengiri* (*Andropogon nardus java* de Jong), the so-called "mahapengiri," from which the bulk of the Java oil and a very small proportion of the Ceylon oil are derived.

"Mahapengiri" can be recognized by the form of its leaves which are usually shorter and broader than those of the "lenabatu." On distillation it gives a higher yield of oil than "lenabatu"; moreover, the oil is of better quality (higher geraniol and citronellal content) than that of "lenabatu." However, "mahapengiri" requires a more fertile soil, more rainfall, and more cultural care than the hardier "lenabatu."

Oil of Citronella Ceylon

History and Development.—Perhaps the earliest note, in Europe, of Ceylon citronella oil was by Nicolaus Grimm, an army surgeon, who practiced medicine in Colombo at the end of the seventeenth century. Grimm named the grass from which the oil was derived *Arundo Indica odorata.*

The first small shipments of *"Oleum siree,"* as it was then called, arrived in Europe at the beginning of the eighteenth century. However, the oil seems to have been exported only sporadically at that time. In 1851 and 1855 samples were displayed at the World's Fairs held in London and Paris; the oil became more generally known in Europe and found increasing employment in the scenting of soaps and technical preparations. Demand for the oil grew, and large quantities were produced in Ceylon, which remained practically the world's sole supplier until about 1890, when Java started to produce a citronella oil of superior quality. Today the supply of the Java type of oil (produced in Java, Formosa, Guatemala and Honduras) by far exceeds that of the Ceylon type. It is only because its price is usually lower that the Ceylon oil can withstand the competition of the Java type of oil.

Botany.—The bulk of the Ceylon citronella oil is distilled from *Cymbopogon nardus* Rendle (*Andropogon nardus ceylon* de Jong), locally called "lenabatu." This plant, cultivated on a large scale in the south of Ceylon, grows to a height of about 1.5 m. Its leaves are long and slender. It is hardier, has a longer life span, flourishes in a less fertile soil, and requires less cultural care and moisture than "mahapengiri" (see above, section on "Botany," and below). However, the quality (i.e., total geraniol and citronellal content) of the oil derived from "lenabatu" is inferior to that of the oil distilled from "mahapengiri."

In addition to the "lenabatu" just discussed, Ceylon also produces a small quantity of the Java type citronella *Cymbopogon winterianus* Jowitt (*Andropogon nardus java* de Jong), locally called "mahapengiri." Commercial shipments of Ceylon citronella oil consist either of oil derived exclusively from "lenabatu," or of mixtures of "lenabatu" with "mahapengiri," in which, however, the former very largely predominates. In some localities of the citronella producing regions of Ceylon the two types of grass grow almost side by side, but the quantity of the "mahapengiri" is negligible.

It has been suggested repeatedly that in Ceylon the "lenabatu" be abandoned completely, and that the acreage be replanted with "mahapengiri," in order to improve the quality of the Ceylon citronella oil. This, however, is not possible because climatic and soil conditions are not generally favorable for the cultivation of "mahapengiri." Under the conditions prevailing in Ceylon the latter type of grass gives a very poor yield of oil.

Cymbopogon winterianus Jowitt ("mahapengiri") owes its species name to the fact that years ago a Mr. Winter, an important citronella oil distiller in Ceylon, tried to cultivate the "mahapengiri" (and for a time actually succeeded) for the purpose of distillation. Later it was replaced by the hardier "lenabatu." This development also led to the local designation "Winter's grass" or "old grass" for "mahapengiri."

"Lenabatu," also called "new grass," is, perhaps, a cross [2] between "mahapengiri"—which, according to Jowitt,[3] occurs in Ceylon in the wild as well as the cultivated state—and the entirely wild growing so-called "mana" grass (*Cymbopogon confertiflorus* Stapf). The latter is probably the parent plant of all types of citronella grass.

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[2] Cf. *Bull. Impt. Inst.* **10** (1912), 299.

[3] *Ann. Roy. Bot. Gardens, Ceylon* **4** (1908), 183.

Producing Regions.—The citronella producing regions of Ceylon are located in the extreme south of the island. Starting near the beautiful bay of Weligama, the southern limits follow the coast of the Indian Ocean eastward toward the port of Tangalla; from the coast the section stretches north into the mountains of the Southern Province. In this area about 30,000 acres are planted with citronella. In 1946 the exact figure was 30,033 acres.[4] Two subsections of production may be distinguished:

1. The larger and more important of these subsections stretches, in the form of a huge triangle, from Matara to Tangalla and north. Most of the grass here is grown on well-kept plantings.
2. The smaller subsection lies to the north of Weligama. The grass here grows partly semiwild on old and neglected plantings, which have not been properly weeded, with the result that more than one type of citronella grass is harvested and distilled.

The oils produced in the two subsections resemble each other closely, except in respect to specific gravity, which is occasionally lower in some batches of oil from the Weligama district.

The localities where citronella is grown are for the greater part slightly hilly and rather infertile. The annual rainfall amounts to 60–70 in., but for the larger part of the year there is very little rain.

Planting and Cultivating.—All plantings are owned by Singhalese, none being operated by European producers or exporters. The fields range from scattered small patches (about ½ acre) up to 300 and more acres on large estates, which are owned by wealthy natives. These landowners sometimes rent a part of their fields, as well as the necessary distillation posts, to small producers on a crop-sharing basis. The owner then receives one-sixth of the oil produced on the rented fields, while the sharecropper retains five-sixths; from this he must pay all expenses of cultivation, harvesting, and distilling.

Except for the small quantities of semiwild grass growing on old, neglected fields (which are not carefully weeded during years of low prices), all the grass is cultivated. Plantings are located usually on the poorer type of soil, particularly on the slopes of hills. Prior to planting, the soil is prepared by burning old grass and weeds, and by hoeing.

For planting, stools of fully grown, healthy plants are divided, and set out 1.5 ft. apart. This is done during the two rainy (monsoon) seasons, which last from the end of April to the end of June, and from middle of October to middle of December.

Depending upon the quality of the soil and the amount of rainfall, from six to eight months are required for the new plants to reach a sufficient size

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[4] Agricultural census of 1946.

(3 to 5 ft. tall) to be harvested. The cutting is done with sickles, by women and girls. Three harvests a year are possible on the same field, the date of cutting depending upon the time of planting. Harvesting thus goes on throughout the year, but there are three main seasons, i.e., May to June, August to September, and December to the middle of January. The grass is never cut during rain spells, because it may ferment while lying in the fields after cutting. Moreover, the distillation of wet (or fresh) grass requires long hours and a great amount of fuel. The cut grass is therefore allowed to dry in the fields, which requires from 1 to 3 days, depending upon sunshine and atmospheric conditions. The dried grass is then tied into bundles, stacked up in the fields for further drying, and finally hauled on bullock carts to the distilleries.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 9. Citronella oil production in Ceylon. Harvest of the grass.

The plantings should be weeded out annually, and fertilized biannually with the ashes of citronella grass which has been distilled and burned (as fuel). Frequent fertilization encourages the growth of the plant and increases the yield of oil per acre. If well taken care of, a field of "lenabatu" may be productive for as long as twenty-five years, at the end of which time it must be replanted. In most cases, however, the yield of grass and oil diminishes substantially after the tenth year, and the field becomes unprofitable. If not properly cultivated a planting may show signs of decline after five years.

Exceptional fields are said to be more than fifteen years old. While surveying the production of citronella oil in Ceylon, the author heard of fields for which an age of fifty years was claimed. It seems probable that such claims represent an exaggeration.

Yield of Grass and Oil per Acre.—According to Volkart Brothers,[5] the average yearly yield of Ceylon citronella oil per acre amounts to about 50 lb. "Lenabatu" grass contains approximately 0.5 per cent of oil. The yearly yield of dried grass per acre amounts, therefore, to about 90 cwt. Other sources report yields ranging from 60 to 90 cwt. of grass per acre.

The maximum yield of a plantation is obtained in the third year, at which time it reaches 60 or 80 lb. of oil per year per acre. After the fifth year the yield diminishes. Between the fifth and the fifteenth year it amounts to only 40 lb. of oil per year per acre. After the twenty-fifth year the field is usually replanted.

The opinion has been expressed [6] that the yield, as well as the quality, of the Ceylon oil could be improved by more intensive methods of cultivation (green manuring, proper shading, etc.) and more selective methods of propagation.

Distillation.—The dried plant material is processed in numerous distillation posts distributed throughout the citronella regions of Ceylon. These distilleries, which resemble one another closely in construction, are usually located at the base of hills, where a sufficient supply of cool water is available. A typical distillation post consists of two stills connected with one and the same condenser, the latter being inserted in a rectangular water basin made of concrete and imbedded in the ground. The stills, of galvanized iron, are usually 8 ft. high and 4.5 ft. wide; a few are larger. The two stills are operated alternately—while one still is being charged or discharged, the other remains in operation. For this reason the two stills have only one helmet (with an attached gooseneck). Distillation is carried out with live steam generated in a separate and simple steam boiler, the latter partly imbedded in the ground. Warm water drawn from the condenser tank serves for feeding the steam boiler. For heating, exhausted and sun-dried plant material is used. The ashes are dumped in the fields for fertilization purposes.

The oil separator and the container holding the separated oil are housed in a locked subterranean room, accessible through an underground passage, to which only the proprietor or trusted foreman has the key.

The entire distillation post is housed within walls, and protected by a protruding roof.

Only dried plant material is used, as distillation of fresh material requires too much fuel and is said to yield an oil of less agreeable odor. During dry-

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[5] Private communication of Volkart Brothers, Galle Agency, Galle, Ceylon.

[6] Cf. *Perfumery Essential Oil Record* **26** (1935), 88.

ing of the cut plants in the fields, care has to be exercised to prevent fermentation and rotting.

Distillation of one charge lasts about 6 hr. This rather protracted distillation is necessary because of the low steam pressure in the boiler, the limited capacity of the latter, and the comparatively large charge of plant material in the still.

According to the industrial census of 1946, there were in the Southern Province 321 citronella distilleries, but 64 of these distilleries were not operating in 1946.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 10. Citronella oil production in Ceylon. A typical distillery.

Trade of Oil.—In the larger and well-managed distilleries the oil is handled carefully and stored properly. The estate owners who produce large quantities of oil may deliver their output directly to exporters, but small operators or sharecroppers usually sell their lots to field brokers. In many cases the small producers are financed by middlemen, who may make substantial profits by charging interest on the advanced funds.

The leading Ceylon exporters have agencies in Galle or Matara, purchasing copra, rubber, coir yarn, cinnamon, oil of citronella, and other products of the island from the native producers. The buying of citronella oil is by no means a simple matter, because the manager of the agency, although no chemist, is expected daily to evaluate numerous small lots of citronella oil brought in by field brokers. Unless the latter receive an immediate acceptance, they simply go next door and offer the lot to a competing purchasing agency. The analytical assays must, therefore, be simple, yet as reliable as possible. Determination of the specific gravity, a test for the presence (absence!) of alcohol, and a simple solubility test for the presence (absence!) of kerosene are all that can be expected of a rough and ready test for the quality of each lot. Beyond that the purchasing agent cannot possibly go.

If a lot is accepted, the field broker is paid in cash, or credited against loans advanced. If refused, he usually offers his oil to a competing exporter nearby. In the course of these transactions a good deal of oriental business craftiness is exercised: frequently intermediaries succeed in playing competing exporters one against the other, particularly if one exporter is short of oil. It is surprising how well the intermediaries are informed about the stocks, commitments, and requirements of competing exporters.

When a certain amount of oil has been purchased, the accumulated small lots are bulked in the warehouses of the exporter's branches in Matara or Galle. These large lots are then stored in tanks until the oil is sufficiently clear to permit easy filtration. Impurities settle to the bottom of the tank, and the supernatant liquid may often be so clear that filtration becomes unnecessary.

On aging, the oil undergoes certain changes: the specific gravity increases slightly, and the solubility in 80 per cent alcohol decreases. Genuine oils which contain no added kerosene (see below) retain their originally good solubility for about three months. The color also changes, particularly when the oil is exposed to air and light. The color may range from yellow to slightly green.

As a rule, the exporters standardize their bulkings, or make them up on the basis of orders from abroad. The oil is shipped in second-hand lubricating oil drums of 45 gal. capacity, and a small percentage (about 6 per cent) in galvanized iron drums. Shipping ports are Galle and Colombo, where most of the exporters have their main offices and warehouses ("Go-downs"). Some of the larger exporters operate their own very simple testing laboratories, where the outgoing shipments are submitted to a few routine tests. When there is doubt as to quality, a sample of the lot is submitted to the city analyst in Colombo. No government control is exercised over outgoing shipments of citronella oil, and purity and quality are matters of contract between exporters and foreign buyers.

Quality of Ceylon Citronella Oil.—In respect to quality, the Ceylon citronella oil industry differs considerably from that of Java, where every shipment of essential oil is submitted to a rigid analysis in the government laboratories, before an export permit is granted, any adulterated or substandard batch being rejected. To the lack of government control over exports of Ceylon oils may be attributed, at least in part, the fact that even today much of the Ceylon citronella oil reaches foreign markets after it has been adulterated with about 6 per cent of kerosene. This practice came into vogue years ago when some exporter had the "bright" idea of adding a small quantity of kerosene to the oil in order to reduce its price by a few pennies. The surprising part is that the idea took hold, with the result that the trade became used to adulterated citronella oil from Ceylon, and for many years has accepted this quality readily under the label of "ordinary" or "market" or "fair average quality" (f.a.q.). Needless to say, this practice has greatly handicapped the Ceylon oil in its competition with the Java citronella oil which, aside from its purity, offers the added advantage of a higher citronellal and total geraniol content. In the course of years, many efforts have been made, on the part of serious exporters and importers, to put a stop to this nuisance. Among other measures the establishment of government control over outgoing shipment of the Ceylon oil has been suggested, but these efforts have met with little success. Several arguments have been advanced in favor of retaining the old practice of adding kerosene to the Ceylon oil. It is asserted, for example, that the trade has become used to this type of oil and likes it because of its lower price, or that without the benefit of a lower price the Ceylon oil could not compete with the Java oil, or that government control would mean a government monopoly, etc. All of these points are obviously irrelevant: by the same logic most essential oils could or should then be adulterated, and instead of (say) 10 per cent of kerosene, any quantity could be added, to suit the purse of the buyer! It would seem more logical for the buyer to do the cutting of the oil himself, when necessary, or to use less oil in his preparation, rather than to purchase an oil cut with a neutral kerosene fraction, which adds nothing to the odor strength of the oil. Moreover, since the kerosene fractions used in Ceylon for the purpose of adulteration originate chiefly from the United States, they are shipped overseas for a long distance only to be shipped back to America or Europe. It would be more economical, under the circumstances, to save the cost of transport of the kerosene fractions and add them to the pure oil in America or Europe, if this should really be desired.

As a result of the practice of adulteration, there are now two distinct types of commercial Ceylon citronella oil:

1. The so-called "estate" oils, which are generally pure, containing no kerosene. These oils are produced on extensive estates, chiefly in distilleries of large capacity, whence their name "estate" oils. These oils are usually exported on a contract basis which stipulates a minimum of 60 per cent total geraniol content. Until recently the quantities of estate oils shipped abroad accounted for only about 30 per cent of the total annual export of Ceylon

citronella oil, but an improvement of this figure can be expected in the near future, for reasons explained below.

Serious exporters prefer to trade in estate oils, because the purchase of such pure oils in large quantities from the estates is much easier than the collection of numerous small lots (all of which have to be examined) from many intermediaries, who may not be altogether reliable. Moreover, exporters often enjoy close personal connections with the owners of large estates, and know them to be reliable suppliers of all kinds of products.

2. The so-called "ordinary," or "market," or "fair average quality" (f.a.q.) oils. They contain 5 or slightly more per cent of kerosene fractions, and are often cut down to the extreme limit permissible with the "Schimmel solubility test" (see below), upon which contracts for this type of oil are usually based. Some lots of the f.a.q. oils are produced on the larger estates, but most of the batches consist of bulkings of numerous small lots, purchased by the exporters from middlemen or field brokers. Until recently, about 70 per cent of the total annual exports of Ceylon citronella oil consisted of f.a.q. oils. It should be mentioned that the kerosene is added by the producers, but frequently, and where possible, the field brokers, middlemen, and even the exporters add some more kerosene until the limit permitted by the "Schimmel solubility test" is reached.

To put an end to the practice of adulteration of Ceylon citronella oil with kerosene, Schimmel & Co., over a period of years, introduced three simple solubility tests, which show the presence of kerosene or petroleum fractions in the oil. Details of these tests will be found below. Of the three tests, only the first, or "old Schimmel test," has been adopted by the trade, but it is powerless to detect adulteration with kerosene amounting to less than 5 per cent. Moreover, pure oils occasionally fail to pass this test. Consequently, adulterated oils continue to reach the market in large quantities, and, because of legal complications, even the U. S. Customs authorities are unable to stop the entry of such lots into the United States.

It is only recently that the Scientific Section of the Essential Oil Association of U.S.A. (E.O.A. No. 12) has established definite standards for Ceylon citronella oil, specifying that the test for the presence of mineral oil (saturated hydrocarbons) be negative. Details will be given below in the section on analysis. Although the specifications of the Essential Oil Association of U.S.A. have as yet no legal standing, they have nevertheless been of great benefit to the industry, insofar as most American essential oil houses now try to supply oils which meet these specifications. To this end, American importers now insist upon pure Ceylon citronella oils and purchase chiefly estate oils. Thus, there is hope that the old practice of adding kerosene to Ceylon citronella oil will gradually be abandoned, at least as far as the imports to the United States are concerned.

Physicochemical Properties.—The odor of the Ceylon citronella oil is coarser than that of the Java oil. Its content of total geraniol (geraniol + citronellal) and citronellal is substantially lower than that of the Java oil, which fact is the principal reason for the lower quality and value of the Ceylon oil. (Cf. the monograph on "Citronella Oil Java, Physicochemical Properties.")

The color of the Ceylon oil ranges from yellow to light brown. A green color indicates the presence of copper. The copper can be removed by treatment of the oil with aqueous solutions of acids, particularly tartaric acid (cf. Vol. I of this work, p. 378).

There is no purpose in recording the limits of the physicochemical properties of Ceylon citronella oils that have been adulterated with mineral oil fractions ("f.a.q.," "ordinary," or "market" oils).

Gildemeister and Hoffmann[7] reported the properties quoted below, but did not state specifically whether these values include also "market" oils:

Specific Gravity at 15°	0.900 to 0.920, exceptionally as low as 0.898
Optical Rotation	−7° 0′ to −22° 0′
Refractive Index at 20°	1.479 to 1.494
Total Geraniol Content	In oils of good quality not below 57%, but occasionally as low as 54% in otherwise normal commercial oils
Geraniol Content	26 to 38.8%
Citronellal Content	5.4 to 15.8%
Solubility	Clearly soluble in 1 to 2 vol. of 80% alcohol. The solution remains clear or turns slightly opalescent on dilution up to 10 vol. In the latter case, however, no separation of oil droplets takes place even after prolonged standing in a closed vessel (Schimmel Solubility Test)

Six samples of pure citronella oils ("estate oils") distilled under the author's supervision in Ceylon (1939), had these properties:

	"A"	"B"	"C"	"D"	"E"	"F"
Specific Gravity at 15°	0.907	0.908	0.907	0.899	0.900	0.900
Optical Rotation	−11° 42′	−9° 40′	−13° 45′	−14° 10′	−14° 36′	−14° 40′
Refractive Index at 20°	1.4826	1.4842	1.4837	1.4792	1.4799	1.4800
Total Geraniol Content	61.1%	60.4%	59.3%	59.3%	57.6%	57.6%
Aldehyde Content, Calculated as Citronellal	9.2%	7.7%	8.9%	14.2%	12.3%	12.3%

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[7] "Die Ätherischen Öle," 3d Ed., Vol. II, 343.

	"A"	"B"	"C"	"D"	"E"	"F"
Solubility in 80% Alcohol, at 20°	Soluble in 1 vol.; opalescent in 4.5 vol. and more	Soluble in 1 vol.; opalescent in 3.5 vol. and more	Soluble in 1 vol.; opalescent in 5 vol. and more	Soluble in 1 vol.; slightly opalescent in 10 vol.	Soluble in 1 vol.; slightly opalescent with more	Soluble in 1 vol.; slightly opalescent with more

(The solubility of samples "A," "B" and "C" was determined according to the "new Schimmel test"; for samples "D," "E" and "F" the "old Schimmel test" was applied.)

Shipments of "estate oils" analyzed by Fritzsche Brothers, Inc., New York, had properties varying within the following limits:

Specific Gravity at 15°/15°	0.898 to 0.910
Optical Rotation	−9° 0′ to −18° 0′
Refractive Index at 20°	1.4790 to 1.4850
Total Geraniol Content	55 to 65%
Aldehyde Content, Calculated as Citronellal	7 to 15%
Solubility	Clearly soluble at some dilution between 1 and 2 vol. of 80% alcohol. When diluted to 10 vol., the solution should remain clear, or become not more than slightly opalescent

Analysis.—Details regarding the methods of analysis of citronella oil will be found in the monograph on "Citronella Oil Java," under the sections dealing with "Physicochemical Properties" and "Analysis." These methods apply also to the Ceylon oil. They include the so-called "oleum test" for the detection of added mineral oils or petroleum fractions, and determination of the flash point.

A few years ago the Essential Oil Association of U.S.A., Scientific Section (E.O.A. No. 12) suggested the following test for the presence of mineral oil (saturated hydrocarbons):

Place 20 cc. of fuming sulphuric acid, containing 15 per cent free SO_3 in a graduated, narrow neck Babcock bottle, 50 cc. capacity, cool in ice bath 10 min., keep bottle in ice bath and add 5 cc. of Oil Citronella Ceylon dropwise at such a rate that the bottle remains cold. Incline the bottle and rotate continuously during the addition, which should require about 5 min. When no further reaction is apparent remove from ice bath, bringing slowly to room temperature with frequent cautious shaking. Wash down neck with 3 or 4 cc. of fuming sulphuric acid.

When no further reaction is apparent on shaking, shake vigorously for 30 seconds. Place bottle in water bath and heat slowly to 60° C. with frequent agitation. (Caution is required, as escaping gas may force some solution from bottle.) Heat at 60°–65° C. for 15 min., shaking the contents carefully but vigorously 8–10 times during this period. Remove from bath and without cooling, carefully add sulphuric acid (specific gravity about 1.84) until the bottle is about three-fourths full. Shake well. No material should adhere to stem and sides at this point; cool to room temperature, add sulphuric acid (specific gravity about 1.84) until the level is about two-thirds up in neck of flask. Centrifuge 10 min. at 1,200 revolutions per minute or stand overnight and read, centrifuge an additional 10 min. Pure Oil Citronella Ceylon should have no readable separation.

Solubility.—These oleum tests (which, except for slight modifications, are fundamentally the same) practically supersede and eliminate the various solubility tests which were developed years ago by Schimmel & Co. for the special purpose of detecting the presence of mineral oil fractions or kerosene in Ceylon citronella oil. Details pertaining to the "old Schimmel test," the "new Schimmel test," and the "raised Schimmel test" will be found in Vol. I of this work, p. 332. As has been pointed out, the "new" and the "raised" Schimmel tests have never been adopted by the industry. The "old Schimmel test," often referred to simply as "Schimmel test," offers a rough and ready means of detecting addition of kerosene amounting to more than 5 to 7 per cent; oils containing less kerosene will usually pass this test. Many contracts for Ceylon citronella oil, particularly in Europe, are still based upon this test. It is primarily for this reason that the test is mentioned here.

A few years ago, the (British) Essential Oil Sub-Committee of the Society of Public Analysts' Analytical Methods Committee issued a report dealing with a solubility test for citronella oil.[8] The Sub-Committee found the "Schimmel test" to be unsatisfactory, because it is not sufficiently well defined to give concordant results in different hands. Hence the following test (which should be known as the "London Solubility Test") has been recommended:

> One volume of citronella oil should form a clear solution at 20° C. with from one to two volumes of 80 per cent v/v alcohol, and with a total of four volumes of 80 per cent v/v alcohol; the solution should not be more than faintly opalescent and there should be no separation of oily drops on standing overnight in a stoppered cylinder at 20° C.

In practice this test is actually very similar to the "new Schimmel test" (see Vol. I of this work, p. 333) based on the description given in the Bericht Schimmel & Co. of 1923.[9] In the "new Schimmel test," 80 per cent alcohol is added drop by drop to the point of maximum cloudiness or turbidity, the mixture then being permitted to stand undisturbed to ascertain whether or not any separation of oily droplets occurs. In actual practice, the point of maximum turbidity usually occurs after 4 or 5 volumes of 80 per cent alcohol have been added. In the full description of this Schimmel test, the analyst

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[8] *Perfumery Essential Oil Record* **37** (1946), 30.

[9] *Ber. Schimmel & Co.* (1923), 18.

is cautioned that violent shaking should be avoided to prevent the separated oil from being so finely divided that separation into droplets will not be noticed until some considerable time afterward. Such a warning might well have been included in the "London test," to hasten the routine examination of many samples in a commercial laboratory.

Total Production.—

Annual Exports of Ceylon Citronella Oil 1939–1948 (10 Years)[10]

Year	*United Kingdom*	*U.S.A.*	*India*	*S. Africa*	*Other Destinations*	*Total Tons*
1939.........	221	270	31	8	161	691
1940.........	262	138	68	4	124	596
1941.........	259	115	176	18	50	618
1942.........	275	232	157	20	112	796
1943.........	199	138	53	62	153	605
1944.........	71	321	69	44	82	587
1945.........	91	169	79	84	87	510
1946.........	412	139	58	33	128	770
1947.........	84	219	69	45	153	570
1948.........	173	134	115	51	227	700
Average 10 Years......	205	187	87	37	128	644
Average Percentage....	31.8	29.0	13.5	5.8	19.9	100

From these figures it can be seen that during the past ten years the average export figures amounted to 644 tons per year.

The yearly production of citronella oil in Ceylon ranges normally from 650 to 700 tons. Unusual droughts may reduce this quantity occasionally by about 100 tons.

Chemical Composition.—The chemical composition of the Ceylon type of citronella oil (derived from *Cymbopogon nardus* Rendle, *lenabatu*) has not been investigated as thoroughly as that of the Java type of citronella oil (derived from *Cymbopogon winterianus* Jowitt, *mahapengiri*), large quantities of the latter being processed technically for the isolation of geraniol, citronellal and other components.

The following substances (listed approximately in order of their boiling points) have been observed in oil of citronella Ceylon:

Camphene. From the terpenes, which constitute 10 to 15 per cent of the oil, Bertram and Walbaum,[11] and Schimmel & Co.[12] isolated camphene. Conducting gaseous

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[10] Courtesy Volkart Brothers, Inc., New York.

[11] *J. prakt. Chem.* [2], **49** (1894), 16.

[12] *Ber. Schimmel & Co.*, October (1899), 12; April (1912), 40.

hydrochloric acid into an ethereal solution of the fraction b. 157°–164°, Bertram and Walbaum obtained a solid hydrochloride which, on heating with water to 100° under pressure, readily yielded camphene. Treating the same fraction with a mixture of glacial acetic acid and sulfuric acid, Schimmel & Co. prepared isoborneol m. 212°; they isolated camphene in solid form also directly by careful fractionation of the oil. According to Naves,[13] Ceylon citronella oil contains from 5 to 6 per cent of camphene (formylation by the Ljubomilov method).

Limonene. Identified by Schimmel & Co.[14] by preparation of the tetrabromide m. 104.5°, and of the nitrolbenzylamine derivative m. 92°–93°.

Dipentene. Characterized by Bertram and Walbaum,[15] and by Schimmel & Co.[16] through the tetrabromide m. 124°–125°.

Other Terpenes(?). When fractionating the oil, the last named workers [17] noted the presence also of other terpenes which had a very low specific gravity; these could not be identified (possibly myrcene was among these.—The author).

Methyl Heptenone. The forerun of the oil furthermore contains traces of methyl heptenone, which, in the course of the above cited investigations, was identified by preparation of its semicarbazone m. 134°–135°.

d-Citronellal. The aldehyde $C_{10}H_{18}O$, forming one of the main constituents of Ceylon citronella oil, has been the subject of considerable controversy (cf. the monograph on "Citronellal" in Vol. II of this work, p. 336). Dodge [18] expressed the opinion that the compound in question was an aldehyde, and suggested the empirical formula $C_{10}H_{18}O$; definite proof for its aldehydic nature was offered by Semmler.[19] Ceylon citronella oil contains 5–16 per cent of citronellal in dextrorotatory form. According to Naves,[20] the citronellal present in Ceylon citronella oil is slightly racemized: $[\alpha]_D^{20}$ $+12° 6'$ to $+12° 36'$. The statement that citronellal appears to have a very slight rotatory power, contrary to what is known of citronellal derived from Java citronella oil, is a myth (Naves.).

l-Borneol. In the citronellal fraction Schimmel & Co.[21] observed *l*-borneol, which was identified by preparation of its phenylurethane m. 138°. According to Naves,[22] the *l*-borneol contained in Ceylon citronella oil is stereochemically pure: $[\alpha]_D^{20}$ $-32° 42'$ (c = 20, in acetic acid); $-34° 13'$ (c = 20, in chloroform); $-36° 43'$ (c = 20, in benzene).

A Substance(?) with linaloöl odor. The same fraction was found to contain a substance with an odor reminiscent of linaloöl, which on oxidation yielded citral.

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[13] *Perfumery Essential Oil Record* **39** (1948), 346.

[14] *Ber. Schimmel & Co.*, April (1912), 40. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 344.

[15] *J. prakt. Chem.* [2], **49** (1894), 16.

[16] *Ber. Schimmel & Co.*, October (1899), 15.

[17] *Ibid.*, April (1912), 40.

[18] *Am. Chem. J.* **11** (1889), 456.

[19] *Ber.* **26** (1893), 2254.

[20] *Perfumery Essential Oil Record* **39** (1948), 346.

[21] *Ber. Schimmel & Co.*, April (1912), 43. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 345.

[22] *Perfumery Essential Oil Record* **39** (1948), 346.

Nevertheless, the substance in question does not seem to be linaloöl, contrary to the early opinion of Schimmel & Co.[23]

Thujyl Alcohol(?). When oxidizing this linaloöl-like substance with chromic acid, Schimmel & Co. noted, aside from citral, a compound, the odor of which recalled thujone, which gave a semicarbazone m. 179°–182°. Attempts were made, using permanganate, to oxidize the fraction b. 202°–210° (which possessed an odor of thujyl alcohol) to thujaketonic acid; these were not successful, however.

Nerol. In the fraction b. 218°–230°, after it had been freed of borneol, the same investigators [24] identified small quantities of nerol by preparation of its tetrabromide m. 116°–118°.

Geraniol. From the next fraction, which forms a large part of the oil, Schimmel & Co.[25] isolated geraniol by preparing its calcium chloride compound and regenerating the pure alcohol by decomposition of the addition product with water.

Geranyl Acetate, Citronellyl Acetate, and Citronellyl-*n*-butyrate(?). The next fraction of the oil contains geranyl acetate, accompanied by citronellyl acetate and citronellol esterified probably with *n*-butyric acid. According to Schimmel & Co.,[26] citronellol does not occur in the oil as a free alcohol, but in ester form only. Citronellol was identified by preparation of the silver salt of the acid phthalate, m. 125°–126°. According to Naves,[27] the free alcohols occurring in the oil include only small proportions of citronellol.

Methyl Eugenol. Eugenol methyl ether is present in the higher boiling fractions of Ceylon citronella oil, and was characterized by Schimmel & Co.,[28] who oxidized it with potassium permanganate to veratric acid m. 179°, and also converted it to methyl isoeugenol. The latter yielded a dibromide m. 102°.

Sesquicitronellene. Removing the methyl eugenol from the high boiling fractions by extraction with 70 per cent alcohol and redistilling the residue, Schimmel & Co.[29] obtained two fractions consisting chiefly of two dextrorotatory sesquiterpenes.

The lower boiling compound b. 270°–280° (with much decomposition), b_{15} 157°, d_{15} 0.8643, α_D $+1° 28'$, n_D^{15} 1.51849 which, however, still contained some oxygenated substances, apparently belongs to the aliphatic series and, according to Gildemeister and Hoffmann,[30] is most likely identical with sesquicitronellene.

This sesquiterpene was later identified by Semmler and Spornitz [31] as a natural component of Java citronella oil (cf. the monograph on "Sesquicitronellene" in Vol. II of this work, p. 83).

A Sesquiterpene(?). From the higher boiling of the two above-mentioned fractions Schimmel & Co.,[32] by careful fractionation, isolated another sesquiterpene b. 272°–275°, b_{16} 170°–172°, d_{15} 0.912, α_D^{17} $+5° 50'$, which, however, could not be

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[23] *Ber. Schimmel & Co.*, October (1899), 17.

[24] *Ibid.*, April (1912), 40.

[25] *Ibid.*, October (1893), 12.

[26] *Ibid.*, April (1912), 40.

[27] *Perfumery Essential Oil Record* **39** (1948), 346.

[28] *Ber. Schimmel & Co.*, October (1898), 17; Oct. (1899), 18.

[29] *Ibid.*, October (1899), 19.

[30] "Die Ätherischen Öle," 3d Ed., Vol. II, 346.

[31] *Ber.* **46** (1913), 4025.

[32] *Ber. Schimmel & Co.*, October (1899), 19.

freed entirely of the lower boiling fraction (sesquicitronellene), as the difference in the boiling points was only 8°.

Farnesol. When isolating geraniol from Ceylon citronella oil, Elze[33] obtained a small quantity of a fraction b_5 150°–165°. After saponification, and on steam distillation, this fraction yielded a minute portion of an oil, which on treatment with phthalic anhydride and decomposition of the phthalate gave farnesol, b_5 145°–146°, d_{15} 0.895, $\alpha_D \pm 0°$. According to Elze,[34] Ceylon citronella oil contains 0.2 to 0.3 per cent of farnesol, free and in ester form.

Use.—Ceylon citronella oil is used chiefly for the scenting of soaps, sprays, disinfectants, polishes, and all kinds of technical preparations where price is of prime consideration.

SUGGESTED ADDITIONAL LITERATURE

F. Sorges, "Essence of *Cymbopogon nardus* of Sicily," *Chim. ind. agr. biol.* **16** (1940), 21. *Chem. Abstracts* **34** (1940), 3013.

OIL OF CITRONELLA JAVA

History and Development.—Java's citronella oil industry dates back to about 1890, when, during a hunting trip near Cheribon, A. K. J. Kaffer discovered a primitive native still in which wild growing sereh (citronella) grass was distilled. Interested in the possibilities of such an oil, Kaffer later experimented with raising the grass on his own fields. Although its origin is obscure, this grass was of such good quality that in 1890 a small planting was started in the Buitenzorg Botanical Garden. Aside from Kaffer, there were other pioneers in this field, M. Treub, and P. V. van Romburgh among them, who initiated production of the grass in western Java. A. W. K. de Jong[35] and later H. W. Hofstede[36] contributed greatly to the development of the industry by their detailed studies of Java citronella oil.

In 1899 the "mahapengiri" type of citronella, introduced from Ceylon, was first planted in Buitenzorg and then propagated widely. Kaffer extended his own plantations, which were not very far from Buitenzorg. At that time it was extremely difficult to compete on the European market with the well-established Ceylon oil. In their annual report of 1900, however, Schimmel & Co. commented very favorably on a Java oil distilled by van Romburgh from plants grown in the Botanical Garden of Buitenzorg. In 1902, there

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[33] *Chem. Ztg.* **37** (1913), 1422.

[34] *Ibid.*

[35] "The Ethereal Oil Yielding Plants of the Netherlands East Indies and the Preparation of Their Oils," *Ber. van de Afd. Handelsmuseum van het Koloniaal Inst.* No. 7, 183. *Indische Mercuur* **45** (1922), 1.

[36] "Citronellaolie," *Mededeelingen van de Afdeeling Nijverheid* No. 4, Buitenzorg, Archipel Drukkerij (1928).

were two citronella distilleries in Java, one of them, "Odorata," located in Tjitjoeroeg and owned by Kaffer, the other "Tjikantjana," in Tjandjoer. Between 1900 and 1910 the European consumers began to realize that the Java oil, being superior in quality, deserved a higher price than the Ceylon oil; also, Europe's new and rapidly growing industry of aromatic isolates and synthetics could use the Java oil to far greater advantage than the Ceylon oil. As a result, Java's citronella industry expanded steadily, and in 1919 Java for the first time surpassed Ceylon in the production of citronella oil. The banner year of 1924 saw prices higher than fl. 7 per kilogram, and from then on production increased rapidly until in 1926 Java produced twice as much oil as Ceylon. At the end of 1933, during the world-wide depression, prices fell to about fl. 1 per kilogram, but even then expansion continued until about 1,800 metric tons of oil were produced in 1934, when prices fell below fl. 0.80. This increase in production despite declining prices was a result of the even more depressed condition of all other agricultural products, which induced many small growers to turn to citronella, which was still relatively remunerative.

It might be well at this point to consider the effect which the enormously increased production had on the quality of the oil. In the early years of Java's citronella industry, all oil was distilled under peculiarly uniform conditions, dependent upon identical plant material (consisting exclusively of "mahapengiri"), identical soil, altitude, stills, and working methods. The only distilleries existing at that time were large, European-owned and managed, and processed grass grown only on their own plantations. Freshly cut grass of best quality was distilled with direct steam of relatively high pressure, and for only a short time. Hence, the oils were uniform in quality, and the physicochemical properties of Java citronella oil varied within only very narrow limits.

In the early 1900's the narrow-leafed, hardier and longer-lived "lenabatu" variety of citronella was introduced from Ceylon, probably with the idea of raising it experimentally on some of the poorer soils of Java. It was hoped that this variety, although giving a lower yield and an inferior quality of oil, might nevertheless offer a solution to the problem of opening new terrains for planting. Unfortunately, however, during the years when citronella plantings were being vastly expanded and the demand for planting material was great, the inferior "lenabatu" was propagated along with the "mahapengiri." This, of course, brought about a lowering of the quality of the Java oil which had gained such a high reputation on the world markets. It is not in the interest of Java to produce this type of oil, and even today growers must guard against gathering their young plants ("bibit") from "lenabatu" fields.

The rapid expansion of the citronella industry in Java between 1910 and

1934 had still other consequences. Many Chinese, and wealthier natives, took up distillation in competition with the European producers. They had to purchase their planting material ("bibit") from existing plantations, which frequently supplied the worst quality. New plantations were started on different soils, at different altitudes, and in regions with different weather conditions. The newcomers could not afford to erect large and modern steam distilleries; they used more primitive (direct fire) stills, and often distilled leaf material purchased from native growers instead of grass grown on their own plantations. The idea was to obtain as much oil as possible from the plants without paying much attention to quality; and when prices finally fell to unprofitable levels, plantings were neglected and old fields were not renewed. It is easy to understand that buyers abroad had reason to complain about the quality of the Java citronella oil. Conditions finally became so serious that the Netherlands administration had to step in and, by enacting a number of strict control measures, save the industry which had been a source of considerable income to the colony.

Botany.—The bulk of the Java type of citronella oil is distilled from *Cymbopogon winterianus* Jowitt, *mahapengiri* (*Andropogon nardus java* de Jong), called "mahapengiri" in Java. The plants, recognizable by their broad leaves, require good soil and much care in growing and cultivating. They must be renewed after a few years, because the root stocks work themselves out of the ground. Young shoots, growing from the axillary leaves of the mother plant, develop into large clumps of grass with leaves (3 to 4 ft. high) that bend outward until their ends almost touch the ground. The plants would flower if left in the natural state. Tall plants usually contain less essential oil than normal ones.

At present, most citronella plantings in Java consist of "mahapengiri" grass, but there are still a few of "lenabatu" (which accounts for the substandard lots of Java citronella oil that occasionally reach the exporters in Java).

"Mahapengiri" is not indigenous to Java. As has been mentioned, it was imported from Ceylon in the early years of the twentieth century, when several types of citronella grass were experimented with in Buitenzorg. The wild "mana" grass, *Cymbopogon confertiflorus* Stapf, which is said to be the parent plant of all commercial (cultivated) citronella grasses, does not occur in Java.

Soil, Climate, and Altitude.—There exist in Java several varieties of wild growing sereh grass, but they are not utilized for distillation. All plant material which serves for recovery of oil originates from numerous plantings, both small and large.

Altitude, climate, and soil conditions profoundly affect the vitality and life span of the plant, as well as the yield and quality of the oil (particularly its citronellal content). Uniformity cannot then be expected from oils which originate from different producing regions. For a long time citronella was considered a very sturdy plant which could get along even on poor soil. This belief caused many costly errors, because such soils, after a promising start, were quickly exhausted; poor soils do not support citronella for several consecutive years without crop rotation, rest, and ample green fertilization. It is true that even exhausted plantings yield a fair amount of oil, if other favorable factors intervene, an ideal succession of rain and sunshine, for example. As a rule, however, the yield and quality of oil from plants raised on poor soils are normal only for the first three years, and then decline rapidly.

Citronella grass grows in low as well as in high altitudes (up to 2,000 ft. and more). All kinds of soils, provided they are sufficiently fertile, suit the purpose. Rich, alluvial soil, at 600 to 700 ft. altitude, and *in a humid climate with regular rainfalls,* would probably offer most favorable conditions for good yield and quality of oil, and guarantee longevity of the plantings. At lower altitudes the plants grow very slowly during the dry season, with constant danger of dying off if cut in the beginning of, or during, that period. Heavy and loamy soils of poor texture are not suited for citronella. Neither are waterlogged soils, partly submerged, partly dry, unless they are carefully drained. According to Hischmann,[37] calcareous soils, with only a thin sand layer, yield good grass and good oils for a time, but are quickly exhausted. As soon as the roots reach the lime subsoil, the citronellal content of the oil starts declining. Hischmann believes that sandy soils, on which the grass does not grow too high, offer the natural precondition for a good oil; moreover, such soils are less afflicted with weeds. Deep sand, sufficiently rich, is often better than loamy or even fertile soil. Although the growth of the plants on such sands is meager and the quantity not large, the proportion of oil in relation to weight of leaves is more favorable. When the plants grow too quickly, the formation of oil becomes a secondary function and, after all, the leaves *per se* are only ballast. It is more advantageous to obtain a higher percentage of oil from a smaller amount of leaves because bulk increases cost of transportation, labor, and steam. Virgin soil, reclaimed from jungle, yields, like irrigated land, a very large amount of grass for the first years, to the detriment of oil formation. Such was the case in Sumatra with newly established plantings, which produced insignificant quantities of citronella oil.

Soils really suitable for citronella are not restricted in number and not always highly valued. Most producers seem to be impressed by an abundant yield of leaves, rather than by a thinner growth, and a better yield of oil.

[37] *Ber. Schimmel & Co.* (1938), 20.

Planting and Cultivating.—There are no fixed rules for laying out plantations, because of the great variations in nature of terrain, labor available, and wages.

After being cleared of trees, the land is burned over and planting holes are dug. If a planter can afford extra labor, the field, after being burned, should be gone over with a mattock. The more intense the cultivation, the more favorable will be the results. In slightly hilly ground, square fields of about 4 hectares are laid out. Wagon roads should not be forgotten. In very hilly regions, conditions are entirely different, and citronella must frequently be planted on slopes which are not suitable for rice or other crops. Sereh grass may grow quite well there, provided the soil is not too poor.

It is possible to raise citronella successfully in young rubber plantations four or five years old, with the rows of high pruned trees more than 24 ft. apart. Citronella grows in the sun and in the shade, but in the latter case few new shoots appear; the growth is retarded and, consequently, there will not be more than one yearly harvest. The blades become hard and woody, so that cutting yields too much stalk material in proportion to leaves. Shade is also detrimental to the yield of oil and its total geraniol content.

Since the grass requires a fairly large amount of moisture, planting must take place only during the rainy periods. Thus, new fields are usually laid out in December-February, i.e., during the first part of the rainy season. No grower would dare to start planting in April-October because of the risk of losing his investment during the dry season. New plants which have not developed sufficiently during the latter part of the rainy season, that is up to May, usually die early in June-September. Those that survive are subnormal.

Planting material ("bibit") for sereh grass is obtained by dividing old clumps. The best type originates from the Experiment Station in Buitenzorg. Although sereh grass does flower, it is difficult to grow it from seed. When shipping "bibit," the leaf must be torn off beforehand, and the segments dried a little in the shade. Wet planting material, that has been rained upon, spoils easily.

About ten sturdy divisions ("seed pieces") can be obtained from each clump. Calculating two divisions to each planting hole, one acre of old plants would yield material for five acres of a new planting. On good soil, the plants should be set out 3 by 3 ft. apart; the interval may be less in poorer soil. If a planting is to last only a short time, 2 by 2 ft. will be sufficient. The period between harvests should also be considered, because a longer growing time requires wider planting.

Sereh grass is usually planted by digging holes with a mattock or dibble. It is necessary to plant the segments fairly deep, as otherwise the clumps easily work themselves out of the ground. Hilling up, loosening of the soil.

and weeding are advisable to improve the yield, and maintain the plantation. In actual practice, however, little care is exercised, and it even seems doubtful whether the expense is worth-while during periods of low oil prices.

With regular cutting at intervals of about three months, starting from the beginning of the second year after planting, a plantation should be discontinued after the fourth year, because citronella is rather soil-exhausting, and any prolonged growth would be detrimental to the soil, the plants, the yield, and quality of the oil. After the fourth year, the yield of grass and oil diminishes considerably, and from the fourth to the eighth year only 40 per cent of the initial quantity of leaves, at most, can be expected. Fields older than five years are rarely profitable. Nevertheless, one frequently encounters plantations which are renewed only when they no longer give a sufficient yield; there even exist fields which are harvested up to the twelfth year. This, of course, is quite uneconomical in most cases. The natives, who plant small patches (from one-quarter hectare to two hectares) and on cheaper ground, often discontinue sereh grass after the third year, and rotate the crop by raising peanuts or tapioca. It is a fact, however, that only poor yields are obtained when citronella is regrown later on these same fields, because this type of rotation does not rebuild the soil. For this reason native plantings seldom last longer than three years, whereas large estate plantings last from four to five years, and sometimes longer, because their soil is usually more fertile and greater care is taken in laying out the sereh fields. It is difficult to make definite statements regarding the life span of a sereh plantation. In 1939 there existed a few twenty-year-old plantings which were still good, but, in general, one-quarter to one-third of the European owned plantations consisted of fields four to eight years old.

In the years prior to World War II, the very low prices of the oil made it unprofitable to plow under old citronella fields and lay out new plantings. Changing over to the cultivation of other crops was even more costly. The financial difficulties caused by the world depression had gradually forced the large estates to turn over the growing of sereh to the natives and to rely upon the purchase of native-grown grass. As a result, the large distilleries on the old European owned estates had to process ever greater amounts of leaf material grown by the natives from seedlings which had been supplied by the estates. Once the natives had their own plants it was easy for them to continue propagating, with the result that the native plantings in the vicinity of the old estates increased largely. The natives, with the help of their families, can operate at much lower cost than the plantation owners, for which reason it became more and more difficult for the estates to maintain their sereh plantings. Prior to World War II, native plantings, two to three years old, supplied about two-thirds of the total amount of leaf material harvested. According to Hischmann's[38] analysis of government statistics from 1932 to 1936, European owned estates then comprised far more older plantings than in former years.

When a planting of sereh grass is to be renewed, the soil must first be regenerated. The fertilizers which would seem most appropriate cannot be used in Java for several reasons. The distilled and exhausted grass serves as fuel for distillation, coal being almost unknown in Java, and wood being too expensive in many sections, or having little fuel value. Chemical fertilizers, such as are used on sugar plantations, are costly, and stable dung is not available in sufficient quantity. At one time the estates used imported fertilizers when the fields were replanted after the first four years. The result was that, while the yield of grass increased, the yield of oil remained subnormal, as compared with plantings on fresh soil.

For green fertilizers Hischmann[39] suggested using *Tephrosia candida, Tephrosia vogelii, Crotalaria,* and various mimosa varieties, because they throw off a very large amount of leaves. After these bushes have grown on a field for two years, the ground, when plowed, becomes loose and almost springy, like mossy forest soil, and recuperates beautifully. The estates tried to leave these bushes on the plantings for at least one year, but the small native growers, often on the verge of starvation, are not able to employ this method at all. They simply cannot afford to leave their ground unproductive for one year, or rather for two years actually, because a new sereh planting yields nothing for the first eight or nine months.

During the war years the government of Java could do nothing to improve the quality of the grass by selective breeding. In fact, the grass has suffered by the continued growing for many years and seems to be less hardy and less resistant to diseases than formerly. When plantings are expanded during periods of high oil prices, owners of old and poor fields offer their "bibit" to other growers for new plantings, and, since it is cheaper, inexperienced prospective planters sometimes buy such inferior planting material. Obviously, this does not help to retain the original good qualities of the plant, its resistance to disease, and the yield and quality of the oil.

Harvest.—Citronella planted in December or January can be harvested for the first time in September or October, and today the native growers generally follow this procedure. At one time, the estates waited a full year until the plant had developed its full root system, which is important for a long life span. During the peak of production, a healthy sereh plantation looks like a meadow, although the plants are about 3 ft. (1 meter) apart. Each plant forms a sturdy, big bunch, from which the leaves are cut off progressively and ever higher from the soil. The harvesters cut each plant

[38] *Ibid.* (1936), 15; (1937), 18; (1939), 15.
[39] *Ibid.* (1936), 16.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 11. Production of citronella oil in Java. Harvesting of the plants on a small field.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 12. Production of citronella oil in Java. The harvested and bundled plant material is carried to a distillery.

separately, using knives for the purpose. Proper timing for the cutting is advisable, in order to prevent the grass from flowering.

It is very important to choose the most opportune time of harvesting in order to increase the yield of the planting. A too short growing period decreases the productivity, and seems to affect the plants to such an extent that a field can perish within a short time. If, on the other hand, the grass is left standing for more than three months, the lower leaves wither and considerable oil will be lost; moreover, the content of geraniol and citronellal decreases. Thus, an average between the two extremes should be chosen. However, a definite cutting period cannot always be indicated, because the climate of Java, and the rainy and dry seasons are quite irregular. The best time for cutting seems to be the moment when the stems bear six adult leaves with the seventh leaf in rolled up position. The grass should be harvested three times or, under very favorable conditions, four times a year, but since the small native growers have learned that it is quite easy to transform their grass into ready money, they make four and even more cuttings without waiting for the proper harvesting time. (If a native grower needs cash, he simply cuts from his fields as much leaf material as he requires for distillation, without giving consideration to the proper maturity of the fields.)

Western Java has its rainy season from October to February, and its dry season from May to September of which, however, only July, August, and September are actually dry. The citronella harvest is larger during the rainy season than during the dry season. If old fields are harvested at the beginning of the dry season, and on days without previous early morning dew, the plants suffer much, and the fields are soon in such poor condition that it is often necessary to plow them under in order to treat the soil for the next crop.

The practice of cutting the plants too short, especially of cutting below the knot where the leaves are implanted in the stalk, is very harmful, and involves the risk, particularly during dry weather, of the blade stalks dying off. Low cutting, practiced frequently by the native growers, has another disadvantage: many nearly oil-free parts of the blades are collected which, when distilled, diminish the yield of oil. After the grass is cut, the harvesters remove the old, dried out leaves and tie the fresh leaves in bundles so that they can be carried or hauled to the distillery.

Yield of Oil.—It is difficult to express the yield of oil per acre of grass in definite figures because it depends upon so many factors: climate, fertility of the soil, age of the planting, and method of distillation, among them.

The figures on yield given by de Jong in 1922 probably apply to the time when the first citronella estates existed in Java. As average production on normal soil during the second year, de Jong indicated about 400 piculs (1 picul = 136 lb.) of leaves per bouw (1 bouw = 1.7537 acres) or about 35 metric tons per hectare which, taking 0.7 per cent as average yield of oil, amounts to 247 kg. of oil per hectare, or almost 220 lb. of oil per acre. (One hectare = 2.471 acres.) This figure appears very high, when compared with the estate yields of 1932 to 1936, and is probably due to the fact that in those early days the very high price of the oil permitted extensive care of the citronella fields on the estates. Hischmann,[40] in 1939, confirmed such high yields on new plantations in the second year, but only in rare cases. As a rule, the yield of oil from leaves growing profusely in rich soil is substantially below 0.7 per cent. Fields which give an exceptionally high yield of oil usually consist of sandy soils, where citronella grows not as tall and more slowly. Sereh fields four to seven years old contribute only very little to the total production of an estate, and during periods of low oil prices such old fields are not economical at all. As long as the oil prices were high, an estate could carry on with some old fields, but even then an estate consisting chiefly of old fields could not be considered a paying proposition.

The natives, on the other hand, raise their grass mostly on poor soil, which in some cases has been under cultivation with various crops for generations and without any fertilization. Their leaf production during the second and third years is, on the average, 12 metric tons per hectare and per year. Based on a yield of 0.7 per cent of oil, this amount of grass represents 84 kg. of oil per hectare, or about 75 lb. per acre. Some native growers uproot their citronella fields at the end of the third year because in the fourth year the yield is too low. Thus the planting will be productive for only slightly more than two years. Most natives, however, try to keep their fields in citronella somewhat longer, which delay results in even lower average yields.

Citronella grass grown on estates is of about the same quality as that grown by natives and contains approximately the same percentage of oil. It has been claimed that the average yield of oil per acre from estate grass is higher, but this seems quite exceptional. It is difficult to arrive at comparative figures (ratio) between the quantity of leaf material produced per acre on the estates and that grown per acre on native-owned lots. Prior to World War II the total acreage of the estate plantings was known, but even then figures pertaining to the numerous small citronella plots owned by native growers were not exact. Today the picture is even more confused. According to Hischmann's analysis of the Java Government statistics,[41] only

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[40] *Ibid.* (1939), 17. According to a recent private communication dated March 1st, 1949, by Dr. J. A. Nijholt, Buitenzorg, prior to World War II a yield of 250–300 kg. of oil per hectare was considered very good. At present the yield is much lower because estates no longer exist, and the native fields are in a poor condition, partly overgrown with weeds.

[41] *Ibid.* (1936), 15.

about 20 per cent of the sereh grass in 1936 was produced on large plantations, the rest being grown by small-scale, native farmers, some of whom did not distill their crops but sold them to the numerous distilleries. The average yield of oil was then 0.6 per cent, which means that, based on the 1935 statistics, 276,000,000 kg. of leaves were required to distill the oil produced in that year.

When purchasing citronella grass, the distillers base their estimates on a yield of 1 lb. of oil per 150 lb. of dried leaves. Wet material is not accepted as it requires a great amount of steam for distillation. It can be assumed with certainty that all the oil not declared by the estates as own distillation is produced from leaves grown by natives, because there exists no third producing party. Thus Hischmann[42] concluded from the 1938 statistics that 7,578 hectares of citronella grown on the estates at that time yielded only 343 metric tons of oil per year, or 45 kg. per hectare, whereas 14,608 hectares of native grown citronella yielded 1,175 metric tons of oil, or 80 kg. per hectare. In view of these figures the yield (in 1938) of 45 kg. per year and per hectare on the estates was much lower than the yield obtained in the early years of Java's citronella industry when the plantations on the estates were young, vigorous, and well kept. The statistics show clearly how the low prices brought ruin to the operations of the estates during 1932 to 1936. Compared with estate yields in former years, 80 kg. of oil per hectare of native-grown grass is not unusually high. The data published about citronella production on the estates prove that nearly one-half of their citronella acreage in 1938 consisted of fields at least four year old. Half of the citronella acreage on the estates had passed the peak of normal grass production.

There exist no data on the age of the native plantings, but it is generally known that the natives plow under a sereh field as soon as the yield of grass declines considerably, whereas the estates usually started their plantings carefully in order to secure a longer life span. For this reason the peasants generally have younger fields and obtain a better average yield. In years preceding World War II, the estates could not renew their sereh fields to the same extent as formerly, and could not spend much for the upkeep of their existing fields, suffering a good deal from the low price of the oil. This lack of care was reflected in the yield. Young fields, even though not so well kept as old ones, have a much larger grass production. This very fact partially explains the discrepancy in the production figures, the other factor being that the published areas for peasant grass have always been much smaller than the actual ones. At present the basis for estimates is even more complicated, but the fact remains that the natives uproot their citronella

[42] *Perfumery Essential Oil Record* **29** (1938), 168.

fields whenever it seems advisable and much more quickly than estates would or could, in order to change to other more remunerative crops.

In 1937 almost 24,000 hectares of citronella grass were under cultivation, chiefly in western Java, especially Priangan. The estates distilled the grass in their own distilleries, and there were almost 100 such distilleries, about 12 of them buying the grass from native growers. Furthermore, there existed in that year almost 80 native distilleries, quite small, and nearly all located in Priangan. In addition, there is a native home industry, in which small and rather primitive stills are used.

The figures on yield of grass and oil given above all refer to the years preceding World War II. Since the war, the Japanese occupation and the civil strife after the war, further changes have taken place in Java's citronella oil industry. At the time of this writing (1949) comprehensive and exact data are not yet obtainable, but from general information reaching Batavia it appears that the yield of oil has declined from the former 0.6–0.7 per cent to 0.4–0.6 per cent; moreover, the total citronella acreage in western Java has been reduced to less than 8,000 hectares. According to latest reports,[43] there are now in western Java altogether 7,573 hectares of citronella plantings. Of this total acreage 4,025 hectares are old patch plantings that have not yet been restored to production; 2,963 hectares are in actual production, and 585 hectares have been replanted but are not yet in production. Of this total of 7,573 hectares 6.2 per cent is of an inferior grass variety, the rest is high-grade grass. Because of the fact that most of the fields need replanting the average production of the plantings is low. Java's total production of citronella oil in 1948 amounted to about 300 metric tons only. Based on the present total acreage of about 7,500 hectares in western Java, this would mean approximately 40 kg. of oil per hectare and year, or about 35 lb. of oil per acre and year. However, when calculating on the basis of the 2,963 hectares that are actually in production (see above), the yield of oil per hectare and year would be almost 100 kg., or almost 90 lb. per acre. All of the citronella fields are at present (temporarily ?) in the hands of the natives, the estates having been divided up. Only 25 per cent of the distillation capacity in western Java is at present utilized; the rest is idle, because of several circumstances. Main centers of production now are Tasikmalaja, Tjiamis, Tjitjalengka, Bandoeng in the Priangan, and Bantam.

Harvest and Distillation.—The leaves are usually harvested in the early morning and then dried on the ground outside of the distilleries. Drying requires only 3 to 4 hr. in bright sunlight but, of course, much longer during the rainy season. While drying, the leaves must be turned over occasionally to prevent fermentation. Careful short drying of the leaves is said to benefit

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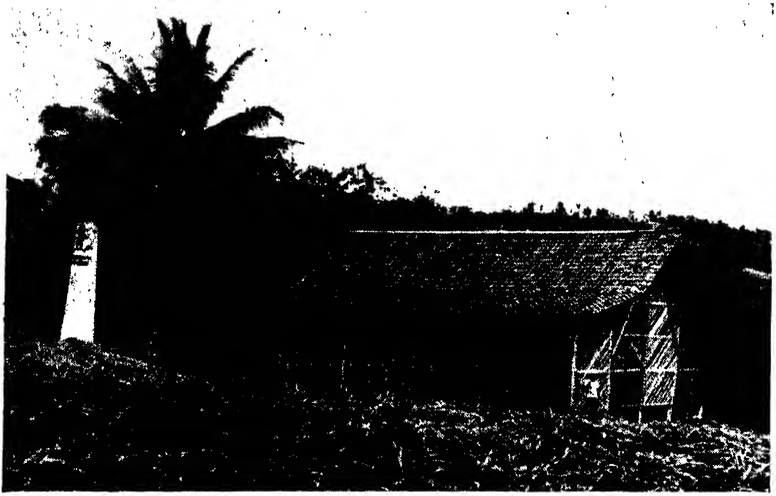
[43] Private communication from Dr. J. A. Nijholt, Director of the Laboratory for Chemical Research, Buitenzorg, Java, March 24, 1949.



Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 13. Production of citronella oil in Java. A native-owned distillery.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 14. Production of citronella oil in Java. A distillery on one of the large estates.

the quality of the oil, whereas long drying, especially in the rain, is harmful. It is claimed that the leaves should not be exposed for any length of time to sun or rain, and that the material should be distilled the same day that it is harvested. If this cannot be done, it should be dried inside the factory or under sheds or on platforms near the boiler.

The distillers prefer to distill dried leaves, because they can charge more into a still and also because the distillation of dry leaves requires less steam and fuel. During periods of continued rain the crop would have to be distilled in a wet condition and, for this reason, most distillers today stop operating in rainy weather. It would be advisable to eliminate weeds from the sereh grass during the drying process, but when oil prices are low few distillers can afford this precaution. Many distillers do not bother to cut the leaves into short pieces prior to distillation. They seem to forget that whole leaves occupy more space in the retort than chopped material, and that, because of uneven distribution in the still, steam channeling and a lower yield of oil will result. Chopping of the leaves increases the economy of a still.

The faster the steam passes through the charge, the lower is the oil percentage per kilogram of condensed steam. If, on the other hand, the steam passes too slowly through the charge, the time of distillation will be longer and the hourly yield of oil per kettle lower. As was pointed out above, most distillers today use distilled and exhausted leaves as fuel, low priced wood being available only in a few localities.

Distillation starts rapidly and slows up gradually after about two-thirds of the oil has been distilled. The average yield of oil is about 0.7 per cent;[44] it fluctuates from 0.5 per cent in the rainy season to 1.2 per cent in the dry season. A still charged with 1,500 kg. of dried, chopped leaves of good quality yields about 12.5 kg. of oil.

If an oil with a high content of geraniol and citronellal cannot be obtained in a certain locality, with plants raised from good stock, other factors such as soil, climate, season, and age of the plants must be blamed.

From the above statements it would appear that the native distillers, who raise their own sereh grass, should be able to produce a better grade of oil than those large-scale distillers who have to buy their leaf material from numerous native growers. In the latter case the distillers cannot be very selective, because the competition for grass is keen, and the native planters usually play one distiller against another. It should be mentioned, however, that not all small native grower-distillers produce a very high quality of oil because their sereh grass is often contaminated with weeds, or is cut too young or too old. In order to obtain a maximum yield of oil, the small dis-

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[44] These figures apply to prewar years. Lately yields of only 0.4 to 0.6 per cent have been reported (cf. above).

tillers often dry the leaves in the sun too long prior to distillation, and extend the time of distillation until the charge is completely exhausted, which, of course, gives an inferior quality of oil with a low citronellal content.

Distillation Apparatus.—Three types of stills are employed in Java—water *and* steam stills, steam stills, and the so-called "godokkans," a sort of intermediate between the first two types.

A. Water and Steam Stills.—One of the advantages which water *and* steam distillation possesses over direct steam distillation is that the danger of steam channeling in the retort is diminished. The steam develops along the entire water surface, and consequently penetrates the charge of grass quite evenly (for details see Vol. I of this work, pp. 120, 147).

The process is now used widely by the native producers. During the early years of citronella oil production in Java, distillation was carried out exclusively with direct steam, but after 1910, when natives and Chinese entered the industry, the process of water *and* steam distillation was introduced, because stills of this type are lower priced and the process itself simple. Operation of these stills is economical; moreover, the stills are not subject to the rules of the Java government applying to steam boilers.

The water *and* steam stills are imbedded into stone hearths and are provided with a grid, which supports the grass. The water beneath the grid is heated with direct fire. One manhole on top and one on the side permit charging and discharging of the plant material. The leaves are tramped into the still quite firmly, to prevent formation of steam channels; the volume of the charge diminishes greatly during distillation. Between the still walls and the plant charge—especially in stills not properly insulated—cooling and some internal condensation may take place and the condensate, which contains dark, nonvolatile extraction matter, collects beneath the grid, at the bottom of the still, and accumulates after a number of operations. It is advisable, therefore, to draw off the water in the still (beneath the grid) after each charge has been distilled, and to replace it with fresh water for the distillation of the next batch.

The ratio of the diameter of a retort to its height should be at least 1 to 1.5 or 2. Steam channels form more readily in low, wide retorts than in narrow and high ones, but that danger is remedied if a wide retort tapers conically toward the top. Such stills, although vastly superior, are not yet being used very much in Java. It is highly advisable to insulate the retorts with a layer of kieselguhr or other material; even finely chopped sereh grass can be used. A retort of 1.10 m. diameter and 2.40 m. height holds 8 to 9 piculs (1 picul = 136 lb.) of grass, which is quite sufficient for one charge.

Water *and* steam distillation requires a separate fire for each still. Thus, the fuel consumption is relatively greater than in one separate steam boiler, which supplies steam for a whole battery of stills. Water *and* steam distillation (with direct fire) can thus be recommended only if small quantities of grass are processed daily, and if the price of fuel is low, as in the case of exhausted sereh grass. Operating a retort holding 8 piculs of grass, by water *and* steam distillation, requires 3 to 4 hr., which is twice as long as would be required with direct steam distillation. Distillation of citronella with water *and* steam in very large retorts, where the steam must go a long way to penetrate the entire grass mass, gives no better a yield than distillation with direct steam.

B. Distillation in Godokkans.—Distillation in the so-called godokkans represents a modified version of water *and* steam distillation. This type of installation is usually owned by wealthier natives or Chinese. The fire hearth and the water boiler are separated from the retort. The capacity of the godokkans varies from 400 to 4,000 kg. of grass. Retorts holding more than 1,500 kg. of leaves are less economical than those holding 1,000 to 1,200 kg. Retorts of small capacity require a shorter distillation time. It has been the practice to distill a charge of 1,000 to 1,200 kg. for 5 to 6 hr., although 3 to 4 hr. would be more satisfactory. After the rapid separation of a few rather unimportant volatile aldehydes, citronellal and geraniol distill over. The yield of total geraniol, particularly citronellal, diminishes after a few hours, and from then on only the less desired compounds, such as sesquiterpenes and sesquiterpene alcohols, can be collected. Under normal conditions, the composition of the oil, after 4½ hr. of distillation, is just slightly above the limit of Contract "A," which specifies a minimum of 85 per cent of total geraniol and 35 per cent of citronellal. Evidently, then, a distillation of 5 to 6 hr. would result in an oil which does not meet these requirements.

C. Distilling with Direct Steam.—In their papers on the production of citronella oil De Jong [45] and Hofstede [46] referred primarily to steam distillation, because at the time of their writing the cultivation of sereh was carried out chiefly by the large estates, which distilled the crop in steam stills. When the natives started cultivating and distilling citronella grass, they used water *and* steam stills chiefly, with the result that today the number of the latter exceeds that of the former. In the case of direct steam distillation, the steam is generated in a separate boiler heated by wood or exhausted sereh grass. The retort resembles that of water *and* steam stills.

As regards the question of steam pressure, it was formerly believed that a high steam pressure would give best results. (Cf. the monographs on

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[45] "The Ethereal Oil Yielding Plants of the Netherlands East Indies and the Preparation of Their Oils," *Ber. van de Afd. Handelsmuseum van het Koloniaal Inst.*, No. 7, 183. *Indische Mercuur* **45** (1922), 1.

[46] "Citronellaolie," *Mededeelingen van de Afdeeling Nijverheid,* No. 4, Buitenzorg, Archipel Drukkerij (1928).

"Citronella Oil from Honduras" and "Citronella Oil from Guatemala—Distillation.") De Jong, for instance, recommended a pressure of 3 to 4 atmospheres (measured in the steam boiler), but later the producers came to realize that such high pressure, while giving a greater yield, affected the quality of the oil adversely. Confirming this view, Hofstede actually proved by experiments that a higher yield was accompanied by a lower quality of the oil. His tests showed clearly that a high steam pressure increased the yield of the oil, but lowered the percentage of geraniol and citronellal in the oil. Instead of 3 to 4 atmospheres steam pressure, 1 to 2 atmospheres were then recommended; and after Hofstede, the distillers went even further and advocated pressures of from only ½ to 1 atmosphere (above atmospheric pressure). The loss in yield of oil obtained by the use of low pressure steam is more than compensated by a high total geraniol content of the oil. Nevertheless a few producers still prefer a larger yield to a higher quality of the oil and hence apply high steam pressure, or extend the period of distillation.

If distillation is continued sufficiently long, all the volatile oil present in the plant will distill over; such oil, however, will contain also the less desirable constituents. Experimenting in Celebes, De Graaf conducted a distillation lasting 2 hr. only. Distilling with a steam pressure of 4 atmospheres (in the steam boiler), and cutting his fractions every 10 min., he found that, with the third fraction, three-quarters of the total yield had already been obtained. After 36 min., the oil fraction contained less than 85 per cent of total geraniol. If the sereh grass used by De Graaf had not been of such excellent quality, the lower limit specifying 85 per cent of total geraniol would have been passed much sooner. After years of experience the producers finally became convinced that an oil of good quality can be obtained by using steam of normal pressure and by limiting the length of distillation. At present, the direct steam stills holding 1,000 to 1,200 kg. of leaves are operated with steam of ½ to 1 atmosphere (above atmospheric pressure, measured in the steam boiler) throughout the distillation, which lasts not longer than 3 hr. The length of distillation obviously depends not only upon the steam pressure, but also upon other factors such as condition (moisture content) of the plant material.

The steam should rise through the charge with sufficient force to penetrate all parts evenly; otherwise, complete distillation will not take place. On the other hand, if the steam is forced through the charge, channels are likely to form. In general, the steam pressure in the stills should not be too high—first, because most stills are not constructed for high steam pressure, and second, because the oil is apt to be decomposed by high temperatures, as well as by too long a contact of the odoriferous substances with steam.

In distilling citronella oil, the most important feature is to maintain a uniform temperature and steam pressure, which should not drop during the process.

The expenses of operating a steam still are usually higher than those connected with water *and* steam distillation. Competition on part of the natives is keen, and some of the estates were forced to follow their example and install water *and* steam stills, in order to produce oils of normal quality as economically as possible. Native oil originating in some of the Priangan districts has been, and still is, of good quality. Provided the natives raise high-grade sereh grass, their oils need not be inferior to the best estate oils; in fact a few of the estate producers made the mistake of emphasizing yield at the expense of quality. Moreover, oil obtained by direct steam distillation is occasionally cloudy and must be stored, prior to shipment, in a tank containing taps at various heights, through which the clarified oil can be drawn off into drums or tins.

D. Tilting Stills.—Tilting steam stills, mounted on trunnions (see Vol. I of this work, p. 130), are not indispensable for citronella distillation, but they can be discharged (emptied) very quickly and offer much saving in labor. However, their installation is considerably more costly than that of stationary stills, and the large citronella distilleries of Java, because of sharp competition with the small operators, can hardly afford them.

Citronellal Content of the Oil.—The chief merit of the Java type of citronella oil lies in its high citronellal content. To understand the problem of varying citronellal content, it is necessary to realize that the distillation of citronella oil from the leaves is actually a fractionation process; in other words, by cutting the distillate at certain intervals, fractions of different composition are obtained. This presents no unusual feature in the production of essential oils in general, but is particularly important in the distillation of citronella because it permits modifying the process in such a way as to obtain oils (in reality fractions) of high and low citronellal content. The usual citronellal content of commercial Java citronella oil is 35 per cent (Contract "A," see below). However, oils containing 40, 45, 60 and more, per cent of citronellal can be obtained by shortened distillation, and by the sacrifice of yield or, more effectively, by fractionation of the distillate during the distillation of the leaves. The first fraction, which contains the bulk of citronellal, is separated. The second fraction consists mostly of geraniol and a little citronellal. Thus, oils of variant citronellal content can be obtained, but care must be exercised that the second fraction retain sufficient geraniol to meet the requirements of Contract "B" (see below), by which the trade specifies an oil containing at least 85 per cent of total geraniol.

The so-called "total geraniol" content, on the basis of which the various commercial contracts are written, is a collective term for all the constituents which are assayed as apparent geraniol, by means of acetylation (cf. Vol. I of this work, p. 274). Not only citronellal and geraniol, but other compounds such as citronellol, citronellol esters, geraniol esters, borneol, and sesquiterpene alcohols fall into this group. This accounts for the fact that the sum of the analytical values for total geraniol, citronellal, and nonacetylizable constituents exceeds 100 per cent. The sesquiterpene alcohols in Java citronella oil amount to about 5 per cent.

The process of distilling citronella oil from the leaves resembles that of fractionating the complete oil *in vacuo*. The principal constituents distill over approximately in the following sequence:

1. Low-boiling terpenes.
2. Citronellal.
3. A mixture of citronellal, geraniol, and various alcohols and esters.
4. Geraniol.
5. Sesquiterpenes and sesquiterpene alcohols.

From what we have said under "Cultivation," it is evident that not all citronella grasses lend themselves to fractional steam distillation for the purpose of obtaining fractions of very high citronellal content. Poor leaf material simply does not contain sufficient citronellal. According to Hischmann,[47] the factors which make for a normal citronellal content may be summarized as follows:

1. Good leaf material grown in high altitudes and with proper care is generally higher in citronellal than that grown in the lowlands.

2. The soil does not have to be rich in humus; it may consist of light sand, but it must not be exhausted. If the roots strike lime subsoil through a thin layer of sand, the oil soon will exhibit a low citronellal content.

3. From the start the planting material should be healthy and vigorous. It must consist exclusively of "mahapengiri" and contain no "lenabatu."

4. The plantings should be well cared for. Green fertilizing, for instance, has a very favorable influence upon the citronellal content of the oil.

5. Days of sunshine alternating with days of light rain are most beneficial. A few months' period of light rainfall every other day, with intervening sunshine, favors the development of high-grade oils, even on relatively poor soil. During very dry or very rainy months, with only a few days of sunshine, the citronellal content is abnormally low.

6. The leaves must be cut at the proper moment and should not be withered.

7. The total area of a citronella plantation should comprise mostly young fields, planted on virgin or regenerated (green fertilized) soil. The citronellal

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[47] *Ber. Schimmel & Co.* (1938), 19.

content of the oil declines considerably in old fields, or on exhausted soils, although the total geraniol content may remain normal for quite some time.

8. The harvested leaves should be distilled as soon as possible, and distillation should not be pushed too far. It should be carried out under carefully controlled conditions.

At present, the state of Java's citronella oil industry does not permit adherence to all these points and, therefore, it is not possible to find throughout the producing regions the same uniform quality of oils as existed during the years prior to the industry's great expansion about twenty years ago.

We have seen that a high citronellal content is usually obtained by fractionation during the distillation of the leaves. While in Java, the author collected an oil assaying about 63 per cent of citronellal and 83 per cent of total geraniol which was said to have been obtained by distillation for only 1½ hr., without any fractionation. It was produced from leaves cut only 45 days after the previous harvest, instead of the normal 65- to 80-day interval. The plants were one and one-half years old, raised on an estate at 2,400 ft. altitude, and were dried 2 days prior to distillation. It should be noted, however, that harvesting every 45 days exhausts a planting in less than three years.

In the years before the outbreak of World War II, the Association of Citronella Oil Producers in Java made efforts to introduce on the world market two new types, in addition to the regular type of oil, so that the trade could choose between three types of Java citronella oil:

1. The standard type of oil which was to assay not less than 85 per cent of total geraniol, and not less than 35 per cent of citronellal.
2. An oil of very high quality, containing 50 to 60 per cent of citronellal. This oil was to serve chiefly as raw material for the making of hydroxycitronellal and synthetic menthol.
3. An oil of low quality, assaying 80 to 85 per cent of geraniol, and only 10 to 20 per cent of citronellal. This oil was to be employed in technical products, for the scenting of soaps, and for the extraction of geraniol.

The same leaf material which, by normal distillation, would yield, let us say, two drums of an oil assaying 35 per cent of citronellal, by proper fractionation will yield approximately one drum of an oil with 60 per cent of citronellal, plus one drum of an oil with 10 per cent of citronellal.

The essential oil industry did not react too favorably to the proposed new types of citronella oil, and considerable criticism was voiced. The oils with a very low citronellal content were called "skimmed" oils, and those with a very high citronellal content were criticized as being less stable than the normal oils. It was said that the removal of part of the citronellal throws an oil off its natural balance.

What the outcome of the controversy might have been is of little importance, because the occupation of Java by Japanese forces completely stopped the exports of citronella oil to Europe and America for several years.

Summary.—Let us now briefly review the fundamental changes which Java's citronella oil industry has undergone since its beginning at the turn of the century.

In the early days, almost all of the oil was produced by a few large estates which worked under similar conditions—soil, altitude, climate, planting material, apparatus, and methods of distillation. The abnormally low prices prevailing during the depression of 1931 did not even permit the large estates to cover their expenses in producing the oil. On the other hand, small native growers, who do not count their own or their families' labor, found even the low prices attractive, because other agricultural products were still less remunerative. Thousands of native growers started to supply the leaf material to numerous new, small-scale native and Chinese distillers. It was grown on poor soil chosen because of cheapness, the fertile and expensive terrains being needed for the production of rice. The sereh grass often was of inferior quality because of admixed "lenabatu," and it was planted at different altitudes with a different distribution of rain and sunshine. The newly established distilleries competed keenly in the buying of leaf material, those paying the highest prices and accepting the worst quality receiving the most supplies. Distillation, too, was carried out less carefully, and in all kinds of primitive stills. No wonder then that the sereh grass and the oil underwent a continuous lowering of quality. As a result, the physiochemical properties of the oil lots no longer were the same as those indicated in the literature of thirty years ago.

Another disturbing factor, aside from outright adulteration, was the practice of mixing oils of good and poor quality. Many newcomers, some of them of questionable integrity, went into the citronella oil business as intermediaries and speculators. Shrewd Chinese dealers, to whom citronella oil meant just another article of speculation, bought up oil, mixed old and freshly distilled lots, and stored them for long periods, with resulting deterioration of the oil. These factors led to a gradual lowering of the quality of the Java citronella oil, which had once enjoyed such a high reputation on the world market.

An increasing number of complaints from buyers abroad finally induced the exporters in Java to take steps to end the unhealthy conditions, and at a meeting held by the Chamber of Commerce in Batavia, it was decided to subject the citronella trade to strict regulations. The result was the Standard Contract and the Arbitration Regulations of March 1, 1935, which have been revised several times since, and adapted to changed conditions, the most important revision being that of April 1, 1938. Highly efficient administrators as the Dutch officials are, they not only set out most energetically to remedy existing abuses in the citronella oil trade, but went much further and by practical supervision, advice, and financial help to the native growers and distillers, combined with a strict supervision of production, trained them to produce oils of normal quality.

To assure the bulk of native-produced oil meeting the requirements of Contract "A" (85 per cent of total geraniol and 35 per cent of citronellal), it became necessary to raise the native sereh cultivation to a higher level by advancing credit, giving advice about planting, and supplying selected plant material for propagation. In 1935 only about 20 per cent of the exported oil originated from estate plants; 80 per cent came from native-grown plants. Special attention had, therefore, to be paid to the native production. In the elaborate government laboratories in Buitenzorg, next to the world-renowned botanical garden, the Netherlands Administration for years has carried out research on all of Java's products, and subjected every shipment of citronella oil to painstaking analysis. A large staff of highly qualified European and native chemists, botanists, and biologists occupies this remarkable institute.

It is not surprising that this efficient organization soon succeeded in reestablishing the former high standing and the reputation of Java's citronella oil industry. One of the important functions of the laboratory's Essential Oil Board was to determine the requirements for the standard export qualities:

Contract "A" (standard contract of the Chamber of Commerce in Batavia) prescribed a total geraniol content of not less than 85 per cent, and not less than 35 per cent of citronellal. When selling other qualities, the total geraniol percentage as well as that of citronellal had to be entered on the certificate.

Contract "B" required a minimum of 85 per cent of total geraniol, but no minimum percentage of citronellal.

Contract "C" permitted less than 85 per cent of total geraniol, with no minimum percentage of citronellal.

The Buitenzorg Experimental Station also tests citronella oil for the presence of adulterants such as kerosene, mineral oil, and fatty oils. Only pure lots are cleared for export.

It is quite possible to detect outright adulteration by chemical means; but the mixing together of heterogeneous oils—such as oils of high and low citronellal content, or oils originating from the highlands and from the lowlands, or old (speculative) lots and new oils (all of them detrimental to the quality of a lot)—are, unfortunately, difficult to check.

During the Japanese occupation, the functions of laboratories in Buitenzorg were temporarily suspended. Considerable damage was done to the Station in the course of the fighting attendant upon the liberation by Allied forces. After that, the Station for a time was occupied by adherents to the newly established revolutionary government. In these turbulent after-war years many of the shipments of oil which reached the market abroad were substandard. During the Japanese occupation metal drums were not readily available in Java, and the limited quantities of oil produced had to be stored under most unfavorable conditions, and for several years. After the war numerous lots of oil were smuggled from Java to Singapore (via Sumatra, on Malayan proas) and transshipped to Europe and America. None of these smuggled lots, of course, underwent any analytical check by the government of Java, and the oils were often of poor quality—caused by age, autoxidation, presence of kerosene and fatty oils, etc.

In 1948 more normal conditions were established in Java with an agreement between the government of the Netherlands and representatives of the Javanese natives. "Indonesia" was made the official name of the former Netherlands East Indies, effective as of September 20, 1948. To protect the reputation of the Java citronella oil, the Indonesian Government decided that, as of October 1, 1948, every shipment of citronella oil of 270 kg. and more must be accompanied by a certificate of analysis, issued by the Laboratory for Chemical Research at Buitenzorg, as had been the practice before the Japanese occupation of Java. These analysis certificates, which must not be older than three months at the date of export, are to state the total geraniol and citronellal content of the oil; they also certify the oil not to be adulterated, and specify the steam distillation residue, if the latter represents more than 2.5 per cent. The analysis number of the certificate must be painted clearly in white letters on the drum or container used.

So far as the commerce in Java type citronella oil is concerned—and this applies also to the oils from Central America—the standard contracts are now written on a minimum basis of 85 per cent of total geraniol and 35 per cent of citronellal. Occasionally, somewhat different qualities are offered, at price differentials; for example, an oil of 92/44 per cent at an advanced price, or a lot of 82/32 per cent at a reduced price.

Physicochemical Properties.—As was pointed out above, the factors conditioning the production of citronella oil in Java have changed during the past twenty or twenty-five years. Formerly, a good part of the oil was produced on large, well-kept estates and was of quite uniform quality. At present, however, production is chiefly in the hands of native growers and distillers, many of them operating on a small scale. Cultivation of the plant has been shifted to different regions, altitudes, and less fertile soils, obviously, not without influence upon the quality of the oil. The physicochemical properties described in earlier literature must therefore be accepted only with reservations. Moreover, up until a few years ago, analytical methods were imperfect and had not been standardized (as they are today).

In 1929 Gildemeister and Hoffmann[48] reported these properties:

Specific Gravity at 15°	0.885 to 0.901; oils with a high citronellal content occasionally exhibit a specific gravity as low as 0.881
Optical Rotation	Usually laevorotatory up to −4° 0′; slightly dextrorotatory oils (+1° 47′) have been observed in very rare cases
Refractive Index at 20°	1.463 to 1.475
Total Geraniol Content	Not below 85% in good oils; occasionally as high as 96%
Actual Geraniol Content (Phthalic Anhydride Method)[49]	26.6 to 45%
Citronellal Content	25 to 54%; in good oils 40% and higher
Solubility	Clearly soluble in 1 to 2 vol. and more of 80% alcohol; occasionally opalescent on dilution
Color	Colorless to light yellow

The odor of Java citronella oil is much superior to that of the Ceylon oil.

After a careful examination of a pure oil obtained by special, exhaustive distillation, Hofstede[50] in 1928 arrived at the conclusion that the properties of the best Java citronella oil, as it supposedly occurs in the plant, are approximately as follows:

Specific Gravity at 27°	0.897
Optical Rotation at 28°	−2° 34′
Refractive Index at 27.5°	1.4654
Total Geraniol Content	88.8%
Actual Geraniol Content	36.0%
Citronellal Content	42.7%
Solubility	Clearly soluble in 2.5 to 7.5 vol. of 70% alcohol; cloudy with more. Clearly soluble in 1.5 vol. and more of 80% alcohol. Miscible with 90% alcohol

Numerous shipments of citronella oil from Java analyzed by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.887 to 0.895
Optical Rotation	−0° 35′ to −5° 6′
Refractive Index at 20°	1.4685 to 1.4728

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[48] "Die Ätherischen Öle," 3d Ed., Vol. II, 364.

[49] See Vol. I of the present work, p. 275.

[50] "Citronellaolie," *Mededeeling van de Afdeeling Nijverheid,* No. 4, Buitenzorg, Archipel Drukkerij (1928).

Total Geraniol Content	82.3 to 89.4%, very seldom below 85%
Total Aldehyde Content, Calculated as Citronellal	28.8 to 43.9%, very seldom below 35%
Solubility at 20°	Clearly soluble at all dilutions between 1 and 2 vol. of 80% alcohol; occasionally slightly opalescent on further dilution up to 10 vol.

On the basis of analysis of a great many lots, the Government Control Laboratories in Buitenzorg (Java) established the following limits for normal Java citronella oil:

Specific Gravity at 15.5°	0.885 to 0.895
Optical Rotation	0° to −3° 0′
Refractive Index	1.468 to 1.472
Total Geraniol Content	80 to 92%
Citronellal Content	35 to 46%
Steam Distillation Residue	0.5 to 3.0%

On prolonged storage of the oil, particularly under poor conditions, the citronellal content and the originally good solubility of the oil decrease; the specific gravity increases.

According to observations made by Hischmann [51] over a period of years, a poor solubility may also result from any of the following causes:

1. Presence of weeds and other spurious grasses in the distillation material, because of improper cultivation or neglect of the serch fields.
2. The use of old plants with woody stalks. The workers cut the leaves as low as possible in order to obtain greater weight (they are paid on the basis of quantity of leaves harvested).
3. The presence of an inferior variety of citronella grass, difficult to distinguish from true "mahapengiri."
4. Occasionally, the presence of overground parts of the root system in the leaf material.
5. Improper storage of the leaves before distillation. Prolonged storage is detrimental, particularly if fermentation has occurred. In order to save steam and fuel, the native distillers often dry the grass for several days, and fermentation may occur.
6. Improper distillation. Some large producers, distilling with direct steam, use excess pressure to obtain a high yield of oil. The small producers, using low pressure steam, sometimes distill for too long a period.

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[51] Conversation with Dr. A. Hischmann in Batavia (Java), 1939.

7. Lack of cleanliness in distillation apparatus and storage tanks.

8. Improper storage of the distilled oil. After distillation, the oil is often permitted to stand unfiltered for weeks. Solubility of an oil decreases with age, particularly if the oil is left exposed to the air.

9. General climatic conditions. Oils produced during the last weeks of an exceptionally dry period and during the first weeks of the rainy season are apt to show a poor solubility.

10. Soil conditions. These also may affect the solubility of the oil.

Hischmann has made a careful investigation of more than 50 oils that were not clearly soluble in 80 per cent alcohol. In only two cases could mineral oil fractions or fatty oil be detected, and in both cases the adulteration consisted of mere traces of these adulterants. The latter were introduced by the use of unclean storage tanks and containers, which had been used previously for other materials, and which had not been properly cleansed. In all other (48) cases the poor solubility of the oil therefore was attributable to some of the factors cited above.

Analysis.—The technically most important constituents of citronella oil (which determine its quality and commercial value) are geraniol (an alcohol) and citronellal (an aldehyde). In the commercial analysis of an essential oil the alcohols are usually determined by acetylization (see Vol. I of this work, p. 271). In the case of citronella oil it should be kept in mind, however, that under analytical conditions not only the geraniol but also the citronellal is affected by acetylization, the citronellal being converted quantitatively into saponifiable compounds (see also Vol. I, p. 274). Thus the total alcohol content of a citronella oil assayed by acetylization comprises both the geraniol and the citronellal. To express this apparent "alcohol" content, the trade has adopted the term "total geraniol." This represents the percentage of all acetylizable constituents of the oil—geraniol (free and esterified), all other alcohols (free and esterified), citronellal and other aldehydes. Exact procedures will be found in Vol. I of this work, pp. 271 ff. Note that in the case of citronella oil acetylization requires *two* hours.

The citronellal content of the oil may be determined by either of the two hydroxylamine methods described in Vol. I of this work, pp. 285 ff. The value obtained comprises not only the citronellal, but also small quantities of other carbonyl compounds. The commercial term "citronellal content" is therefore not quite accurate; "total aldehyde content, calculated as citronellal" would be more exact.

The *actual* geraniol content of the oil may be approximated by subtracting the citronellal content from the total geraniol content. If a more exact value for the actual geraniol content is desired, the phthalic anhydride method for determining primary alcohols will be of help (see Vol. I of this work, p. 275). However, it is seldom used in the commercial routine analysis of citronella oil.

As regards the detection of added ethyl alcohol or methyl alcohol, details of procedure will be found in Vol. I of this work, pp. 338 and 340.

A simple method for the detection of ethyl alcohol in citronella oil has been developed in the Government Laboratories of Buitenzorg, Java (Zimmermann [52]):

> Shake 2 cc. of citronella oil with a crystal of fuchsin for 2 min., during which time the oil should remain colorless. (The fuchsin must first be treated by shaking with pure, unadulterated citronella oil, until no violet color is visible.) In cases of doubt, the refractive index of 1 cc. of water that has been shaken with 10 cc. of the oil is determined.

Occasionally citronella oils are adulterated or contaminated with kerosene, petroleum, or mineral oil fractions. Their presence can be detected by two means: (a) the so-called oleum test, and (b) the determination of the flash point.

(a) Details of the so-called oleum test are given in Vol. I of this work, p. 332.

(b) The determination of the flash point is described in Vol. I of this work, p. 261.

Another method serving for the same purpose has been suggested by Van Hulssen and Koolhaas: [53]

> A special cylindrical vessel with a total capacity of 56 cc. is closed by a tightly fitting stopper, carrying a thermometer and provided with three holes, lying in a row, which may be closed by a sliding cover. The vessel is supported by an asbestos ring, the lower part hanging in an air bath.
>
> In carrying out the determination, 35 cc. of the citronella oil are placed in the vessel and slowly heated. At intervals the lid covering the three holes is drawn aside and an attempt is made to ignite the gas by means of a small test flame (about 3 mm.) kept near the middle hole. The lowest temperature of the oil, at which the mixture of gases ignites to give a flash, is defined as the flash point. For a normal citronella oil the flash point is 84° C. (average of 2,000 determinations), whereas admixture of gasoline lowers the flash point according to the following table:

Percentage of Gasoline in Citronella Oil	*Flash Point* (°C.) *Lower Than*
5	30
2	38
1	56
0.5	66
0.25	70

> Oils with a flash point below 75° C. are suspected as adulterated.

[52] *Chem. Weekblad* **31** (1934), 132.

[53] Private communication from Dr. D. R. Koolhaas, Buitenzorg, Batavia (1939).

Pure Java citronella oils are clearly soluble at all dilutions between 1 and 2 volumes of 80 per cent alcohol, but may become opalescent on further dilution. Turbidity or separation of oil droplets on standing indicates the presence of mineral oil fractions or fatty oils. Such oils should be viewed with suspicion and should be tested for mineral oil (see above) or for fatty oils (determination of the evaporation residue and its saponification number, separation of the fatty acids, etc.—cf. Vol. I of this work, p. 344).

As regards the evaporation residue, all citronella oils—whether freshly distilled or old stock—contain a certain amount of oxidation and polymerization products, which are nonvolatile, and on steam distillation of the oil remain as residue in the flask.

The experience of chemists in the Buitenzorg research laboratories indicates that the steam distillation residue in pure citronella oils varies from 0.5 to 3.0 per cent. Prior to World War II, when the high quality of the Java oil was unquestioned, no attention was paid to the steam distillation residue of a given lot. After World War II, however, when many lots of oil adulterated with fatty oils or lubricating oils appeared on the market, the Department of Economic Affairs in Batavia, in collaboration with local exporters, decided to determine the steam distillation residue (S.D.R.) of each shipment, but to mention it on the certificate of analysis only when it exceeded 2.5 per cent. The latter figure may be accepted as a fair limit.

The specific gravity, optical rotation, and refractive index of the oil are determined in the usual manner (cf. Vol. I of this work, pp. 236, 241, and 244). In the case of normal oils, the specific gravity and the refractive index decrease as the percentage of citronellal increases.

Influence of Metals upon the Oil.—Meyer[54] investigated the influence of various metals upon Java citronella oil and arrived at the conclusion that zinc has the most, and aluminum and tin the least, harmful influence upon the oil.

Exposing iron, copper, nickel, and aluminum to the influence of citronella oil at 100° C., the same author, in another series of experiments, found that iron is most readily attacked by the oil, copper and nickel less, and aluminum least of all.

The findings of Meyer should be helpful in the choice of metals for stills, storage tanks, and shipping drums.

Shipping of the Oil.—The production of citronella oil in Java is concentrated chiefly in the western part of the island. In normal times 95 per cent of the oil, therefore, used to be shipped from Tandjong Priok, the port of Batavia. The balance of the oil was shipped from Surabaya and Cheribon.

Prior to World War II the oil was packed in galvanized iron drums, holding 100 to 250 kg. of oil, or occasionally in tin containers holding 16 kg.

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[54] *Deut. Parfümerieztg.* **17** (1931), 434.

Total Production and Exports.—In the last years prior to the occupation by Japanese forces, Java exported these quantities (in gross weight) of citronella oil:[55]

	Kilograms
1938	1,893,944
1939	2,508,734
1940	2,114,076
1941	2,412,000 (net weight)

Of these three years, 1938 may be chosen as the year in which exports abroad were fairly normal:

	Kilograms
United States	648,937
France	436,522
France, option	157,827
Britain	140,109
Germany	135,734
Holland	91,776
Holland, option	39,897
Argentina	60,713
China	47,941
Italy	28,193
Poland	16,077
India	12,914
Singapore	11,724
Etc.	etc.

No reliable figures were available about the production of citronella oil in Java during World War II and years just after the war. As was pointed out above, the total acreage planted with citronella was greatly reduced (to less than 8,000 hectares in 1948) and only about 300 metric tons of oil were produced in 1948. In the same year 469 tons of oil were exported, 271 tons of which quantity went to the United States (quantities in gross weight).

It can be expected, however, that with the establishment of more normal conditions the production of citronella oil in Java will rise substantially. It may never reach the prewar figure of about 2,000 metric tons per year again, but Java will always be one of the most important, if not the leading, citronella oil producer in the world.

Chemical Composition.—The chemical composition of the Java type of citronella oil (derived from *Cymbopogon winterianus* Jowitt, the so-called "mahapengiri") is quite well known, chiefly because large quantities of this oil are processed yearly for the isolation of its main constituents. These are geraniol, citronellal, and, to a much lesser extent, citronellol. The Java

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[55] Courtesy Dr. J. A. Nijholt, Laboratorium Voor Scheikundig Onderzoek, Buitenzorg, Java.

type of citronella oil contains a substantially higher percentage of these components than the Ceylon type of oil (derived from *Cymbopogon nardus* Rendle, the so-called "lenabatu"), and is therefore more valuable. It also has a stronger odor. Otherwise the two oils are similar except, perhaps, for the content of methyl eugenol, which amounts to more than 8 per cent in the Ceylon oil, and to less than 1 per cent in the Java oil.

The first reliable investigations of Java citronella oil were carried out by Schimmel & Co.,[56] paralleling and following their work on Ceylon citronella oil. Since then, however, relatively few papers have appeared on the chemical composition of this oil, which may seem surprising in view of its commercial importance. The reason is probably that most manufacturers of aromatic isolates have preferred to keep their knowledge for their own use only, rather than to publish it.

According to the literature, the following substances (listed *approximately* in order of their boiling points and according to groups) have been observed in the Java type of citronella oil which also includes the oil produced in Formosa:

Using the same method which he had employed for his investigation of the foreruns of Réunion geranium oil, Bohnsack[57] studied foreruns of Java citronella oil, 52 kg. (b_8 up to 55°) distilled from 2,400 kg. of Java citronella oil. Bohnsack removed the alcohols from 25 kg. of this forerun by the borate method, and obtained three fractions of which he investigated only the first, b_{15} about 45°–80°. (The odor of the second fraction resembled that of borneol and menthol, the odor of the third fraction that of geraniol and citronellol.)

Isobutyl Alcohol and Isoamyl Alcohol. From the first fraction b_{15} 45°–80° Bohnsack obtained isobutyl alcohol and isoamyl alcohol as a uniform boiling fraction, after he had purified these alcohols through their phthalic esters. The two alcohols were identified by means of their α-naphthylurethanes m. 97°–98°, and 63°–64°, respectively.

3-Hexen-1-ol. As main constituent of the fraction b_{15} 45°–80°, Bohnsack isolated 3-hexen-1-ol, which had previously been observed in Japanese mint oil, in the volatile oil of black tea, in raspberry oil and in Réunion type geranium oil (cf. the monograph on "3-Hexen-1-ol" in Vol. II of this work, p. 158).

l-3-Methyl-1-pentanol(?). The fraction b_{15} about 45°–80° also contained a laevorotatory primary, saturated hexanol, b. 154°–156°, b_{10} 52°–54°, d_{15}^{21} 0.8270, $[\alpha]_D^{13}$ about $-2°$; α-naphthylurethane m. 97°–98°. This was probably *l*-3-methyl-1-pentanol. Oxidation of this alcohol with potassium permanganate gave an acid b_{11} 91°–93°, which yielded an amide m. 115°–117°. Little is known in literature about the laevorotatory 3-methyl-1-pentanol. Viebel et al.[58] prepared it synthetically; Levene and Rothen[59] reported its specific optical rotation as $[\alpha]_D^{25}$ $-3° 12'$.

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[56] *Ber. Schimmel & Co.,* April (1900), 11, 13; April (1902), 14; April (1910), 29.

[57] *Ber.* **76** (1943), 564. Cf. *Ber.* **74** (1941), 1575.

[58] *Biochem. Z.* **252** (1932), 401. *Bull. soc. chim.* [5] **6** (1939), 990.

[59] *J. Biol. Chem.* **115** (1936), 415.

n-1-Hexanol. In the fraction b_{12} 60°–67° of the above-mentioned alcohol mixture b_{15} about 45°–80°, isolated from the foreruns of Java citronella oil, Bohnsack[60] also identified *n*-1-hexanol b_8 53°–55° (α-naphthylurethane m. 60°–61°), after he had first removed the unsaturated components by shaking with a cold solution of potassium permanganate.

Methyl Heptenone. In the course of his work on the foreruns of Java citronella oil Bohnsack[61] also investigated the aldehydes and ketones present. Removing the oil from the borates (see above) by distillation, Bohnsack noted aldehydes and ketones of sharp odor, which were lost in the vacuum pump. To identify these compounds Bohnsack treated the other half of the first runs (27 kg.) with bisulfite solution, and was able to isolate citronellal (see below) and methyl heptenone from the solid bisulfite compound.

Isovaleraldehyde. When further processed, the bisulfite lye yielded the above-mentioned oil of sharp odor; in its first fraction Bohnsack identified isovaleraldehyde through its semicarbazone m. 119°–120°.

Furfural. Treating the other fractions b_{17} 40°–75° with sulfite-bicarbonate, the same author identified furfural through its semicarbazone m. 197°.

Benzaldehyde and *d*-1-Methyl-3-cyclohexanone. The oil which did not react with sulfite-bicarbonate was fractionated. One of the fractions consisted of benzaldehyde (semicarbazone m. 213°–215°), another of benzaldehyde and *d*-1-methyl-3-cyclohexanone b_{16} 58°, d_{15}^{16} 0.9176, $[\alpha]_D^{20}$ $+1°\ 12'$ (2 g. oil + 3 g. ether in a 5 cm. tube). The latter was identified through its semicarbazone m. 181°–182°. Oxidation with potassium permanganate in alkaline solution gave β-methyl adipic acid m. 85°–86°. *d*-1-Methyl-3-cyclohexanone had previously been observed only in oil of pennyroyal.

2-Hexen-1-al(?). The four lowest boiling fractions of the portion which had not reacted with sulfite-bicarbonate contained unsaturated substances. Oxidation with silver nitrate in an alkaline medium, according to the method of Curtius and Franzen,[62] yielded (besides *d*-1-methyl-3-cyclohexanone and benzoic acid) some low boiling fatty acids b_{10} 105°–108°, among them a small quantity of an unsaturated acid. The latter probably corresponded to 2-hexen-1-al, but the quantity available was not sufficient to permit identification of this unsaturated aldehyde.

l-3-Methyl-1-pentanal(?). After removal of the above-mentioned unsaturated acid from the fraction b_{10} 105°–108° by the action of potassium permanganate, Bohnsack[63] obtained a slightly laevorotatory saturated acid b_{11} 93°–95°. Its amide m. 115°–117° was identical with the amide m. 116°–118° of the acid which had resulted from oxidation of the above-described primary *l*-hexanol (*l*-3-methyl-1-pentanol). The saturated parent aldehyde of the acid was therefore the *l*-hexanal (probably *l*-3-methyl-1-pentanal) corresponding to the primary *l*-hexanol.

Previously, an *l*-3-methyl-1-pentanal had only been once mentioned in literature, viz., the synthetic product b. 122°, d_4^{25} 0.810, $[\alpha]_D^{25}$ $-8°\ 42'$ (heptane), prepared by Levene and Rothen.[64]

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[60] *Ber.* **76** (1943), 564.

[61] *Ibid.*

[62] *Liebigs Ann.* **390** (1912), 100. Cf. Walbaum and Rosenthal, *Ber. Schimmel & Co.* (1929), Jubiläums Ausgabe, 214.

[63] *Ber.* **76** (1943), 564.

[64] *J. Biol. Chem.* **111** (1935), 739.

l-Limonene and Dipentene. As regards the terpenes, Chiris[65] identified *l*-limonene and dipentene through their nitrolpiperidines m. 109°–110°, and m. 150°–152°, respectively.

Citronellal, *d*-Citronellol, and Geraniol. Schimmel & Co.[66] found that the Java type of citronella oil contains larger quantities of these chief constituents than the Ceylon oil. According to Gildemeister and Hoffmann,[67] the citronellal content of Java citronella oils ranges from 25 to 54 per cent; in normal oils it is not less than 35 per cent, in very good oils higher.

Using the phthalic anhydride method of isolating geraniol, Schimmel & Co.[68] arrived at the conclusion that the oil contains from 26.6 to 45 per cent of geraniol (cf. "Physicochemical Properties").

Citral. Identified by Schimmel & Co.[69] who prepared the naphthocinchoninic acid compound m. 197°–198°. Only about 0.2 per cent of citral occurs in Java citronella oil.

Chavicol(?). Furukawa[70] has claimed that the Java type of citronella oil contains chavicol.

Methyl Eugenol. According to Schimmel & Co.,[71] the Java oil contains less than 1 per cent of eugenol methyl ether, the Ceylon oil more than 8 per cent.

Eugenol, Geranyl Butyrate, and Citronellyl Citronellate. Investigating Java citronella oil, Glichitch[72] found that it contains 5 to 10 per cent—and occasionally more—of a fraction b_{10} above 135°, which includes small quantities of eugenol, geranyl butyrate, and citronellyl citronellate.

Elemol. As chief components, however, this fraction contains two tertiary sesquiterpene alcohols $C_{15}H_{26}O$. One of these two alcohols is monocyclic and was found to be identical with the elemol previously observed in oil of elemi. In its crude form the alcohol melted at 46°; but when purified through its phenylurethane m. 112.5° the melting point of elemol could be raised to 52.5°.

In a later investigation of the Java type of citronella oil produced in Formosa, Kafuku, Ikeda, and Fujita[73] isolated 15 per cent of a high boiling fraction, which contained 50 per cent of elemol.

Doll and Nerdel[74] enriched the elemol content of the last runs of Java citronella oil by fractional distillation, and removed the alcoholic components from a fraction containing about 50 per cent of sesquiterpene alcohols by using the borate method. On standing, 10 kg. of the separated oil, which contained 86 per cent of sesquiterpene alcohols, precipitated 2 kg. of crude elemol (for purification of the elemol see the monograph on "Elemol" in Vol. II of this work, p. 262).

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[65] *Parfums France* No. 18 (1924), 234.

[66] *Ber. Schimmel & Co.*, April (1900), 11, 12; April (1902), 14; October (1912), 40.

[67] "Die Ätherischen Öle," 3d Ed., Vol. II, 364.

[68] *Ber. Schimmel & Co.*, April (1900), 12; October (1912), 40.

[69] *Ibid.*, April (1910), 29.

[70] *J. Chem. Ind. Tokyo* **21** (1918), 515. *J. Soc. Chem. Ind.* **37** (1918), A. 716.

[71] *Ber. Schimmel & Co.*, April (1900), 13.

[72] *Parfums France* **4** (1926), 253.

[73] *J. Chem. Soc. Japan* **53** (1932), 636. *Chem. Abstracts* **27** (1933), 280.

[74] *Ber. Schimmel & Co.* (1940), 46.

Cadinol. The other of the two sesquiterpene alcohols described by Glichitch [75] and mentioned above was bicyclic (b_3 134°–135°, α_D^{18} −12° 12′). It could not be obtained in crystalline form, but on heating with concentrated formic acid it yielded a sesquiterpene, which gave two derivatives m. 118.5°–119° and m. 123°–124°, identical with cadinene dihydrochloride and cadinene dihydrobromide, respectively. The sesquiterpene alcohol in question, therefore, was probably a cadinol, perhaps in impure form.

In their above-mentioned investigation of the Java type of citronella oil produced in Formosa, Kafuku, Ikeda, and Fujita [76] obtained 15 per cent of a high boiling fraction which contained 10 per cent of what they considered γ-cadinol.

More recently, Plattner and Márkus [77] isolated from the last runs of Java citronella oil about 2 per cent of a crystalline cadinol m. 72°, $[\alpha]_D$ −39° 24′ (c = 1.32 in chloroform) which was perhaps the β- or γ-isomer (cf. the monograph on "Cadinol" in Vol. II of this work, p. 276). It could not have been torreyol m. 140°, $[\alpha]_D$ +107° 0′, another crystalline sesquiterpene alcohol.

The cadinol (or the elemol) observed by the above authors is perhaps identical with the tertiary sesquiterpene alcohol $C_{15}H_{26}O$, containing two double bonds, which Semmler and Spornitz [78] noted in Java citronella oil years ago.

Cymbopol. In the course of their above-mentioned work, Kafuku, Ikeda, and Fujita [79] isolated 15 per cent of a fraction which contained 10 per cent of cymbopol b_{759} 292°, d_4^{30} 0.9515, $[\alpha]_D^{22}$ −8° 24′, n_D^{30} 1.495 (cf. monograph on "Cymbopol," Vol. II of this work, p. 273).

γ-Cadinene. From this high boiling fraction (15 per cent of the total oil) the same authors [80] also isolated 15 per cent of γ-cadinene (aside from 15 per cent of geraniol, 10 per cent of γ-cadinol, and 50 per cent of elemol—see above).

Sesquicitronellene. Removing the methyl eugenol from a sesquiterpene fraction of Java citronella oil by extraction with 70 per cent alcohol, and redistilling the residue repeatedly over metallic sodium, Semmler and Spornitz [81] obtained an aliphatic sesquiterpene $C_{15}H_{24}$ in pure form, which they named sesquicitronellene. It had these properties: b_9 138°–140°, d_{20} 0.8489, α_D +0° 36′, n_D 1.53252 (cf. monograph on "Sesquicitronellene," Vol. II of this work, p. 83).

Dicitronelloxide. In the high boiling fractions of Java citronella oil Spornitz [82] observed dicitronelloxide $C_{20}H_{34}O$, b_{12} 182°–183°, d_{20}^{20} 0.9199, α_D −4° 0′, n_D 1.49179 (cf. monograph on "Dicitronelloxide," in Vol. II of this work, p. 718).

Vanillin. Identified by Takens,[83] who reported a mixed melting point of 81°–82°.

According to Bohnsack,[84] the distillation water of Java citronella oil contains *diacetyl*.

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[75] *Parfums France* **4** (1926), 253.

[76] *J. Chem. Soc. Japan* **53** (1932), 636. *Chem. Abstracts* **27** (1933), 280.

[77] *Helv. Chim. Acta* **25** (1942), 1674.

[78] *Ber.* **46** (1913), 4025.

[79] *J. Chem. Soc. Japan* **53** (1932), 636. *Chem. Abstracts* **27** (1933), 280.

[80] *Ibid.*

[81] *Ber.* **46** (1913), 4025. Cf. *Ber. Schimmel & Co.,* October (1899), 19.

[82] *Ber.* **47** (1914), 2478.

[83] *Riechstoff Ind.* **3** (1928), 210.

[84] *Ber.* **76** (1943), 564.

Use.—Oil of citronella, Java type, is one of the most important essential oils.

Oils with a high content of citronellal are used chiefly for the isolation of citronellal, and for conversion of the latter into citronellol, citronellol esters, hydroxy citronellal, and synthetic menthol.

Oils with a low citronellal and high geraniol content are used for the extraction of geraniol, and conversion of the latter into its esters. This type of oil is lower priced, and therefore serves well for the scenting of soaps and technical preparations where cost is of prime consideration. In many cases it can replace the Ceylon type of citronella oil.

The bulk of Java type citronella oil, however, is of the usual, normal quality, i.e., assaying 35 per cent of citronellal and 85 per cent of total geraniol. These oils are employed for the extraction of aromatic isolates, as well as for the scenting of soaps and all kinds of technical preparations.

Citronella Oil from Formosa

Development.—The development of Formosa's citronella industry, like that of Central America, has been remarkable. It owes its success chiefly to the members of one Japanese family—the Iwamotos—who dominated the industry until they were forced to leave when Japan lost possession of Formosa after World War II. In 1912 Kiyoshi Iwamoto, through the Taipeh Agricultural Institute in Formosa, procured one mat (root stock) of citronella grass from Java. This he planted in the district of Shin-Chiku (southwest of Taipeh), and in the course of years managed to propagate it on a large scale, at the same time inducing a number of natives to grow and distill the grass, so that in 1940 Formosa produced about 360 metric tons of citronella oil. In his efforts to expand Formosa's citronella industry, Iwamoto and his family were assisted by the Takasago Perfumery Co.,[85] which contributed greatly to the success of the venture. Prior to, and during, World War II most of the Formosa oil was absorbed by Japan's essential oil industry, and comparatively few lots reached the United States or Europe. Immediately after the war, stocks in Formosa were so plentiful that large lots were shipped to Shanghai and Hong Kong, and from there exported to Europe and the United States, often without indication of the origin. Since 1940 production of citronella oil in Formosa has fallen off substantially because of the general political confusion, but local experts are of the opinion that production will revive and may soon reach 200 metric tons per year. The future, obviously, will depend upon the quantity and the price of the oil

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[85] The author is greatly obliged to his friend Dr. Teikichi Hiraizumi, President of the Takasago Chemical Industry Co., Ltd., Tokyo, Japan, for much of the information contained in this monograph.

produced in Java, as well as upon the continuance of the supply of genuine, unadulterated lots from Formosa itself. Under Japanese rule and control, the quality of the Formosa oil was always excellent and enjoyed a very good reputation.

Producing Regions.—In tropical and semitropical Formosa any locality below 500 m. altitude seems to be well suited to the cultivation of citronella grass.

At present about 85 per cent of the total output of oil originates from the district of Shin-Chiku (southwest of Taipeh), where the grass was first planted in 1912. Cultivation is now distributed as follows:

District	*Percentage of the Total Oil Production*
Shin-Chiku[86]	85
Tai-Chung	7
Tai-Nang	3
Karen-Ko	3
Tai-Toh	2

Most of the production is now in the hands of native growers and distillers.

Climate, Soil, and Altitude.—The grass grows best in a warm climate and in localities with a southern exposure admitting plenty of sunshine. Rainfall is necessary during the growing period, but during the harvest the weather should be dry. Citronella does not suffer as much from wind as do other crops.

The plant thrives better in loamy or clayey soil than in sandy soil; in good soil its life span will be longer and the yield of oil higher. Slopes of hills are suited for plantations, but level ground facilitates soil management.

Citronella can be grown in altitudes above 700 m., but the life span of the plants and the yield of oil will be only half that of plants grown below 500 m. altitude.

Planting, Cultivating, and Harvesting.—In the middle of March the old root stocks develop new roots of yellowish color. These are divided and planted 0.6 m. apart, in rows 1 m. apart. One hectare should contain about 10,000 plants. The root cuttings are imbedded 10 cm. into the ground, while 6 cm. remain aboveground.

For fertilization, ammonium sulfate and potassium phosphate have been recommended, but in general the growers in Formosa use no fertilizers.

During the first year, a new plantation should be weeded twice (in May and in August). Older fields are weeded only once a year (in July or August).

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[86] Names given are those employed formerly, under Japanese rule.

A fully matured plant grows as high as 1.7 m., while the stump attains a diameter of about 0.45 m. A planting may last ten years, but the practice of not fertilizing generally shortens the life span, and after five years a field becomes uneconomical.

A new plantation started in March can be harvested for the first time in October. A field two years old, or older, can be cut twice a year, i.e., in June and October. The grass is cut rather short, only about 12 cm. being left aboveground. The harvested material is permitted to dry in the field for 3 days, during which it loses about 75 per cent of its weight, 100 kg. of fresh grass (leaves) yielding 25 kg. of dried grass.

Distillation.—The stills used for the distillation of citronella grass in Formosa resemble those employed in Japan for the distillation of mint (*Mentha arvensis*—cf. monograph on "Japanese Mint Oil," Vol. III of this work, p. 647). They are movable field stills, the retorts in many cases consisting of simple wooden barrels. It should be noted that fresh grass material cannot be processed in this type of low pressure still, as the fresh grass adheres together and prevents penetration of the steam. Therefore, only dried grass is used for distillation. It must be packed into the stills tightly. The principle of citronella distillation in Formosa is that of water *and* steam distillation (cf. Vol. I of this work, pp. 113, 120 ff., 125, 147 ff., and 150), which means low pressure (and hence prolonged) distillation. The distillation water is automatically returned to the retort during operation; in other words, the aqueous condensate is cohobated. Distillation of one charge requires about 6 hr. During the height of the season four charges are processed daily in each still. For reasons of economy, exhausted and sun-dried grass material is used as fuel, although coal or wood would be preferable.

Yield of Oil.—The yield of oil (from dried grass) varies with the season. Grass (leaves) cut during the June harvest yields about 2.4 per cent of oil, whereas grass cut during the October harvest yields only about 1.2 per cent of oil. Thus, the yield of oil from dried grass averages from 1.8 to 2.0 per cent.

The quantity of oil produced per year and per hectare depends upon the age of the planting:

1st year	50 kg.	One harvest
2nd year	150 kg.	Two harvests
3rd year	120 kg.	Two harvests
4th year	100 kg.	Two harvests
5th year	80 kg.	Two harvests

On a richer soil, and with fertilization, the yield of oil per hectare could probably be increased, but in Formosa the soil used for the growing of citronella is quite exhausted and, as was pointed out above, fertilizers are not used for reasons of economy.

Total Production.—The following figures illustrate the development of Formosa's citronella oil industry from its beginning to 1941 inclusive:

	Kilograms
1917	25
1918	50
1919	120
1920	200
1921	300
1922	350
1923	500
1924	500
1925	700
1926	800
1927	1,000
1928	1,200
1929	2,000
1930	3,000
1931	5,000
1932	10,000
1933	20,000
1934	40,000
1935	80,000
1936	110,000
1937	160,000
1938	220,000
1939	345,000
1940	360,000
1941	310,000

Physiochemical Properties.—An oil of citronella Formosa examined by the Takasago Chemical Industry Co., Ltd., Tokyo,[87] had these properties:

Specific Gravity at 15°	0.8862
Optical Rotation	−4° 8′
Refractive Index at 20°	1.4700
Total Geraniol Content	85%
Geraniol Content	37%
Citronellal Content	39%

An oil analyzed by Fritzsche Brothers, Inc., New York, exhibited the following properties:

Specific Gravity at 15°/15°	0.886
Optical Rotation	−1° 43′
Refractive Index at 20°	1.4687
Total Geraniol Content	84.2%
Aldehyde Content, Calculated as Citronellal	45.1%
Solubility at 20°	Soluble in 1 vol. of 80% alcohol; opalescent in 10 vol.

A sample of oil procured by the author in Japan (1939) had these properties:

Specific Gravity at 15°/15°	0.886
Optical Rotation	−2° 22′
Refractive Index at 20°	1.4673
Total Geraniol Content	87.4%

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[87] Private communication.

Aldehyde Content, Calculated as Citronellal	45.0%
Solubility at 20°	Soluble in 1 vol. of 80% alcohol; opalescent in 4 vol. and more

In general, the properties of Formosa citronella oil resemble those of the oils produced in Java. There is no way of telling what results might be obtained if other methods of distillation were employed in Formosa, since all oil is produced there by one and the same method (see above). According to reports,[88] there is no marked difference in properties between oils distilled from fresh (green) and oils distilled from dried plant material. Nor does the age of a planting (up to five years) exert any influence upon the quality of the oil.

Chemical Composition.—The chemical composition of the Formosa citronella oil is identical with that of the Java type. (Cf. the monograph on "Oil of Citronella Java, Chemical Composition.")

SUGGESTED ADDITIONAL LITERATURE

Hirozo Nobori and Atsuo Kohashi, "Reduction of Citronella." *Koryo* (1948), No. 4, 3. *Chem. Abstracts* **43** (1949), 2160.

Citronella Oil from Guatemala [89]

Development.—The citronella oil industry of Guatemala (C. A.) was established about 1930. At that time Mr. René Keilhauer, a banana grower in Los Cerritos near Escuintla (not far from the Pacific Coast, about 50 miles from Guatemala City), was forced to discontinue his banana plantations as a result of damage by heavy storms (blowdown) and the banana disease (*Cercospera musa* or "sigatoka"). He decided to plant other crops, before weeds and the jungle invaded his fields. A small number of Java type citronella and West Indian type lemongrass plants, introduced during World War I by Mr. Julio Samayoa, pointed toward a solution of the problem. Accordingly, in the course of several years a large acreage near Los Cerritos and adjacent La Maquina was planted with citronella and lemongrass. The sponsors of the new industry, however, probably did not sufficiently estimate the factor of competition on the part of the oils from Java and India from which their venture was later to suffer gravely. It was only because of the stubborn pioneer work of Mr. René Keilhauer and his son

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[88] *Ibid.*

[89] The author is greatly indebted to Mr. Carlos Schaeuffler, Retalhuleu, Guatemala, for much of the data contained in this monograph. As a large-scale producer Mr. Schaeuffler is well qualified to furnish reliable information on citronella oil.

Minor Keilhauer that production of oils of citronella and lemongrass could be continued until 1940. The outbreak of World War II brought about a substantial rise in the prices of the two oils and alleviated the serious plight of the producers in Guatemala. With the conquest of Java by Japanese forces, and with the increasing difficulties of shipping from India, Java citronella oil and Indian lemongrass oil became practically unobtainable in the Western Hemisphere, and the American essential oil industry had to rely almost entirely upon the new production in Guatemala. Prices of the two oils rose to about $5.00 per pound, and, attracted by the profits to be obtained, many other planters turned to the production of citronella and lemongrass on a large scale. Favorable climatic and soil conditions in tropical Guatemala, and prevailing low wages, contributed to the success of the new industry which represents one of the most spectacular chapters in the American essential oil industry.

In 1949 there were 46 individual citronella oil producers in Guatemala, supplying about 770,000 lb. of oil. Of this quantity, 244,000 lb. of oil were produced by three large-scale operators.

With the reappearance of the oil from Java, and with the new competition from Formosa and Honduras, prices of the oil dropped to about $1.00 per pound in 1948, and at the time of this writing (1949) it appears that quite a number of the smaller and less efficient citronella oil producers will be forced out of business. Nevertheless, the Guatemala citronella oil, which is of excellent quality, has become firmly established, and after Java, Guatemala is now the most important producer of citronella oil. In 1950 about 4,500 hectares were under citronella in Guatemala.

Producing Regions.—Citronella plantings in Guatemala are located near the Pacific Coast, from the border of Mexico south to the region of Escuintla, the chief producing regions being Los Cerritos, Retalhuleu, and San Felipe.

Climate, Altitude, and Soil.—Citronella requires a tropical climate with abundant sunshine and occasional but regular rains. Long spells of drought or excessive rainfall are harmful. In this respect citronella is much more sensitive than the hardier lemongrass.

Citronella grows best at altitudes ranging from 600 to 1,500 ft. above sea level; there the leaves can be cut four times per year. At higher altitudes the growth is slow and permits only two or three harvests per year.

The soil most suited to the cultivation of citronella is black humus, provided it is well drained and does not stay wet all year around. Citronella dies quickly in swampy land, but is more resistant on dry land. On soil which contains clay, citronella grows very poorly.

Planting, Cultivating, and Harvesting.—Citronella is planted at the beginning of the rainy season (in May) by means of root division. For this purpose the stools (mats) of mature plants are divided into ten segments about 2 ft. long. When preparing the root segments, any large pieces of woody stalk material and dry blades should be cut off and discarded. Three or four clean and healthy root segments are then planted into holes dug in rows 1 m. apart. This distance permits the use of cultivators between the rows; if the distance is less, the plants will not grow as tall as when planted 1 m. apart. The holes should be about 6 in. deep; deeper planting is dangerous, as the young plants may develop root rot during the rainy season. The

Courtesy of Oficina Controladora de Aceites Esenciales, Guatemala, C. A.

FIG. 15. Production of citronella oil in Guatemala. A citronella plantation 600 feet above sea level.

Courtesy of Oficina Controladora de Aceites Esenciales, Guatemala, C. A.

FIG. 16. Production of citronella oil in Guatemala. A citronella grass harvester recently developed and patented in Guatemala.

root segments should be planted in such a way that the base of the lowest leaf (which is not removed) lies at ground level.

Because of abundant growth of all kinds of weeds, particularly during the rainy season, frequent cleanings or weedings of the fields are necessary. No fertilizers are used in Guatemala; but some producers dump the exhausted (distilled) leaves into the fields.

The first harvest can be made approximately eight months after planting, but this cutting does not yield much leaf material, as citronella reaches full maturity only twelve months after planting. In most cases the grass is cut by hand with machetes; this constitutes the largest item in the cost calculation of the oil. However, efforts are now being made to introduce mechanical harvesters.

Distillation.—The stills used in Guatemala for the distillation of citronella and lemongrass are usually about 10 ft. high and 6 ft. wide, but stills of other sizes are also employed. The steam pressure ranges from 40 to 70 lb. (measured in the steam generator).

Depending upon the prevailing weather conditions, the cut leaves are distilled either fresh or semidried. To pack the leaf material into the stills as tightly as possible, it is first run through heavy hay or fodder cutters which must be solidly constructed to stand the prolonged strain of processing large quantities of grass.

According to the size of the stills and the steam pressure applied, distillation of one charge requires from 45 to 75 min. Longer distillation increases the yield of oil, but the oil will then have a lower content of citronellal, the most valuable constituent of the oil. Since most of the citronellal distills over during the first 15 to 30 min., several distillers in Guatemala have reduced the length of distillation to 45 min., thus obtaining a better quality of oil and saving a great deal of fuel. In times of low oil prices it simply does not pay to prolong distillation.

Yield of Oil.—According to Ippisch,[90] in commercial production, yield of oil per acre per year decreases with the age of a field. For example, with three or four cuttings per annum, the yearly yield of oil per acre (in large-scale production) was found to be 136 lb. in the first year, 103 lb. in the second, 83 lb. in the third, and 66 lb. in the fourth year. After the fourth year, yield is so low that the plantation should be renewed.

One acre yields on the average about 97 lb. of oil per year. It should, however, be pointed out that it is very difficult to indicate the exact yield of oil per acre, as this depends upon the age of the planting and weather conditions. Since cut leaf material arriving at the distilleries is never weighed, only several years' experience can give an idea as to the average yield of oil per acre.

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[90] Private communication from Mr. F. J. Ippisch, Manager, Oficina Controladora de Aceites Esenciales, Guatemala, C. A. (March, 1950).

In general, it may be said that the yield of oil during the dry season is higher than during the rainy season.

In experiments conducted by Loustalot and Pol,[91] Java citronella grass consistently outyielded the Guatemala grass in all harvest treatments. The percentage of *oil* in the Guatemala grass was, however, higher in all treatments, and the average yield of oil per acre was somewhat higher for the Guatemala grass than for the Java grass, when harvested at maximum or low heights. At medium height, the percentage of oil in the Guatemala grass was not much greater than in the Java grass. Guatemala grass harvested eleven times over a four year period yielded 154.4 lb. of oil per acre compared to 141.6 and 136.0 lb., respectively, for plots harvested fifteen and eight times during the same period. Java grass cut at medium height yielded 170.7 lb. of oil per acre per year compared to 138.6 and 119.6 lb., respectively, from plots cut at low and maximum heights. In the Java and in the Guatemala grass the percentage of oil was higher when the grass was harvested at 4.5 ft. than when it was harvested at 3.5 ft. or at maximum height. The percentage of geraniol was slightly but consistently higher in the Guatemala grass than in the Java grass, and there was a tendency for the geraniol to be somewhat higher when the grass was cut at maximum or medium heights.

Physicochemical Properties.—As was pointed out above, the citronellal content of the oil depends chiefly upon the length of distillation. It is higher in oils distilled during the dry season than in oils produced during the rainy season, and in oils derived from plants older than one year.

The duration of distillation is carefully controlled in Guatemala, and oils shipped from there contain about 35 per cent of citronellal and 85 or more per cent of total geraniol. Lately substantial quantities of oil containing as high as 45 per cent of citronellal and the usual 85 per cent of total geraniol have been received on the market. The latter type of oil is particularly appreciated by manufacturers of aromatic isolates.

Genuine citronella oils imported and examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°...	0.886 to 0.901
Optical Rotation............	−1° 0′ to −5° 30′
Refractive Index at 20°......	1.4660 to 1.4738
Total Geraniol Content......	85 to 97%
Aldehyde Content, Calculated as Citronellal.............	28 to 45%
Solubility at 20°............	Clearly soluble at all dilutions between 1 and 2 vol. of 80% alcohol; occasionally slightly opalescent on further dilution up to 10 vol.

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[91] *Agron. J.* **41** (1949), 375. *Chem. Abstracts* **43** (1949), 8448.

Shipping.—The Guatemala oil is usually shipped to the United States by boat in galvanized iron drums holding 53 gal.

Analysis and Chemical Composition.—The methods of analysis are the same as those employed with Java citronella oil. As regards the chemical composition of the oil, no special investigation has been published in literature, probably because it is generally assumed that the composition of the Guatemala oil is practically identical with that of the Java oil (cf. the monograph on "Oil of Citronella Java").

Total Production.—The following quantities of citronella oil have been produced in Guatemala since 1935:

	Pounds
1935	25,730
1936	30,992
1937	57,050
1938	87,154
1939	165,865
1940	145,044
1941	107,125
1942	21,060
1943	111,178
1944	155,357
1945	158,936
1946	315,756
1947	251,095
1948	650,000
1949	770,000

Exports.—Early in 1948 the Oficina Controladora de Aceites Esenciales, Guatemala City, Guatemala, C. A., an association authorized by a government decree of May 11, 1948, was organized on a voluntary basis by the producers of citronella and lemongrass oils in Guatemala. The functions of the association, as set forth in its statement of policies, are:

1. To assure that all essential oils exported from Guatemala are of guaranteed quality.
2. To promptly and fully meet all contractual obligations to purchasers of essential oils.
3. To arrange for advance payments to members, for oils delivered to the association's warehouse in Guatemala City.
4. To establish prices which are fair both to the producers and consumers.

The association acts as consolidated shipping agency, handling all essential oils produced in Guatemala. The government decree which created the O.C.A.E. also granted the organization a blanket export license covering shipments of all essential oils consigned to points outside the country. Members of the association ship their oils by rail or truck to Guatemala City where they are received by the manager and placed in the association's own warehouse. The oils are then inspected, analyzed, water and other impurities are removed, small lots are mixed to insure a uniform quality, and the product is filled in best available, clean containers. Every precaution is taken to insure purity and to provide oils with the chemical content desired by the purchasers. Important technical and agricultural projects have been started in order to increase and improve this industry.

Citronella Oil from Honduras

During World War II, Honduras (C. A.) became a producer of substantial quantities of citronella oil, Java type. The development of this industry must be credited to the Tela Railroad Company,[92] La Lima, Honduras, a firm affiliated with the United Fruit Company, the well-known growers and shippers of bananas. The idea of growing citronella in Honduras was motivated by the impossibility of exporting bananas, due to lack of shipping facilities, during the war years, and by the necessity of raising other crops in order to keep the great number of laborers in the banana plantations occupied.

To one familiar with the excellent research, development, and vast production facilities of the Tela Railroad Company, it is not surprising that the whole program was carried out most successfully. Many of the citronella plantings were laid out along the narrow-gage railroad tracks which cross the immense banana-growing regions, and on which the cut grass can be transported, at low cost, to a centrally located, modern distillery.

The producing regions are near the Atlantic seashore, in the Sula Valley, which is of alluvial origin and has been built up by the Ulua and Chamelecon rivers. There, citronella grass of the Java type was planted early in 1940 with rootstocks obtained from Puerto Rico and Guatemala.

Soil, Climate, and Altitude.—The highest yield of oil has been reported from grass planted on sandy loam (pH from 6.0 to 6.5), but good yields have been obtained also on sandy clay loam (pH from 7.5 to 7.8). All grass is grown at altitudes ranging from 50 to 100 ft. above sea level. Prolonged droughts at times stunt the plants, but an annual rainfall of 80 to 100 in., well distributed over ten months, appears favorable to yields of leaves and oil.

Planting and Cultivating.—Prior to planting, the land must be cleared, plowed, and harrowed. Citronella is propagated by means of rooted crown divisions of mature grass, the time of planting being the rainy season from June to December. For this purpose clumps of mature plants are pulled from the ground, trimmed of all but 5 or 6 in. of their tops, and divided

[92] The author is greatly obliged to Dr. V. C. Dunlap, Director of Tropical Research, United Fruit Co., and to Dr. E. O. Reif, Chief Chemist, Tropical Research Dept., Tela Railroad Co., La Lima, Honduras, for most of the material contained in this section. Since data on the production of oil of citronella are difficult to obtain and often self-contradictory, the information supplied by these two experts, based as it was on years of practical experience, has been particularly valuable.

into single or double stalked root segments, which should be kept wet until planting. The root segments are set out at intervals of 3 ft., in rows 2 ft. apart. The roots of the new plants must be fixed firmly in the ground and well covered with soil.

In the first three months, i.e., until the grass fills the rows, monthly cultivation is necessary. After the first harvest one cultivation will be sufficient. No fertilizers are used. Shortly before each harvest all weeds should be eradicated in order to reduce competition and eliminate possible contamination of the oil.

Citronella flowers once a year, usually at the end of November in the rainy season. Each flower grows on a separate stalk. Neither the flowers nor their stalks contain any essential oil. Since this inert material would increase the weight of the cut leaves, men have to go through the fields prior to the harvest of the leaves, and cut out the flower-bearing stalks. In actual field practice the grass is harvested before it reaches the flowering stage.

Harvesting.—The leaves can usually be cut for the first time six months after planting. Depending on the rapidity of growth, subsequent harvests may take place at intervals of four months, which permits three harvests per year. The time of cutting is best determined by the development, height, and maturity of the plants. They should not be cut when too young, nor should they be permitted to reach the flowering stage (see above). In Honduras, the grass is harvested when the blades reach a height of approximately 3 ft. It is cut by hand with machetes just above the first node and collected in bundles of about 50 lb. Dry leaves may be hauled to the stills immediately. Wet leaves should be left in the field for one day to dry partly, and to lose excessive moisture, as the processing of wet material entails a great deal of steam consumption and necessitates long hours of distillation, not to speak of the greater cost of transportation. Drying for more than one day is detrimental to the yield of oil and to the citronellal content of the oil, as can be seen from the following experiments carried out by the Tela Railroad Company, La Lima:

DRYING EXPERIMENT

Treatment of Grass	*Percentage of Oil Calculated for Green Grass*	*Citronellal Content of the Oil in Per Cent*
Green Grass	0.625	36.28
1 day sun dried	0.530	34.21
2 days sun dried	0.500	27.23
3 days sun dried	0.370	22.50
4 days sun dried	0.330	24.44
1 day room dried	0.625	35.37
2 days room dried	0.570	25.37
3 days room dried	Oil had putrid odor	...

Distillation.—Prior to distillation, the leaves are reduced to 4-in. pieces by means of twin power cutters placed opposite each other. The material is then fed by gravity into the still and packed tightly. Live steam of 15 lb. pressure (measured at the steam inlet gauge) is injected, but as soon as the first vapor appears at the condenser outlet (usually after 10 min.) the steam pressure is reduced to 5 lb. When the condensate flows evenly, the steam pressure is raised gradually to a maximum of 25 lb., and kept up as long as no vapor appears at the condenser outlet. Distillation is completed when an appreciable amount of oil can no longer be separated from the condensate. The flow of oil may be checked by drawing samples periodically at the condenser outlet. Depending upon the condition of the leaf material, distillation of one charge requires from 3 to 5 hr. at the most. After 3 hr. such small quantities of oil are obtained that contination of distillation pays only when oil prices are high. Moreover, the oil collected after 3 hr. contains very little citronellal, the chief constituent, which determines the price of each lot of oil. It is, therefore, preferable to stop distillation, provided, of course, that a normal yield of oil has been obtained.

The following table shows the percentage of oil obtained during successive hours of distillation, calculated upon the total yield of oil:

Percentage of Oil Distilled after:

1 Hr.	*2 Hr.*	*3 Hr.*	*4 Hr.*	*5 Hr.*
55.0	25.5	10.0	5.7	3.8
53.5	22.6	11.7	7.8	4.6
52.3	26.9	9.5	7.4	3.9
Citronellal Content of Fraction	36.1	10.6	8.6	8.5
Citronellal Content of Total Oil		32.6		31.7

Yield of Oil.—So far as the yield of oil from green (fresh) leaf material per acre and per year is concerned, the following table will be of interest:

Yield per Acre and Year in Pounds

(The numbers in parentheses indicate the number of cuttings per year)

Soil and pH	*1943*	*1944*	*1945*	*1946*	*1947*
Sandy clay loam, pH 6.5	138.4 (3)	129.3 (3)	60.3 (2)	92.1 (2)	54.8 (2)
Sandy clay loam, pH 7.5	59.9 (1)	270.3 (4)	204.6 (4)	205.4 (4)	126.1 (3)
Sandy loam, pH 6.5			57.4 (1)	235.1 (4)	195.3 (3)

Yield of Oil

Soil and pH No. of Harvest	*Percentage of Oil per Weight of Grass*	*Pounds of Oil per Acre and per Cutting*	*Citronellal Content of the Oil (%)*	*Age of Grass in Months*
Sandy clay loam, pH 6.5				
1	1.236	39.8	32.6	6
2	1.330	46.8	33.1	3
3	0.716	50.4	32.3	4
4	0.973	44.0	38.0	3
5	1.119	44.0	37.6	4
6	0.663	41.5	36.0	4
7	1.207	24.3	34.8	4
8	0.628	35.5	37.6	6
9	0.664	44.5	38.7	4
10	0.745	47.6	37.6	4
11	0.709	27.3	36.2	4
12	0.712	27.5	36.3	4
Sandy clay loam, pH 7.5				
1	0.650	54.9	35.0	6
2	0.983	72.5	35.1	6
3	1.007	55.5	35.7	3
4	0.679	47.5	36.0	3
5	0.990	42.5	39.5	3
6	0.653	54.4	38.3	4
7	0.643	58.2	38.2	4
8	0.794	43.8	36.8	4
9	0.818	56.5	36.4	4
10	0.690	56.0	34.4	4
11	0.869	38.8	34.9	4
12	0.771	38.1	34.6	4
Clay loam pH 7.3				
1	0.494	80.6	40.0	7
2	0.704	70.4	41.0	4
3	0.697	48.8	45.0	4
4	0.722	44.7	36.5	6
5	0.923	50.7	35.0	4
6	0.607	44.8	41.3	4
7	0.987	28.3	50.8	4
8	0.653	36.1	41.8	6
Sandy loam pH 6.5				
1	0.602	61.6	38.7	6
2	1.091	54.9	36.5	4
3	0.757	59.0	38.3	4
4	0.501	59.6	34.6	4
5	0.512	53.4	35.2	4
6	0.880	40.3	37.2	4
7	0.883	43.7	35.6	4
8	0.740	57.9	34.8	4

It has been found that the yield of oil is influenced chiefly by two factors—the age of the planting and the amount of rainfall. After ten harvests the yield of oil per acre decreases to a point at which operation becomes unprofitable. Prolonged drought retards growth of the grass and decreases the yield per acre.

The spent leaves are not used as fuel, as the steam boilers are heated with oil. Analysis of the ashes of the spent and burned grass has shown that the ashes possess very little value as fertilizers.

Physicochemical Properties.—The physicochemical properties of citronella oil, distilled under identical conditions (i.e., the same length of distillation) are influenced by both climate and soil. Leaves cut during rainy periods yield an oil with a low citronellal content. Oil derived from grass grown on clay soil exhibits a high citronellal content, whereas oil from plants grown on very sandy soil has a low citronellal content.

Numerous shipments of Honduras citronella oil received and analyzed by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°...	0.882 to 0.899
Optical Rotation............	−0° 28′ to −5° 45′
Refractive Index at 20°......	1.4690 to 1.4740
Total Geraniol Content......	85 to 91%
Aldehyde Content, Calculated as Citronellal............	30 to 45%
Solubility at 20°............	Clearly soluble at all dilutions between 1 and 2 vol. of 80% alcohol; occasionally slightly opalescent on further dilution up to 10 vol.

The quality of the citronella oils imported from Honduras has been excellent.

Total Production.—The total production of Honduras citronella oil from 1942 through 1949 was as follows:

Year	*Pounds of Oil*
1942...........	196
1943...........	7,567
1944...........	29,598
1945...........	45,943
1946...........	107,579
1947...........	76,744
1948...........	58,984
1949...........	40,422

Citronella Oil from Haiti

The citronella plant (Java type) was introduced into Haiti in 1939 from the U. S. Agricultural Experiment Station in Mayaguez, Puerto Rico, by

Shada (Société Haitienne de Développement Agricole). This company was financed by the Import and Export Bank. The citronella plantings in Haiti, which are still small, are located near Bayeux, Plaisance, Aux Cayes, Ducis, and St. Michel. The only plantings which have been increased within the last few years are those near Bayeux, where 80 acres are now (1949) under cultivation, and those near Aux Cayes, where a nursery of 50 acres has been established.

In general, citronella is not as hardy as lemongrass and requires a better soil. According to Dejoie,[93] the plant is very sensitive to the application of nitrogen fertilizers, which reduce the yield of oil per ton of grass and increase the green matter abnormally. This seems to be the result of a disbalance between nitrogen and phosphoric acid (P_2O_5). The best method of fertilization is to apply 300 lb. of superphosphate per acre and to mulch the planting with exhausted (distilled) chopped grass that comes from the same area. In regions of low rainfall the cultivation of citronella is not economical, even if the plants have been set out in the wet season, because the plantings suffer too much during the dry season. Sixty inches appears to be the minimum of annual rainfall necessary at altitudes from sea level to 1,500 ft. At Plaisance 50 in. of rainfall per year was found sufficient. A nursery of 20 acres at that elevation has proved very satisfactory so far as tonnage of grass (leaves) per acre and yield of oil are concerned.

As was pointed out in the monograph on "Oil of Citronella Java," the distillation of citronella grass, Java type, is actually a fractional distillation if an oil containing 85 per cent of total geraniol and 35 per cent of citronellal content is to be produced. It does not matter whether the grass is distilled in the fresh or dried state. Since a normal oil acceptable to the trade cannot be produced if all the oil contained in the grass (leaves) is distilled over, the producer must be satisfied with a yield of 10 lb. of oil per metric ton of fresh grass. With fresh plant material high steam pressures give better results, and distillation can be stopped after 4 hr. With dried grass low pressure steam is preferable.

So far, the production of citronella oil in Haiti has been almost negligible, as can be judged from the following figures:

Fiscal Year	*Quantity of Oil in Kilograms*
1941–1942	...
1942–1943	...
1943–1944	...
1944–1945	186
1945–1946	687
1946–1947	181

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[93] Private communication of Senator Louis Dejoie, Port-au-Prince, Haiti.

Fiscal Year	*Quantity of Oil in Kilograms*
1947–1948	1,294
1948–1949	1,401

Nevertheless, it is safe to assume that once the production of citronella oil, Java type, has been firmly established in Haiti, it will surpass that of lemongrass. So far, however, the Haitian peasants have evinced little interest in the growing of lemongrass or citronella. At present, the plantations belong to the large producer-distillers, who are studying the behavior of the plant, and experimenting with methods of cultivation, harvesting and distillation, in an attempt to establish optimum conditions before starting large-scale plantings.

Citronella Oil from the Belgian Congo

According to the U. S. Department of Commerce,[94] citronella is grown in the Belgian Congo in much the same manner as lemongrass (see the monograph on "Lemongrass Oil from the Belgian Congo") except that the culture of citronella is older and somewhat more specialized. Under ideal conditions, the production of citronella oil per hectare amounts to 50 and even 80 kg., but actual production ranges from 25 to 35 kg. per hectare. In 1947 about 50 hectares were under citronella cultivation; the total output of oil in that year was approximately 3,500 kg. The future of the citronella industry in the Belgian Congo will depend upon conditions on the world market. Like oil of lemongrass, oil of citronella from the Congo has not yet found a definite place on the world market, but if a steady demand should develop, plantations will probably be increased. The government agricultural and economic services are quite anxious to discover new sources of revenue for the colony and would encourage additional plantings of citronella.

OILS OF OTHER *CYMBOPOGON* (AND *ANDROPOGON*) SPECIES

All the *Cymbopogon* (or *Andropogon*) oils described above are commercially important and produced on a large scale. Literature describes a

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[94] *Bur. Foreign Domestic Commerce,* "International Reference Service," Vol. 7, Pt. 3 (1949), No. 16—"The Belgian Congo as a Source of Crude Drugs and Essential Oils."

number of other *Cymbopogon* (and *Andropogon*) oils which have been produced experimentally over a number of years and in various countries, but which have not attained any commercial significance. Moreover, there is considerable confusion regarding their exact botanical origin. It would seem consistent with the policy followed in this work to omit these experimental oils from our discussion, were it not for the fact that the essential oil chemist is occasionally faced with the problem of examining samples of just such oils distilled in tropical and subtropical countries from wild growing *Cymbopogon* (or *Andropogon*) species that seem to the producer to offer commercial possibilities. To aid the analyst in his task we shall briefly describe most of the experimental *Cymbopogon* (and *Andropogon*) oils mentioned in literature. Not included here are still other oils, produced experimentally in the past, about the botanical origin of which nothing is known. They are usually referred to as "an oil distilled from a *Cymbopogon* (or *Andropogon*) species." No purpose whatsoever would be served in enumerating such oils, and any discussion would only add to the already existing confusion.

OIL OF "BOTHA GRASS"

According to Gildemeister and Hoffmann,[1] the so-called "Botha grass" which occurs wild in Madras, and the "Bode grass" [2] which grows in Mysore, belong to certain species of *Cymbopogon* so far unidentified. In the opinion of Rao, Sudborough and Watson [3] the odor of the essential oils distilled from these grasses resembles that of the oil of "Inchi grass" from Travancore. The oils exhibited these properties:

	"Botha Grass" Oil from Madras	*"Bode Grass" Oil from Mysore*
Specific Gravity at 15°	0.9038	0.9231
Optical Rotation at 25°	+39° 18′	−24° 42′
Refractive Index at 25°	1.4748	1.4831
Ester Number	...	1.3
Saponification Number	44.7	45.5
Saponification Number after Acetylation	120.7	112.7
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	36.5%	34.4%

Two "Botha grass" oils from Madras, examined by Schimmel & Co.[4] had the following properties:

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[1] "Die Ätherischen Öle," 3d Ed., Vol. II, 379.

[2] Occasionally the two terms seem to be used interchangeably.

[3] *J. Indian Inst. Science* **8A** (1925), 146.

[4] *Ber. Schimmel & Co.* (1928), 8.

	I	*II*
Specific Gravity at 15°	0.9321	0.9303
Optical Rotation	−18° 28′	−20° 45′
Refractive Index at 20°	1.48693	1.48587
Acid Number	2.2	2.2
Ester Number	46.7	40.1
Ester Number after Acetylation	112.9	110.1
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	33.9%	33.0%
Solubility in 80% Alcohol	Soluble in 2.1 vol. and more	Soluble in 3.8 vol. and more

OIL OF "CAMEL GRASS"

The so-called "camel grass," *Cymbopogon schoenanthus* Spreng. (syn. *Andropogon schoenanthus* L.), is a typical desert plant, which thrives with a minimum of water and moisture. It occurs widely in North Africa, Arabia, Iran, and many other parts of Asia. The plant is the principal grazing food for camels in the desert. In the past the plant was esteemed as a diuretic. Old pharmacopoeias and books on herbs refer to it as *Herba schoenanthi, Juncus odoratus, Foenum,* or *Palea camelorum.* In Arabian the plant is known as "Izkhir." Indian bazaars still handle the dried grass. It contains about 1 per cent of an essential oil, which can be isolated by steam distillation.[5] While the oil is not produced commercially, it is of some theoretical interest.

Dymock[6] observed these properties in a sample of oil: d_{15} 0.905 and α_D −4° 0′. Schimmel & Co.[7] reported d_{15} 0.915 and α_D +34° 38′. The same firm found that the oil distills between 170° and 250°. The odor of the oil recalls that of elemi oil, a result of the presence of phellandrene.

According to Rakshit and Dutt,[8] *Cymbopogon schoenanthus* yields 0.13 to 0.98 per cent of oil (d 0.8575 to 0.8875, acid number 1.0 to 10) which contains 3.1 to 10 per cent of phenols, and 10 to 30 per cent of aldehyde.

OIL OF "INCHI GRASS"

There is considerable confusion in the literature regarding the taxonomy of the plant from which the so-called "Inchi grass" oil is derived. Moudgill and Iyer[9] suggest the white flowering variety of *Cymbopogon caesius* Stapf

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[5] W. Dymock, C. J. H. Warden and D. Hooper, "Pharmacographia Indica," Vol. III (London), 564.

[6] *Ibid.*

[7] *Ber. Schimmel & Co.*, April (1892), 44.

[8] *Indian Soap J.* **13** (1947), 27.

[9] *Perfumery Essential Oil Record* **13** (1922), 292.

(Inchippul or Succunarippul). Rao and Sudborough,[10] however, believe this plant to yield the so-called "Kachi grass" oil (see the monograph on "Kachi Grass Oil"). Perhaps this is a case involving subspecies hard to differentiate morphologically.

According to Stapf, *Cymbopogon caesius* Stapf [11] (*Andropogon caesius*, *α* et *β*, Nees; *A. schoenanthus* var. *caesius* Hack.), also called "Kamakshi grass," is closely related to *Cymbopogon martini*, but sufficiently different to be distinguished. However, there are crosses between the two species in places where both grasses occur. *Cymbopogon caesius* grows widely in the southeastern part of India, particularly in the Karnatik.

Aside from the above-mentioned white flowering variety, there exists also a red flowering variety, which, in the opinion of Rangachariar,[12] is *Cymbopogon flexuosus* Stapf (lemongrass). However, the director of the botanical garden in Kew declared the two varieties to be merely forms of the same grass, viz., *Cymbopogon flexuosus* Stapf *forma albescens*.

According to Gildemeister and Hoffmann,[13] the vernacular name for the plant, "Inchippul" ("Gingergrass"), is due to the fact that the crushed leaves smell like ginger.

Steam distilling the air-dried upper parts of the white flowering variety of "Inchi grass," collected in October from arid slopes of southern Travancore (India), Moudgill and Iyer [14] obtained 0.8 per cent of a light colored, green-yellow oil. It darkened on standing. The odor resembled that of palmarosa oil. The oil had these properties:

Specific Gravity at 30°/4°	0.9187
Optical Rotation at 30°	−38° 54′
Refractive Index at 30°	1.484
Acid Number	1.7
Saponification Number	5.6
Saponification Number after Acetylation	120
Aldehyde Content (Hydroxylamine Method)	4.2%
Solubility	Soluble in 7 vol. of 80% alcohol; soluble in 0.8 vol. of 87% alcohol; insoluble in 70% alcohol

The following compounds were identified in the oil:

l-Camphene.

l-Limonene.

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[10] *J. Indian Inst. Science* **8A** (1925), 8. *Ber. Schimmel & Co.* (1926), 25.

[11] *Kew Bull.* (1906), 341. Cf. Administration Report of the Government Botanic Gardens and Parks, the Nilgiris, for 1901, p. 5.

[12] *Perfumery Essential Oil Record* **13** (1922), 295.

[13] "Die Ätherischen Öle," 3d Ed., Vol. II, 377.

[14] *Perfumery Essential Oil Record* **13** (1922), 292.

l-Borneol.

l-Terpineol.

A Sesquiterpene Compound(?).

An oil distilled exclusively from the flowers (yield 1.5 per cent) had these properties:

Specific Gravity at 30°/4°	0.9380
Optical Rotation at 30°	−37° 30′
Refractive Index at 30°	1.495
Acid Number	0.4
Saponification Number	6.1
Saponification Number after Acetylation	78.0
Solubility	Soluble in 1 vol. of 87% alcohol; insoluble in 70% alcohol

Distilling the red flowering and the white flowering forms of "Inchi grass," Moudgill [15] obtained oils of similar composition and properties:

	Red Form	*White Form*
Specific Gravity at 28°/4°	0.9130	0.9110
Optical Rotation at 30°	−36° 0′	−40° 0′
Refractive Index at 28°	1.4820	1.4815
Acid Number	0	0
Ester Number	11.4	9.2
Ester Number after Acetylation	121.8	117.4

The yield of oil was higher from the flowers than from the leaves.

The following substances were observed in the oils:

A Bicyclic Sesquiterpene, $C_{15}H_{24}$. d_4^{30} 0.9064, α_D^{30} −12° 0′, n_D^{30} 1.5005.

A Tertiary Sesquiterpene Alcohol, $C_{15}H_{26}O$. Optically inactive.

An Aldehyde(?), $C_{10}H_{14}O$ or $C_{10}H_{16}O$. b_{4-5} 92°–94°, α_D^{30} −6° 30′; semicarbazone m. 164° and 181°.

l-Limonene.

l-Camphene.

l-Borneol.

l-Terpineol.

Acetic Acid, Butyric Acid, An Optically Inactive Unsaturated Acid, $C_{16}H_{30}O_2$. In ester form.

An oil of "Inchi grass" from Travancore, investigated in the Imperial Institute [16] had these properties:

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[15] *Quart. J. Indian Chem. Soc.* **2** (1925), 23. Cf. *Bull. Imp. Inst.* **22** (1924), 268.

[16] *Bull. Imp. Inst.* **22** (1924), 268.

Specific Gravity at 15°/15°	0.924
Optical Rotation	−39° 51′
Refractive Index	1.486
Acid Number	1.0
Ester Number	9.4
Ester Number after Acetylation	91.0
Total Alcohol Content, Calculated as Geraniol	26.8%
Aldehyde Content (Bisulfite Method)	3%
Solubility	Insoluble in 70% alcohol

The odor of the oil resembled that of palmarosa oil.

An oil examined by Schimmel & Co.[17] had the following properties:

Specific Gravity at 15°	0.9250
Optical Rotation	−34° 25′
Refractive Index at 20°	1.48895
Acid Number	0.9
Ester Number	11.2
Ester Number after Acetylation	98.9
Total Alcohol Content, Calculated as Geraniol	29.4%
Solubility	Not completely soluble in 10 vol. of 80% alcohol; soluble in 0.3 vol. and more of 90% alcohol, with slight opalescence

The properties of this oil conformed closely to those reported by other investigators. However, the odor of the oil resembled that of Ceylon citronella oil and not that of palmarosa oil.

Oil of "Kachi Grass"

According to Rao and Sudborough,[18] the parent plant of "Kachi grass" is *Cymbopogon caesius* Stapf. It grows wild in Bangalore and in the highlands of Mysore. Steam distilling the whole (dried) grass, Rao and Sudborough[19] obtained 0.22 to 0.53 per cent of oil (I). Distillation of the (dried) flowering tops yielded 1.1 to 1.61 per cent of oil (II). The oils had the following properties:

	I	*II*
Specific Gravity at 15.5°/15.5°	0.9267 to 0.9339	0.9181 to 0.9789
Optical Rotation at 25°	−18° 18′ to −45° 36′	+9° 54′ to −62° 30′
Refractive Index at 25°	1.4846 to 1.4867	1.4838 to 1.4889
Acid Number	0.9 to 2.5	0.5 to 9.2

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[17] *Ber. Schimmel & Co.* (1926), 59.

[18] *J. Indian Inst. Science* **8A** (1925), 9.

[19] *Ibid.*

	I	*II*
Saponification Number	13.2 to 31.2	12.0 to 32.4
Saponification Number after Acetylation	150.4 to 164.0	114.6 to 172.3
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	46.6 to 51.4%	34.5 to 54.4%

These constituents have been identified in the two types of oil:

Geraniol.

Perillyl Alcohol.

Dipentene.

l-Limonene.

In general, the oils derived from the fully developed flowering tops contained a higher percentage of oxygenated compounds than the oils from the immature tops.

"Java Lemon Olie"

Years ago Schimmel & Co.[20] examined a number of oil samples labeled simply "Java Lemon Olie," which had an odor similar to that of citronella oil, yet somewhat different. Nothing is known about the plant from which the oil was distilled. It was probably a species of *Cymbopogon,* perhaps the wild growing "mana grass" (cf. the monograph on "Oil of 'Mana Grass' "). The samples of "Java Lemon Olie" examined by Schimmel & Co. had properties varying within the following limits:

Specific Gravity at 15°	0. 8809 to 0.8914
Optical Rotation	+10° 6′ to +14° 52′
Refractive Index at 20°	1.46466 to 1.46684
Total Geraniol Content	49.1 to 50.9%

As a matter of special interest it should be noted that these oils contained laevorotatory citronellal, which had not previously been observed in any essential oil. When isolated by means of its bisulfite compound, the regenerated aldehyde exhibited these properties:

b	205°–208°	α_D	−3° 0′
d_{15}	0.8567	n_D^{20}	1.44791

Semicarbazone m. 74°

In addition to *l*-citronellal, the oils contained cineole, and probably limonene (or a mixture of limonene and dipentene).

Although "Java Lemon Olie" is not produced commercially, the fact that it contains *l*-citronellal lends it some scientific interest.

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[20] *Ber. Schimmel & Co.,* April (1903), 21.

Oil of "Mana Grass"

The parent plant of the Java and Ceylon citronella grasses, in the opinion of Stapf, is probably the "mana grass," which grows wild on the island of Ceylon. There are two varieties of "mana grass," viz., *Cymbopogon nardus* var. *linnaei* (*typicus*), and *C. nardus* var. *confertiflorus*. However, the oils derived from the two varieties are indistinguishable as regards properties and yield, which vary considerably, depending probably upon local and seasonal conditions, etc. The oils possess no commercial importance whatsoever, but they are interesting scientifically. About thirty years ago Jowitt [21] experimentally cultivated the two varieties in Ceylon and, on distillation, obtained yields of oil ranging from 0.06 per cent to 0.45 per cent. The lowest yield was observed in May.

Examining these oils in London, Pickles [22] observed the following properties (with a wide range within the two types of oil):

1. Oil of *Cymbopogon nardus* var. *linnaei:*

Specific Gravity at 15°	0.894 to 0.926
Optical Rotation	−6° 42′ to +4° 54′
Total Geraniol Content	43.5 to 64.7%

2. Oil of *Cymbopogon nardus* var. *confertiflorus:*

Specific Gravity at 15°	0.900 to 0.929
Optical Rotation	−2° 11′ to +12° 12′
Total Geraniol Content	39.1 to 64.2%

The actual geraniol content of the oils (determined by the phthalic anhydride method) varied considerably.

Oil of Cymbopogon Afronardus Stapf

Beckley [23] reported that there are several species of this plant, with varying oil content. From one species he obtained 0.5 to 1 per cent of a clear yellow oil, rich in geraniol. The odor of the oil resembles that of palmarosa. The Imperial Institute [24] reported these properties for an oil obtained from the plant grown in Kenya:

Specific Gravity at 15.5°/15.5°	0.8940
Optical Rotation at 19°	−0° 10′
Refractive Index at 20°	1.4755

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[21] "*Cymbopogon* Grass Oils in Ceylon," *Circ. Agr. J. Roy. Botan. Gardens Ceylon* **5**, No. 12 (1910), 115.

[22] *Ibid.* Cf. *Bull. Imp. Inst.* **8** (1910), 144.

[23] *East African Agr. J.* **1** (1936), 469.

[24] *Bull. Imp. Inst.* **32** (1934), 220.

Acid Number	1.4
Ester Number	52.0
Ester Content, Calculated as Geranyl Acetate	18.2%
Ester Number after Acetylation	249.1
Total Alcohol Content, Calculated as Geraniol	84.2%
Aldehyde and/or Ketone Content (Neutral Sulfite Method)	3%
Solubility	Soluble in 1.7 vol. of 70% alcohol at 15.5°, without turbidity on further dilution

OIL OF CYMBOPOGON CLANDESTINUS STAPF

Rhind[25] steam distilled *Cymbopogon clandestinus* Stapf, a grass which grows abundantly in Burma, and obtained an oil (yield 0.26 per cent of the dry matter) that was of a light straw color and had a pleasant gingergrass odor.

Two oils investigated in the Imperial Institute[26] (I), and by Schimmel & Co.[27] (II), had these properties:

	I	*II*
Specific Gravity at 15°	0.9319	0.9240
Optical Rotation	+45° 58′	+45° 38′
Refractive Index at 20°	1.495	1.47769
Acid Number	3	0.8
Ester Number	11.3	12.1
Ester Number after Acetylation	167.1	168.9
Alcohol Content, Calculated as Geraniol	52.5%	53.2%
Aldehyde and/or Ketone Content (Neutral Sulfite Method)	18%	...
Solubility	Soluble in 2.1 vol. of 70% alcohol	Soluble in 5.5 vol. and more of 60% alcohol

As regards odor and properties, oil of *Cymbopogon clandestinus* Stapf (= *Andropogon clandestinus* Nees, *A. schoenanthus* subsp. *clandestinus* Hack.) resembles oil of gingergrass, but has a better solubility than the latter.

OIL OF CYMBOPOGON COLORATUS STAPF

Cymbopogon coloratus Stapf (*Andropogon coloratus* Nees; *A. nardus* var. *coloratus* Hook. f.) belongs to the citronella grasses of the Malabar coast; it

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[25] *Agr. J. India* **25** (1930), 327.

[26] *Bull. Imp. Inst.* **27** (1929), 458.

[27] *Ber. Schimmel & Co.* (1930), 20.

occurs in the Tinnevelly district, as far as the Anamalai Hills, and in the region of Karnatik (Madras). The grass differs from *Cymbopogon flexuosus* in being much smaller.[28]

An oil produced experimentally on the Fiji Islands (yield 0.35 per cent) had an odor reminiscent of citronella and lemongrass.

The physicochemical properties and chemical composition of oil of *Cymbopogon coloratus* have been investigated in the Imperial Institute,[29] and by Goulding and Earl.[30]

The properties of the oil vary within these limits:

Specific Gravity at 15°	0.911 to 0.920
Optical Rotation	−7° 43′ to −10° 42′
Solubility	Soluble in 1 vol. and more of 80% alcohol; not clearly soluble in 70% alcohol

In the Imperial Institute geraniol and citronellal were identified as chief constituents. According to Goulding and Earl the composition of the oil is as follows:

23%	Geraniol (determined by means of the phthalic anhydride method)
10%	Geranyl Acetate
7.5%	Terpenes (perhaps a mixture of *l*-limonene and one or several other terpenes)
40%	Aldehydes (chiefly citral)
0.75%	Acetic Acid
0.75%	Phenols (among them an odorless substance m. 142°)

More recently Pilley, Rao and Simonsen [31] distilled the flowering tops of *Cymbopogon coloratus* Stapf, growing in the North Arcot District of India, and obtained an oil that was entirely different from those described above. The oil contained:

15%	*l*-Camphene
7%	*l*-Limonene
Trace	Camphor(?)
8%	*l*-Borneol
10%	Geraniol
35%	Sesquiterpenes
8%	Sesquiterpene Alcohols
2 to 3%	Sesquiterpene Oxide(?)
14%	Unidentified Compounds

On cooling of the terpene fraction most of the camphene separated in crystalline form, m. 51°, $[\alpha]_D^{30}$ −82° 18′ (in chloroform solution).

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[28] O. Stapf, *Kew Bull.* (1906), 321.

[29] *Bull. Imp. Inst.* **8** (1910), 145; **10** (1912), 27.

[30] *Proc. Chem. Soc.* **30** (1914), 10.

[31] *J. Soc. Chem. Ind.* **47** (1928), 52.

Oil of Cymbopogon Densiflorus Stapf

The flower heads of *Cymbopogon densiflorus* Stapf, when steam distilled, yielded about 2 per cent of a yellowish viscous oil, possessing an odor reminiscent of gingergrass oil. Chiris[32] reported these properties:

Specific Gravity at 15°	0.9304
Optical Rotation at 25°	+59° 30′
Refractive Index at 20°	1.4683
Acid Number	2.10
Ester Number	8.42
Ester Number after Acetylation	141.68
Ester Number after Formylation	196.40
Solubility	Soluble in 1 vol. of 75% alcohol, with slight opalescence above 9 vol.; soluble in 0.5 vol. of 80% alcohol without turbidity

The oil reduced ammoniacal silver nitrate.

Oil of Cymbopogon Exaltatus

The volatile oil derived from *Cymbopogon exaltatus* (*Andropogon exaltatus*), native to Western Australia, is reported to be of the gingergrass type,[33] with the following properties:

Specific Gravity at 15.5°	0.9299
Optical Rotation	−18° 22′
Refractive Index at 20°	1.479
Ester Number	60.8
Ester Number after Acetylation	138.7
Solubility	Soluble in 2.5 to over 24 vol. of 70% alcohol (at 20°)

The ester value is higher than that generally met in Indian oils of *Cymbopogon martini* (var. *sofia*), or of "Kachi grass" (*C. caesius*), and the free alcohol content somewhat lower; the solubility is very satisfactory in an oil of this type. The odor is powerful and perhaps gives less of the somewhat unpleasant impression of undiluted gingergrass (possibly due to the larger proportion of esterified alcohols); it tends to a ginger note which is very persistent. The oil should be valuable as a fixative in certain heavier perfumes and for soaps. On the palate it gives a mildly burning sensation followed by a definite gingery flavor, and if its other characters are satisfactory it may have potentialities in flavoring materials.

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[32] *Rev. Marques Parfums France* **17** (1939), 81.

[33] *Perfumery Essential Oil Record* **25** (1934), 136.

Oil of Cymbopogon Georingii Honda

An oil obtained by steam distillation of *Cymbopogon georingii* Honda was investigated by Kariyone and Majima.[34] The oil (yield 1.0%) was of a yellow color and had these properties:

Specific Gravity at 20°/20°	0.9585
Specific Optical Rotation at 13°	−34° 58′
Optical Rotation at 17°	1.52128
Acid Number	0
Saponification Number	12
Methoxy Content	25.42%

On fractional distillation under reduced pressure the oil gave camphene, borneol, terpineol(?), cadinene, elemicin, and isoelemicin.

Oil of Cymbopogon Giganteus Chiov.

Cymbopogon giganteus Chiov., locally called "Tsauri grass," is a plant that grows wild in Nigeria (West Africa). A sample of oil distilled from the flowering tops (yield 1.15 per cent) and examined in the Imperial Institute,[35] London, exhibited an odor reminiscent of gingergrass oil. The following properties were observed:

Specific Gravity at 15°/15°	0.950
Optical Rotation at 20°	−42° 39′
Refractive Index at 20°	1.493
Acid Number	5.8
Ester Number	9.7
Ester Number after Acetylation	194.0
Total Alcohol Content, Calculated as Geraniol	62.4%
Aldehyde Content (Sulfite Method)	10.0%
Solubility	Soluble in 2 and more vol. of 70% alcohol

On steam distillation the flowering tops *and* stalks (60 to 75 cm. long) yielded 0.45 per cent of volatile oil.

Oil of Cymbopogon Iwarancusa Schult.

Cymbopogon iwarancusa Schult. (syn. *Andropogon iwarancusa* Jones) grows wild in the Himalaya Mountains, up to 8,000 ft. altitude, from Cashmir to Assam, and in the plains from the northwestern Himalayas to Bombay. On steam distillation the grass yields an essential oil with a minty

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[34] *J. Pharm. Soc. Japan* **55** (1935), 41. *Chem. Abstracts* **29** (1935), 3112.
[35] *Bull. Imp. Inst.* **22** (1924), 270.

odor. The oil is not produced commercially and therefore offers only scientific interest.

Two oils examined by Simonsen[36] (*I*), and by Simonsen and Rao[37] (*II*) had these properties:

	I	*II*
Specific Gravity	d_{30}^{30} 0.9203	d 0.9228
Optical Rotation	$[\alpha]_D^{30}$ +51° 41′	α +42° 48′
Refractive Index	n_D^{30} 1.481	n 1.4858
Acid Number	0.7	...
Ester Number	12.0	...
Saponification Number after Acetylation	47.4	...
Ketone Content (Bisulfite Method)	77%	44%

According to Simonsen and Rao[38] the oil contains up to 24 per cent of *d*-Δ^4-carene, and up to 80 per cent of *dl*-piperitone. The same author also observed in the oil about 2 per cent of an unidentified alcohol with a rose-like odor, 28 per cent of a sesquiterpene alcohol b_{31} 176°–177°, and small quantities of palmitic, decylic and octylic acids (in free or esterified form).

Berger[39] reported that the root of *Cymbopogon iwarancusa* Schult. contains 0.4 to 0.9 per cent of volatile oil, resin, and bitter principles.

OIL OF CYMBOPOGON POLYNEUROS STAPF

The so-called "Delft grass," *Cymbopogon polyneuros* Stapf (*Andropogon polyneuros* Steud.; *A. versicolor* Nees; *A. schoenanthus* var. *versicolor* Hack.; *A. nardoides β minor* Nees ex Steud.),[40] grows wild in the southwestern part of India, particularly in the Nilgiris. The name "Delft grass" originates from the fact that the plant occurs on the island of Delft, off the coast of Ceylon, where it is used for the feeding of horses. On the island of Ceylon the grass grows in the higher altitudes (up to 1,500 m.).

According to Gildemeister and Hoffmann,[41] the grass has been distilled experimentally on several occasions, the yield of oil ranging from 0.20 to 0.34 per cent. The oils had a peculiar, sweetish odor, quite different from that of citronella or lemongrass. The properties of four Ceylon oils varied within these limits:

Specific Gravity at 15°	0.936 to 0.951
Optical Rotation	+30° 53′ to +55° 15′

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[36] *J. Chem. Soc.* **119** (1921), 1644.

[37] *Indian Forest Records* **9** (1922), 111. *J. Soc. Chem. Ind.* **42** (1923), A. 29.

[38] *Ibid.* Cf. Simonsen, *J. Chem. Soc.* **121** (1922), 2292.

[39] *Scientia Pharm.* **10** (1939), 140.

[40] O. Stapf, *Kew Bull.* (1906), 345.

[41] "Die Ätherischen Öle," 3d Ed., Vol. II, 375. Cf. *Bull. Imp. Inst.* **8** (1910), 144; **10** (1912), 30.

Total Alcohol Content, Calculated as $C_{10}H_{18}O$	38.7 to 51.8%
Solubility	Soluble in 1 vol. of 80% alcohol, opalescent to turbid in 10 vol.

The alcohol content of these oils was calculated as $C_{10}H_{18}O$, but the nature of the alcohols was not determined.

More recently Kotnis and Rao[42] steam distilled the stalks and flowering tops of *Cymbopogon polyneuros* Stapf and obtained 0.38 per cent of a volatile oil with these properties:

Specific Gravity at 30°/30°	0.9329
Specific Optical Rotation at 30°	+49° 18′
Refractive Index at 30°	1.4922
Acid Number	4.8
Ester Number	58.5
Ester Number after Acetylation	124.9

After saponification and distillation at 4 mm., the oil yielded *d*-limonene, *d*-perillaldehyde, and a tertiary sesquiterpene alcohol b_9 138°–153° which was not identified.

OIL OF CYMBOPOGON PROCERUS A. CAMUS

Cymbopogon procerus A. Camus (= *Andropogon procerus* R. Br.) occurs in Australia.

An oil distilled in the Netherlands East Indies and examined by van Eerde[43] exhibited an odor reminiscent of turpentine oil. It had these properties:

Specific Gravity at 20°	1.0334
Optical Rotation at 20°	−8° 15′
Refractive Index at 20°	1.5183
Acid Number	12
Saponification Number	36.99
Saponification Number after Acetylation	124.68
Free Alcohols, Calculated as Geraniol	29.70%
Combined Alcohols	8.33%

The oil also contained: 34.90 per cent of elemicin, pinene(?), formic, propionic and butyric acids as esters, and trimethoxygallic aldehyde.

OIL OF CYMBOPOGON PROXIMUS (HOCHST.) STAPF

Cymbopogon (*Andropogon*) *proximus* (Hochst.) Stapf = *Cymbopogon senaarensis* var. *proximus* (Hochst.) Chiov. = *Andropogon iwarancusa*

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[42] *J. Indian Inst. Science* **18A** (1935), 129.

[43] *Pharm. Weekblad* **61** (1924), 1190.

proximus Hackl. is a plant of the family *Gramineae* that grows wild in Abyssinia and Eritrea (East Africa).

Bruno[44] raised plants experimentally, from imported seed, in the Colonial Garden of Palermo (Sicily), and on steam distillation obtained 0.424 to 0.68 per cent of volatile oil.

A sample of this oil examined by Schimmel & Co.[45] had these properties:

Specific Gravity at 15°	0.9169
Optical Rotation	+59° 22′
Refractive Index at 20°	1.48317
Acid Number	1.2
Ester Number	8.4
Ester Number after Acetylation	25.2
Solubility	Clearly soluble in 0.8 vol. and more of 80% alcohol; turbid in 8 vol. and more of 70% alcohol

The odor of the oil was first reminiscent of pennyroyal, later of celery. The portions isolated by means of sodium bisulfite also had a celery-like odor, but with a note of fatty aldehydes.

Later Bruno[46] investigated other oils distilled (in Palermo) from the leaves of *Cymbopogon proximus* Stapf and reported the following properties:

Specific Gravity	0.9344 to 0.9614
Refractive Index	1.4869 to 1.4892
Acid Number	0.1 to 1.95
Ester Number	21.13 to 54.13

The leaves contained the maximum of oil just before the flowering period, the minimum during the ripening of the seeds. In the latter period the oil content was highest in the flowers.

OIL OF CYMBOPOGON (JAVANENSIS) RECTUS A. CAMUS

Hofmann[47] investigated an oil distilled from a *Cymbopogon* species growing wild on the island of Java, particularly in Kedu. The plant was first named *Cymbopogon javanensis,* but later van Eerde[48] declared it to be identical with *C. rectus* A. Camus.

The oil examined by Hofmann exhibited an agreeable, sweetish odor reminiscent of palmarosa, rather than of citronella. It had these properties:

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[44] *Boll. Studi Informazioni R. Giardino Coloniale Palermo* **8** (1925).

[45] *Ber. Schimmel & Co.* (1927), 24.

[46] *Lavori Ist. botani., Palermo* **3** (1932), 1.

[47] *Pharm. Weekblad* **56** (1919), 1279. *Apoth. Ztg.* **43** (1920), 652.

[48] "Nieuwe Bijdrage tot de Kennis der indische Grasolien," Leyden (1924). *Ber. Schimmel & Co.* (1925), 3.

Specific Gravity at 15°	0.9747
Optical Rotation	−2° 54′
Refractive Index at 20°	1.51352
Acid Number	1.25
Ester Number	30.9
Ester Number after Acetylation	155.1
Total Geraniol Content	48.2%
Free Alcohol Content	33.9%
Solubility	Soluble in 1.9 vol. of 70% alcohol; soluble in 0.6 vol. of 80% alcohol, turbid in 2.8 vol. and more

The following constituents have been observed in the oil:

Phenolic Compounds(?). Traces.

Methyl Vanillin. Small quantities.

An Aldehyde (perhaps Citral). Small quantities.

Formic, Butyric, Valeric, and Caprylic Acids. In ester form.

l-α-Pinene. Hydrochloride m. 126°.

An Alcohol(?). Of agreeable, rosy odor.

Geraniol. Diphenylurethane m. 77°.

Methylisoeugenol. In the high boiling fractions. The oil contains about 30.5 per cent of methylisoeugenol.

According to de Jong,[49] the natives in Java call this oil "Poedoeng" or "Poedoeng semoe merah"; it has an odor reminiscent of roses and contains from 40 to 60 per cent of geraniol. The yield of oil is about 0.15 per cent.

Oil of Cymbopogon Senaarensis Chiov.

Cymbopogon senaarensis Chiov. grows wild in the Sudan. The grass possesses a strong odor reminiscent of pennyroyal. Locally the plant is known as "Mahareb." On steam distillation it yields from 1 to 1.2 per cent of an essential oil. The oil is not produced commercially, but offers some theoretical interest.

Two oils examined by the Imperial Institute [50] (*I*), and by Roberts [51] (*II*) had these properties:

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[49] "De aetherische Oliën leverende planten van Nederlandsch Oost-Indië en de bereiding van haar oliën," *Berichten van de Afdeeling Handelsmuseum van het Koloniaal Instituut* Nr. 7.

[50] *Bull. Imp. Inst.* **10** (1912), 31. Cf. *J. Chem. Soc.* **107** (1915), 1465.

[51] *J. Chem. Soc.* **107** (1915), 1465.

	I	*II*
Specific Gravity at 15°	0.9383	0.9422
Optical Rotation	+34° 14′	+29° 38′ (at 23°)
Acid Number	...	4.2
Ester Number	...	14.5
Saponification Number	14	...
Ester Number after Acetylation	60.2	62.1

The quantitative composition of the oil is approximately as follows:

13%	Terpenes, among them *d*-limonene, and probably pinene.
45%	1-*p*-Menthen-3-one (piperitone).
25%	A sesquiterpene alcohol $C_{15}H_{26}O$, b. 280°–285°, b_{21} 170°–175°, d_{15}^{15} 0.9544, α_D^{24} +10° 48′.
3%	An alcohol with a rose-like odor.
0.2%	Phenols.
2.0%	Acids, among them acetic, *n*-octylic, decylic, and palmitic acids.
11.8%	Residue, consisting probably chiefly of sesquiterpenes.

Oil of Cymbopogon Stipulatus Chiov.

Bruno[52] examined the oil distilled from the leaves of *Cymbopogon stipulatus* Chiov. which had been grown in the botanical experiment garden of Palermo (Sicily). Samples of oil had these properties:

Specific Gravity	0.9428 to 0.9665
Refractive Index	1.5192 to 1.5206
Acid Number	0.07 to 0.1
Ester Number	24.26 to 39.20

The maximum oil content in the leaves is reached just before the flowering period; the minimum during the ripening of the seeds. In the latter period the oil content is highest in the flowers.

An oil distilled from the leaves had the following properties:

Specific Optical Rotation	−30° 22′
Ester Number after Acetylation	28.9
Solubility	Soluble in 1 to 10 vol. of 80% alcohol

Oil of Cymbopogon Virgatus Stapf

On steam distillation of *Cymbopogon virgatus*, a species of grass growing in Burma, Rhind[53] obtained 0.55 per cent of an oil with a somewhat unpleasant odor, reminiscent of that of "Botha grass" oil. The oil had the following properties:

[52] *Lavori Ist. botani., Palermo,* **3** (1932), 1, 10. *Chem. Abstracts* **27** (1933), 1712.

[53] *Agr. J. India* **25** (1930), 327.

Specific Gravity at 15°	0.9556
Optical Rotation	−28° 53′
Refractive Index at 20°	1.49107
Acid Number	1.9
Ester Number	6.5
Ester Number after Acetylation	72.8
Alcohol Content, Calculated as Geraniol	21 to 22%

OIL OF ANDROPOGON ACICULATUS WILLD.

Hosking[54] steam distilled the leaves of *Andropogon aciculatus*, endemic to Samoa, and locally called "Moegalo." Obtained in a yield of 0.41 per cent, the oil had these properties:

Specific Gravity at 19°/19°	0.888
Optical Rotation	+0° 14′
Refractive Index at 19°	1.4879
Acid Number	2.6
Ester Number	12.3
Aldehyde Content (Bisulfite Method)	80%
Solubility	Insoluble in 10 vol. of 70% alcohol; insoluble in 10 vol. of 80% alcohol

OIL OF ANDROPOGON CONNATUS HOCHST.

Andropogon connatus Hochst. is an herb of the family *Gramineae* that grows wild in Eritrea (East Africa). Rovesti[55] investigated an oil obtained from this plant by steam distillation (yield 1.78 per cent), and reported these properties:

Specific Gravity at 21°/15°	0.9355
Optical Rotation at 20°	−54° 31′
Refractive Index at 23°	1.4951
Acid Number	0.13
Ester Number	5.32
Ester Number after Acetylation	138.13
Solubility	Soluble in 2.1 vol. of 70% alcohol

Odor and composition of the oil resembled those of gingergrass oil. The oil contained:

l-α-Phellandrene.

Geraniol.

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[54] *Perfumery Essential Oil Record* **24** (1933), 2.
[55] *Ann. chim. applicata* **17** (1927), 561.

Dihydrocuminyl Alcohol (at least 30 to 35 per cent).

An Aldehyde(?) of penetrating odor.

Hydrocarbons(?).

Sesquiterpenic Compounds(?).

Oil of Andropogon Fragrans

Louveau[56] examined a sample of oil of *Andropogon fragrans,* produced experimentally on the island of Réunion. The species had not previously been reported, and Louveau concluded, from the properties and composition of its oil, that the plant might be a third variety of *Andropogon martini* Roxb., of which the *motia* and *sofia* varieties yield palmarosa and gingergrass oils respectively, or possibly a local subvariety of the *sofia.*

The odor of the oil resembled that of palmarosa and gingergrass oils. Properties were as follows:

Specific Gravity at 15°	0.9572
Optical Rotation	+8° 6′
Refractive Index at 20°	1.4942
Acid Number	12.0
Ester Number	17.5
Ester Number after Acetylation	160.3
Total Geraniol Content	50.1%
Ester Content, Calculated as Geranyl Acetate	6.2%
Free Alcohol Content, Calculated as Geraniol	36.1%
Aldehyde Content, Calculated as Citronellal (Burgess Method)	9.2%
Solubility	Soluble in 0.9 vol. of 80% alcohol

The oil consisted of approximately:

10%	Terpenes (about $\frac{1}{4}$ α-pinene)
6%	Esters of terpene alcohols (chiefly geranyl acetate)
36%	Free alcohols ($\frac{2}{3}$ geraniol; linaloöl, and perhaps citronellol and nerol)
9%	Aldehydes ($\frac{3}{4}$ citronellal; perhaps citral; certainly cuminic aldehyde)
2%	Ketones (particularly methyl heptenone and menthone)
6%	Free solid acids (chiefly abietic acid)
30%	Sesquiterpenes, resinous substances from polymerization, which did not distill over at b_4 155°.

Oil of Andropogon Intermedius R. Br.

Andropogon intermedius R. Br. (= *Amphilophis intermedia* Stapf) occurs in India, the East Indian Archipelago, Indo-China, China, in the Philippine

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[56] *Rev. Marques parfumerie Savonnerie* **11** (1933), 311.

Islands, and Australia. Occasionally the plant grows in large quantities. In Java the plant is known as "Roempot pipit," in Flores as "Poang." The odor of the oil resembles that of vetiver.

A sample investigated by van Eerde [57] had these properties:

Specific Gravity at 20°	0.9850
Optical Rotation at 20°	−9° 30′
Refractive Index at 20°	1.5018
Acid Number	15.65
Saponification Number	72.64
Saponification Number after Acetylation	176.64
Alcohol Content, Calculated as Geraniol	36.15%
Combined Alcohols	15.68%

The oil contained *l*-limonene, acetic, and butyric acids.

Two samples of oil of *Andropogon intermedius* (R. Br. ?) examined in the Botanical Institute of Buitenzorg [58] (Java) had the following properties:

	I	*II*
Specific Gravity at 26°	0.889	0.919
Optical Rotation	−21° 52′	−15° 30′

The yield of oil in the case of the second sample was 0.03 per cent.

Oil of Andropogon Intermedius R. Br. var. Punctatus Hack.

The oil of *Andropogon intermedius* R. Br. var. *punctatus* Hack., known as "Montsukigaya," was investigated by Kafuku, Sebe and Kato.[59] Obtained in a yield of 0.5 per cent it had the following properties:

Specific Gravity at 20°/4°	0.8600
Optical Rotation at 30°	−10° 0′
Refractive Index at 30°	1.4643
Ester Number after Acetylation	130.18

The oil contained 4-undecanone, a dextrorotatory alcohol, an isomer of decyl alcohol, and octyl alcohol. Content of acids after hydrolysis of the esters reached 7 per cent. Among the acids were acetic, butyric, caproic, enanthic and caprylic acids.

Oil of Andropogon Kuntzeanus Hack. var. Foveolata Hack.

By steam distillation of *Andropogon kuntzeanus* Hack., var. *foveolata* Hack., originating near Poona, in India, Rao [60] obtained 0.27 per cent of an

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[57] "Nieuwe Bijdrage tot de Kennis der indische Grasolien," Leyden (1924). Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 386.

[58] *Jaarboek van het Departement van Landbouw Nijverheid en Handel in Nederlandsch-Indië,* 1907 (Batavia, 1908), 67; 1910 (Batavia, 1911), 48.

[59] *J. Chem. Soc. Japan* **59** (1938), 312. *Chem. Abstracts* **32** (1938), 8697.

[60] *J. Indian Inst. Science* **15A** (1932), 75.

oil, dark brown in color and possessing a sesquiterpene odor. It had the following properties:

Specific Gravity at 30°/30°	0.9208
Specific Optical Rotation at 30°	−36° 30′
Refractive Index at 30°	1.4813
Acid Number	1.7
Ester Number	0.3
Ester Number after Acetylation	80.8

The oil contained about 40 per cent of bicyclic, tertiary sesquiterpene alcohols of the cadinene type, about 10 per cent of *l*-camphene, 10 per cent of an isomer of camphene, and small amounts of α-pinene and borneol.

OIL OF ANDROPOGON ODORATUS LISB.

Andropogon odoratus Lisb.[61] (= *Amphilophis odorata* A. Camus) is a grass that grows wild on the west coast of India. In the districts of Poona and Thana the plant, locally known as "Veddigavat," or "Vaidigavat," and "Usadhana," is cultivated by the natives who relish it because of the ginger-like odor and flavor.

De Jong planted the grass in the Experiment Station of Buitenzorg (Java) and, on steam distillation, obtained 0.3 per cent of an oil that had a sharp, bitter flavor and an odor reminiscent of turpentine oil. Van Eerde[62] examined a sample of this oil and reported these properties:

Specific Gravity at 15°	0.9352
Optical Rotation at 20°	−37° 22′
Refractive Index at 20°	1.48511
Acid Number	5.5
Saponification Number	43.72
Saponification Number after Acetylation	155.55
Free Alcohols, Calculated as Geraniol	23.31%
Combined Alcohols	10.51%
p-Methoxycinnamic Acid	0.79%

The oil further contained:

l-Camphene.

l-α-Pinene.

l-Borneol.

Geraniol.

Butyric Acid.

An Aldehyde(?).

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[61] Cf. O. Stapf, *Kew Bull.* (1906), 349.

[62] "Nieuwe Bijdrage tot de Kennis der indische Grasolien," Leyden (1924). *Ber. Schimmel & Co.* (1925), 3.

According to Gildemeister and Hoffmann,[63] a number of oils investigated in years prior to the work of van Eerde cited above, had the following properties:

d_{31} 0.931, α_D −22° 45′ [64]
d_{15} 0.915, α_D −23° 10′ [65]
d_{26} 0.914, α_D −31° 10′ [66]
d_{26} 0.914, α_D −34° 44′, Saponification Number 33.6,
Saponification Number after Acetylation 98.9.[67]

OIL OF ANDROPOGON SCHOENANTHUS SUBSPEC. NERVATUS HACK.

Years ago Schimmel & Co.[68] received, from the Sudan, a small lot of a grass which in the Botanical Institute of Leipzig was identified as *Andropogon schoenanthus* subspec. *nervatus* Hack. On steam distillation the dried grass yielded 1.9 per cent of a brownish oil that had a certain similarity to the usual gingergrass oils, but a much weaker odor. The properties of the oil were:

Specific Gravity at 15°	0.9405
Optical Rotation	+26° 22′
Refractive Index at 20°	1.49469
Acid Number	4.6
Ester Number	9.3
Ester Number after Acetylation	99.1
Solubility	Soluble in 0.5 and more vol. of 80% alcohol; separation of paraffins from the dilute solution

Years later Joseph and Whitfeild [69] steam distilled flowering "Naal grass" (*Cymbopogon nervatus* Chiov. = *Andropogon schoenanthus* subspec. *nervatus* Hack.) and obtained 0.8 to 1.5 per cent of oil. This plant grows widely in the central parts of the Sudan, along the Blue Nile, and in the province of Kordofan. The properties of three oils derived from three different lots of grass varied within these limits:

Specific Gravity at 20°/20°	0.953 to 0.955
Optical Rotation	−31° 0′ to −50° 0′

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[63] "Die Ätherischen Öle," 3d Ed., Vol. II, 385.

[64] W. Dymock, C. J. H. Warden and D. Hooper, "Pharmacographia Indica," Vol. III (London), 571.

[65] *Ber. Schimmel & Co.*, April (1892), 44.

[66] *Jaarboek van het Departement van Landbouw Nijverheid en Handel in Nederlandsch-Indië*, 1910 (Batavia, 1911), 49.

[67] *Ibid.*, 1911 (Batavia, 1912), 44.

[68] *Ber. Schimmel & Co.*, April (1911), 19; October (1911), 17.

[69] *J. Soc. Chem. Ind.* **41** (1922), T. 144.

Refractive Index at 20°	1.492 to 1.495
Acid Number	3.6 to 4.4
Ester Number	21.8 to 29.6
Ester Number after Acetylation	189.2 to 198.1
Solubility	Soluble in 1.2 to 1.6 vol. of 70% alcohol

The properties of these three oils differed substantially from those of the oil obtained by Schimmel & Co. (see above), particularly in regard to the optical rotation.

The oils investigated by Joseph and Whitfeild appeared to consist chiefly of *l*-limonene and perillyl alcohol.

OIL OF *ELYONURUS LATIFLORUS* NEES

(Oil of Espartillo)

Elyonurus latiflorus Nees (*Lygeum spartium*), the rush-leaved *Lygeum*, Feather Grass, or Spanish Grass Hemp, occurs in several parts of South America, particularly in Paraguay and Brazil (from Bahia to Rio Grande do Sul, in Minas Geraes, and Goyaz). The plant is probably native to Paraguay, where it grows wild on enormous tracts of land from the Gran Chaco to Asunción. In Paraguay the grass is known by the common name of "Espartillo Guazú." It serves for the pasturing of cattle, particularly at times when drought and intense cold destroy other pasture grasses that grow together with the espartillo.

Spontaneous propagation by seed results in robust plants reaching a height of 0.6 to 1.2 meters. The leaves are cylindrical, filiform, straight, and hard, resembling straw. Whitish flowers, enclosed in sparse ears, produce small fuzzy seeds that are easily scattered by wind. The root consists of a fibrous, thick, very compact crown.

The plant is said to possess medicinal properties, for which reason the leaves are used for the making of infusions that country people drink to cure leprosy.

As in the case of most grasses belonging to the family *Gramineae*, the leaves, stalks, and roots of *Elyonurus latiflorus* contain an essential oil that can be isolated by steam distillation. For practical purposes, however, only the overground parts (leaves and stalks) of the plant are used for distillation. One ton of this material is three to four times more bulky than 1 ton of lemongrass, which fact adds to the expense of haulage and distillation and plays an important role in the cost calculation of the oil. One hectare of a natural espartillo pasture yields approximately 5 tons of stems and leaves. The use of cutting and reaping machines, and field drying, by a system similar to that employed for hay, would greatly reduce the cost of transportation and distillation.

In Paraguay, much of the espartillo grass grows also in scattered patches east of the Paraguay River, from the town of Emboscada near Asunción, up to the Brazilian border. This would seem to be the region most favorable for developing an espartillo oil industry, because a sure and cheap supply of wood and water for distilling is available. Moreover, in the vicinity of Emboscada, there are already a number of petitgrain distilleries which may be used for the processing of espartillo grass.

Tempted by the generally high price level of essential oils prevailing during World War II, and the enormous quantities of plant material available, a few producers in Paraguay started to distill espartillo grass in 1945–1946, and limited quantities of oil were actually produced at that time. The venture, however, suffered from several handicaps; for example, during periods of continued rainfall the roads become almost impassable and the work at the distilleries has to be interrupted. Harvesting and transport of the very bulky plant material are slow, and relatively expensive, the yield of oil low. Moreover, the odor of the oil is not very distinctive. Essential oil houses in the United States encountered considerable difficulty in introducing the oil on the market, and the hopes of the producers in Paraguay were not fulfilled. As a result, interest waned, and production was heavily curtailed.

Yields of oil in ordinary stills ranged from 0.09 to 0.11 per cent. However, yields as high as 0.27 to 0.30 per cent have been obtained at the Villa Hayes and at the Colonia Primavera in Rosario.

Two samples of espartillo oil from Paraguay examined by Fritzsche Brothers, Inc., New York, had these properties:

		II
Specific Gravity at 15°/15°	0.973	0.950
Optical Rotation	−9° 40′	−1° 20′
Refractive Index at 20°	1.5042	1.5017
Acid Number	3.2	. . .
Saponification Number	17.0	17.3
Solubility	Soluble in 0.5 vol. of 90% alcohol; very cloudy in more	Turbid up to 10 vol. of 90% alcohol

Oil (I), produced in Caraguatay, about 85 km. east of Asunción, was of better quality than oil (II).

Shipments of oil of espartillo from Paraguay analyzed by the same firm had properties varying within the following limits:

Specific Gravity at 15°/15°	0.932 to 0.952 (in one case as low as 0.903)
Optical Rotation	−2° 45′ to −5° 24′ (in a few cases dextrorotatory, up to +3° 42′)
Refractive Index at 20°	1.4928 to 1.5042
Acid Number	0.9 to 1.9
Saponification Number	7.1 to 24.1
Ester Number after Acetylation	21 to 51
Aldehyde Content, Calculated as Citronellal (Hydroxylamine Hydrochloride Method)	3.0 to 5.3%
Solubility	Soluble in 0.5 vol. of 90% alcohol, cloudy with more

The odor of the oils resembled that of carrot seed oil, with a spicy, pepper-like by-note.

Nothing is known about the chemical composition of this oil.

OIL OF *ELYONURUS TRIPSACOIDES* H.B. ET K.

Elyonurus tripsacoides H.B. et K., a grass related to the *Andropogon* species, grows widely in Central America.[1] On steam distillation, it yields about 0.1 per cent of a volatile oil with an odor reminiscent of vetiver.

The following properties have been observed:

Specific Gravity	0.976
Optical Rotation	−10° 0′
Ester Number	10.5
Saponification Number after Acetylation	42

The fraction b. 275°–325° contains, as chief constituent, a sesquiterpene; it also contains a phenol (perhaps eugenol).

[1] *Perfumery Essential Oil Record* 4 (1913), 98.

OIL OF VETIVER

Essence de Vétiver *Aceite Esencial Vetiver* *Vetiveröl*
Oleum Andropogonis Muricati

Introduction.—The vetiver grass (*Vetiveria zizanioides* Stapf (*Andropogon muricatus* Retz., *Anatherum zizanioides* [L.] Hitchc. and Chase)) occurs wild, semiwild and cultivated in many tropical and subtropical countries. The underground part of the plant consists of numerous fine rootlets, light yellow or gray to reddish in color, which contain a viscous essential oil of pleasant, persistent odor. The commercial oil of vetiver is obtained by distillation of the root. The root itself possesses a most agreeable aroma, for which reason the dried root is employed to scent linens, clothes, etc., either by itself or in the form of sachets. In the Orient the root has been used extensively since antiquity; it was described in the ancient Veda of the Hindus. From time immemorial the root has also been employed to make baskets, and to weave mats, which, sprinkled with water and hung like curtains in the house, cool the air and emanate a pleasant odor. In Java the root is often used to support the walls of fish ponds and to protect them against collapse. In Haiti (West Indian islands) the natives employ the overground part of the plant, the dried grass, for the thatching of their huts.

In Java the vetiver root is called "Akar wangi," in India "Cus-Cus" or "Khas-Khas," meaning "aromatic root."

In its wild state the plant flourishes on the slopes of the Himalaya Mountains, in many parts of India, Ceylon, and Malaya. Vetiver is cultivated extensively in Java, on Réunion Island, in the Seychelles Islands, and in some parts of the Western Hemisphere—in Louisiana (U.S.A.), and in São Paulo (Brazil), for example. Cultivation experiments (for the distillation of its oil) have been conducted in Honduras, Guatemala, and Mexico. In Haiti (West Indies) the plant escaped cultivation long ago, and now grows semiwild and scattered over wide areas.

The commercial vetiver oil is distilled from root material grown chiefly on plantations, the principal producing regions being Java, Réunion Island, and Haiti. The trade distinguishes the following types of vetiver oil:

1. Oils produced by modern methods in European and North American essential oil distilleries, from dried root material imported from Java. This type of oil is of excellent quality. Prior to World War II about 60 metric tons of vetiver root were exported annually from Java. Assuming that all[1]

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[1] More likely, a good portion of the exported root was employed for sachets, etc.

of the exported root was used for distillation purposes, this quantity corresponds to an approximate annual production of 1,000 kg. of European or American distilled vetiver oil.

2. Oils distilled in Java from domestic root material. Owing to the strict analytical control exercised by the government of Indonesia (formerly the Netherlands East Indies) over all outgoing shipments, this type of oil is also of good quality. Prior to World War II, annual production amounted to about 20 metric tons of oil.

3. Oils distilled on Réunion Island from roots grown locally by small-scale planters, in large part sharecroppers. The oil is usually of excellent quality. Annual export figures have varied considerably (from 5 to 15 metric tons), depending upon competition from the Java type of vetiver oil.

4. Oils distilled chiefly in Haiti (West Indian islands) and to a small extent in Mexico, Central America (Guatemala and Honduras), and South America (State of São Paulo in Brazil). As we shall see below, this type of oil differs somewhat from the other types of vetiver oil; its quality depends upon the age of the root material and the method of distillation. Haiti has been producing the oil, but in limited quantities only. Production, however, could be increased substantially, should demand and market prices warrant it.

At the time of this writing (1949), the type of oil described under (1) is no longer available. Due to the civil strife and guerrilla warfare raging in the interior of Java, vetiver root cannot be exported from Java. Neither is the type of oil described under (2) readily available. Hearsay reports from the interior of Java indicate that the principal (and quite modern) vetiver distillery was destroyed during the occupation by Japanese forces and many of the vetiver plantings have been discontinued in favor of other, more vital, crops. It will be quite some time before normal conditions are restored in Java. Shipments of Java vetiver oils reaching Europe and the United States at present, represent, in the main, old stocks accumulated here and there during the Japanese occupation. The following monograph on Java vetiver is, therefore, based chiefly upon conditions prevailing in Java prior to the outbreak of World War II, when the author had occasion to visit the island and survey the vetiver producing regions. Undoubtedly the Java oil will again be offered in large quantities, when conditions on the island become normal.

As far as the American vetiver oil industry is concerned, it came into existence during the years of World War II, when the Java and Réunion oils were no longer available, and when very high prices encouraged the production of vetiver oil in certain parts of the Western Hemisphere. However, some of the new plantations were started without previous experience, and in soils not suitable for vetiver. The result was a very low yield of oil, and therefore an excessively high price. Potential production in the Western Hemisphere is large, but future developments will depend entirely upon the availability of the Java and Réunion oils (which are the most important types), and the price the oil brings on the world market. It should also be remembered that the use and consumption of vetiver oil are rather limited, and any overproduction will only cause ruinous competition. Moreover, vetiver root is difficult to distill, giving a great deal of trouble in the separation of the oil from the water, and the yield of oil in general is low. Therefore, any prospective grower of vetiver should first ascertain, by systematic distillation experiments, whether his root material will yield sufficient oil to make commercial exploitation worth-while. The vetiver root grown in Louisiana (U.S.A.), for example, does not contain sufficient oil to permit distillation on a competitive basis. The Louisiana root is therefore sold as dried root, in small bundles, for the scenting of linen in drawers and closets.

An English controlled company in the interior of the State of São Paulo (Brazil), during World War II, began extensive cultivation of the root on its vast properties (mostly coffee plantations), but it is doubtful if this potentially large vetiver industry can survive, once competition from Java is felt again.

Oil of Vetiver Java

Development.—Before World War I, Java exported large quantities of dried vetiver root to Europe, chiefly to Germany, France, and England, where the root was used either for the distillation of its oil, or in the form of sachets, for the scenting of closets, drawers, and chests. The year of 1917, however, brought about such a shortage in shipping space that much root material accumulated in the ports of Java. Since the warehouses were filled to capacity, this material could not even be properly stored. It was principally as a result of this situation that Hischmann [2] conceived the idea of distilling the root material on the spot and of exporting the less bulky oil. Preliminary distillation experiments convinced Hischmann that the root should be distilled with direct steam, and a substantial quantity of the accumulated stocks were then processed in a distillery near Bandoeng. Owing to the fact that the root had already been stored and aged for almost two years, an oil of high specific gravity and very good quality was obtained. It found ready acceptance in Europe and America, and thus Java's vetiver oil industry came into being. Despite occasional setbacks the industry grew, and in 1935 Java surpassed Réunion Island in quantity of vetiver oil exported.

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[2] Interview with Dr. A. Hischmann, Batavia, in 1939.

Producing Regions.—Java's main vetiver producing regions are near Garoet (western Java) and Wonosobo (central Java). Practically all of the root originates from scattered patch plantings and from small holdings, ranging from one-quarter of an acre to twenty acres in rare cases. The production of the root has always been in the hands of natives, few white planters growing vetiver on their estates.

Soil Conditions.—The most suitable soil for the successful growing of vetiver consists of loose sandy ground, or, even better, young volcanic ashes on the slopes of hills. The root can easily be pulled from such soils without parts of the thin rootlets adhering to the ground and being lost. Compact, heavy, loamy soil should be avoided, not only because the root cannot be pulled out readily, but also because root grown in such soil gives a lower yield of oil. Harvesting from heavy soils is a problem. If the root is planted in proper soil, the altitude does not matter. Young volcanic soils, however, do not occur in the plains of Java, but only on the slopes of volcanoes, usually at about 5,000 ft. above sea level.

Good export root is often characterized by the presence of small, black cinders.

Planting.—"Akar wangi," the vetiver plant of Java, is a nonflowering variety of *Andropogon muricatus* Retz.

According to experiments carried out in Buitenzorg,[3] vetiver should not be planted in shaded places, as shade will exert an unfavorable influence upon the development of the root system. Regular cutting of the grass seems to benefit the root.

As on Réunion Island (cf. the monograph on "Vetiver Oil Réunion"), vetiver is planted by root division. The planting takes place in the rainy season. Distance between the plants should be 2 to 3 ft., but, due to local conditions, is frequently irregular. The ground used in Java for the planting of vetiver seldom lends itself to the raising of other crops. It is not always possible to replant vetiver on the same field.

One hectare yields about 1,000 kg. of air-dried root, the quantity, of course, depending upon the soil and the general condition of the planting. Occasionally root fungus (the nature of which has not yet been established) damages the plants and lowers the yield of root.

Harvest.—The harvesting period depends upon the weather. If the same field is to be replanted with vetiver, the roots can be extracted from the ground only during the rainy season, because the root stocks have to be divided and replanted immediately. However, if the field is to be used for some other crop, harvesting of the root will be more convenient during the dry season, not only because the earth can be shaken off the extracted root

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[3] *Jaarboek van het Departement van Landbouw, Nijverheid en Handel in Nederlandsch-Indië* (Batavia 1910), 48.

more easily, but also because the root will dry more quickly. Distillers prefer to purchase dry root material, to avoid any argument with the supplier over weight and water content. The collected root is first washed in a river or fountain, and then dried in the sun, or preferably in the shade.

If intended for local distillation, the dried root is packed loosely; if intended for export, it is pressed into bales of 100 kg. and wrapped in jute bags.

The native growers sell their crop to middlemen, usually Chinese, from whom they have received advance payments. The middlemen, in turn, sell the root to local distillers or to exporters in Batavia and Surabaya.

Quality of the Root.—If a fully developed root system and a high quality of oil are desired, the root should not be extracted from the ground earlier than twenty-four months after planting. Young roots are tender, thin, almost hair-like; on pulling they break easily and stay in the ground. Furthermore, on distillation they yield an essential oil with a low specific gravity and low optical rotation. The odor of these "light" oils is "green," "earthy." Older, more developed, somewhat thicker root, on the other hand, yields an oil of better quality; its specific gravity and optical rotation are higher, the odor fuller, richer, more lasting. Oils derived from older root are usually of darker color than the oils distilled from younger root.

However, for obvious reasons, it is difficult to induce the natives to wait twenty-four months before harvesting the root. Always in need of cash, they are inclined to collect the root as early as eight months after planting; at any rate they expect at least a yearly crop from their vetiver fields.

Any experienced distiller will carefully examine a lot of root material before paying for it. Some "smart" natives or middlemen occasionally admix root that has previously served for mats or other purposes or has already been exhausted by steam distillation. A good quality of root, giving a high yield of oil, can usually be recognized by its slightly reddish-brown color. Very light, almost whitish root as a rule contains very little essential oil.

Distillation.—Prior to World War II, there were in Java several vetiver oil distillers, a few of them Europeans, the others Chinese and Malayan. Two of the distilleries were of large size and equipped with efficient, specially designed stills and oil separators. The vetiver distilleries owned by the natives were not quite so advanced. A few producers used their citronella stills for the distillation of vetiver, which explains why some lots of vetiver oil received abroad were contaminated by a slight by-odor of citronella.

Because of the high boiling points of its chief volatile constituents, and their high viscosity, the distillation of vetiver root is beset with considerable difficulties, particularly in regard to the separation of the oil from the distillation water.

Prior to distillation, the dried root material should be reduced to small pieces in a solidly constructed ensilage cutter. To prevent formation of dust, annoying to the workers, the root is first wetted by sprinkling with water.

Distillation is carried out with live steam of 4 to 5 atmospheres pressure (measured in the separate steam boiler). The stills should be well insulated, to prevent internal condensation and excessive wetting of the plant charge during the long hours of distillation. Depending upon the pressure and amount of steam injected, distillation of one charge requires 12 to 36 hr.

The oil distills over first as a fraction lighter-than-water, and toward the end of distillation as a fraction heavier-than-water. For a time the distillate may run in the form of a whitish, milk-like emulsion which has to be separated (1) by regulating (modifying) the temperature of the water in the condenser, and (2) by using proper oil separators. (For details the reader should consult Vol. I of this work, pp. 137 and 139.) Some distillers in Java employ a series of large tanks as oil separators. At the bottom of each tank is a narrow, tube-like pocket in which the fraction heavier-than-water collects and from which it can be drawn off. The combined fractions of the oil are finally filtered warm in steam-jacketed filters; some producers use small centrifuges for the purpose.

Yield of Oil.—Dried Java vetiver root of good quality yields from 1.5 to 2 per cent, in rare cases as much as 3 per cent, essential oil. Fresh (undried) root, of course, gives a much smaller yield.

Quality of the Oil.—The quality of vetiver oil depends not only upon the age of the root (see above), but also upon the length of distillation. The most valuable constituents of the oil, and most important in regard to odor, are high boiling and can be recovered only by prolonged distillation, which, obviously, means more steam consumption and a higher cost. By the use of slightly superheated steam toward the end of distillation, the hours of distillation may be shortened.

In order to produce vetiver oils of good quality the leading distilleries in Java, prior to World War II, stored their root material for about six months before they processed it, and extended distillation to almost 36 hr. Such oils are quite dark in color, rather viscous, and possess a high specific gravity and optical rotation. The odor of these "heavy" oils is full, rich, and very lasting, quite superior to that of the "light" oils obtained either from young roots or by short distillation.

On aging, the odor of vetiver oil, in general, improves, freshly distilled oils exhibiting a somewhat "green" odor.

The oil is usually shipped in galvanized iron drums of 25, 50, or 100 kg. capacity. In normal times every shipment of Java vetiver oil must first be examined in the government laboratories of Buitenzorg before a certificate of purity is granted to the exporter.

Total Production.—During the last ten years (exclusive of the time when Java was occupied by Japanese forces) the following quantities of vetiver oil in metric tons and gross weight were exported from Java:[4]

1939	34
1940	29
1941	23
1947	2
1948	1

Physicochemical Properties.—Four genuine samples of vetiver oil procured by the author while in Java had the following properties:

	I	*II*	*III*	*IV*
Specific Gravity at 15°	1.009	1.009	1.007	0.991
Optical Rotation	+31° 36′	Too dark	+30° 48′	Too dark
Refractive Index at 20°	1.5260	1.5271	1.5260	1.5258
Acid Number	31.1	32.5	30.2	12.5
Ester Number	2.0	12.6	1.0	4.0
Ester Number after Acetylation	141.5	150	152.1	129
Solubility at 20° in 80% Alcohol	Soluble in 1 vol.; cloudy in 2 vol. and more	Not clearly soluble; but soluble in 0.5 vol. of 90% alcohol and more	Soluble in 1.5 vol.; turbid in 3.5 vol. and more	Very cloudy in 10 vol.

Sample IV was inferior to the other oils in regard to odor as well as to properties.

According to Koolhaas and Rowaan[5] (Buitenzorg Government Laboratories) the properties of Java oil vary within these limits:

Specific Gravity at 15°	0.985 to 1.045
Optical Rotation (10 mm. tube)	+15° 0′ to +45° 0′
Refractive Index at 20°	1.510 to 1.530
Acid Number	8 to 35
Ester Number	5 to 25
Ester Number after Acetylation	100 to 150
Solubility in 90% Alcohol	Soluble in 1 to 10 vol.

Shipments of Java vetiver oil received and examined by Fritzsche Brothers, Inc., New York, had properties which varied within the following limits:

Specific Gravity at 15°/15°	1.002 to 1.003
Optical Rotation	+24° 20′ to +31° 4′

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[4] Courtesy of Dr. J. A. Nijholt, Laboratorium Voor Scheikundig Onderzoek, Buitenzorg, Java.

[5] *Parfums France* **15** (1937), 245, and private communication by Dr. D. R. Koolhaas

Refractive Index at 20°	1.5259 to 1.5260
Acid Number	20 to 33
Ester Number	5.6 to 7.5
Ester Number after Acetylation	137.2 to 140.0
Solubility	Soluble in 0.5 vol. and more of 90% alcohol

Gildemeister and Hoffmann[6] distinguished between commercial Java oils of good quality (I), and the so-called "light" oils from Java (II):

	I	*II*
Specific Gravity at 15°	0.9926–1.0444	0.9852–1.0015
Optical Rotation	+20° 30′ to +46° 0′	+14° 25′ to +24° 10′
Refractive Index at 20°	1.51889–1.53060	1.52236–1.52612
Acid Number	8.4–40.1	7.5–14.9; in one case 27.1
Ester Number	5.6–24.6; in one case 2.8	6.5–14.9
Ester Number after Acetylation	103.7–151.2	98–119.5
Solubility in 80% Alcohol	Soluble in 1 to 2 vol.; occasionally opalescent to turbid with more alcohol	Not clearly soluble. Clearly miscible with 90% alcohol; in exceptional cases opalescent on dilution

EUROPEAN-DISTILLED VETIVER OIL

As was pointed out in the introduction, substantial quantities of baled vetiver root were at one time exported from Java and processed for the recovery of oil in the well-equipped distilleries of Europe. It should be mentioned that, due to shipping difficulties, Réunion Island never exported vetiver root as such. All European-distilled vetiver oils therefore originated from imported Java root.

Vetiver oils distilled under the author's supervision in Southern France had these properties:

Specific Gravity at 15°	1.010 to 1.030
Optical Rotation	+28° 0′ to +40° 0′; usually +33° 0′ to +38° 0′
Refractive Index at 20°	1.5230 to 1.5270
Acid Number	20 to 33
Ester Number	6 to 10
Ester Number after Acetylation	145 to 170
Solubility in 80% Alcohol, at 20°	Usually soluble in 0.5 to 1 vol.; occasionally opalescent and slightly turbid on addition of more alcohol

Owing to the modern apparatus and methods of distillation applied, these oils were of very high quality.

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[6] "Die Ätherischen Öle," 3d Ed., Vol. II, 329.

The cost of transport of the root from Java, however, added substantially to the price of these oils, which could, therefore, be used only in high quality perfumes.

Gildemeister and Hoffmann [7] recorded the following properties of oils distilled in Germany by Schimmel & Co.:

Specific Gravity at 15°	1.013 to 1.040
Optical Rotation	+25° 0′ to +41° 0′
Refractive Index at 20°	1.522 to 1.528
Acid Number	27 to 75
Ester Number	8.4 to 23
Ester Number after Acetylation	120 to 173
Solubility in 80% Alcohol	Soluble in 1 to 2 vol.; occasionally opalescent to turbid on addition of more alcohol

OIL OF VETIVER RÉUNION

For years the oil of vetiver produced on the island of Réunion (located in the Indian Ocean, 400 miles east of Madagascar) has been noted for its good quality, a result of the care applied to the root material prior to distillation. The odor as well as the physicochemical properties of a vetiver oil depend greatly upon the age of the root, i.e., the time which elapses between planting and harvesting.

Producing Regions.—The growing and producing regions on Réunion are located in the southern, eastern, and extreme southeastern parts of the island, the most important centers being La Petite Île (in the southeast), Montvert (in the south), and Les Lianes (in the east).

These are mountainous sections of Réunion and abound with water, drawn from nearby springs or rivulets. This fact is important, as the distillation of vetiver root requires a great amount of water. Stills on Réunion are supplied with water by a system of simple bamboo tubes.

The plantings are located on the slopes of hills and mountains, above sea level, but well below altitudes at which geranium is grown.

Economic Setup.—The bulk of the oil is produced by settlers of French descent, who own large or medium sized tracts of land. With the help of employed labor they grow the crop and distill the root material in their own stills. Often, however, the root is grown by sharecroppers and delivered to the landlord for distillation.

The annual production of vetiver is influenced by several economic factors: (1) the price of the oil on the world market which depends upon competition (chiefly from the Java oil); (2) the cost of labor, which is governed entirely by the social laws of France; (3) the price of sugar.

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[7] *Ibid.*

Since cane sugar and vetiver are grown on the same type of soil on Réunion Island, and at about the same altitudes, the two crops compete with one another, and obviously the planters are inclined to give preference to the more remunerative crop. Most of the sugar produced on Réunion, however, goes to France, where, after the leveling of a very high import duty, it has to compete with beet sugar, which crop fluctuates widely in France.

Planting, Cultivating, and Harvesting.—Most vetiver plantings on Réunion Island are small, patchlike, and widely scattered. The best soil consists of loose volcanic ashes, since the roots can be pulled easily from such soil, and without any portion of the fine roots remaining underground. Vetiver root grown on such soil can be cleaned quickly by simply shaking any adhering soil particles off the extracted root.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 17. Vetiver oil production on Réunion Island. View of harvested root material and freshly replanted root segments.

Whenever a new planting is started, fertilizer is applied in the form of ashes of residual vetiver root, which has been distilled and used as fuel.

A new field is started on the same ground, immediately after, in fact simultaneously with the extraction of the old roots. Harvesting and planting take place from June to November. The leaves and stalks of the old plants are cut with machetes, and the entire root system is pulled out of the ground by hand. The lower, fibrous parts of the root are cut off, and the remaining center parts of the root stocks (stools) are divided for replanting. The root segments are then planted out, 1 ft. apart, in rows also 1 ft. apart. The plants should be so close together that the roots, after growing, touch one another underground. This will facilitate extraction of the ensuing root crop.

Quality and Age of the Root.—The quality and the age (i.e., the length of time between planting and harvesting) of the root are of fundamental importance, and greatly influence the yield, physicochemical properties, and odor of the oil.

In poor soil the root will develop very little oil; hence the necessity of frequent manuring and fertilizing. After one year in the ground the root contains sufficient essential oil, but the oil will be of substandard quality. After two years in the ground, the root yields a little less essential oil, but the oil will be of excellent quality. Three-year-old root yields so little oil that distillation becomes uneconomical. It is questionable whether the content of oil actually decreases as the root stays in the ground. More likely the oil contained in old root is composed chiefly of high boiling constituents (sesquiterpene alcohols) which do not readily distill over, particularly in the low-pressure type of stills (water *and* steam distillation) used on Réunion Island.

Obviously, then, the best distillation material is two-year-old root, and the distiller-producers insist upon such root when purchasing from sharecroppers. The latter, however, are usually in need of cash, and like to reap a yearly crop from their fields. Producers, who have to depend for part of their root requirements upon other growers or sharecroppers, are, therefore, very careful in their selection of material, preferring to buy it from their neighbors, with whose fields they are well acquainted. Good root can be distinguished by very fine black rings, whereas superannuated root (yielding very little oil) possesses a dead, gray-brown color.

Distillation.—The root material grown on Réunion is not exported, but processed locally, in a number of rather primitive stills sheltered under simple roofs, or in wooden shacks, and distributed over the producing regions. The stills operate on the principle of water *and* steam distillation (cf. Vol. I of this work, pp. 120 and 147). Frequently, however, the water rises above the false bottom (usually made of wood) and immerses part of the charge, causing excessive wetting, which means that longer distillation is required.

Many stills are of relatively large capacity, one charge consisting of 300 to 400 kg. of root material, after it has been dried in the sun for one or two days. The water below the false bottom is brought to the boiling point with a fire kindled with wood or exhausted vetiver root.

Distillation of one charge requires 36, or sometimes even 48 hr. Whenever the cost of wood is high, and the price of vetiver oil relatively low, some producers are tempted to shorten the distillation, to the detriment of the quality of the oil (cf. the section on "Distillation" in the monograph on "Oil of Vetiver Java").

Since the larger landowners and producers cannot personally supervise distillation for 36 to 48 hr., the Florentine flasks and oil receivers are sometimes enclosed in a special compartment of which the owner alone has the key. This protects against theft of oil by the laborers who, during the night, must watch distillation, regulate the temperature of the condensers, and keep the fire burning.

In view of the difficulties connected with the distillation of vetiver, the visitor to Réunion is inclined to wonder how the distillers can produce such a good grade of oil with their primitive equipment. It is simply a matter of "know-how," acquired through many years of experience. No facilities for the automatic reflux of the distillation waters (cohobation) existing, the distillation waters are collected in barrels and used again (instead of fresh water) for the next charge. To prevent the flow of the distillate in the form of troublesome emulsions, the water inlet to the condenser is regulated so that the distillate (condensate) runs quite warm. Moreover, fuel will be saved if the warm distillation water is used again for a new batch of root in another still.

While practically all oil of vetiver in Réunion is produced in primitive direct-fire stills, there are on the island two steam distilleries—one in St. Paul, Piton, and the other one in nearby St. Paul, Grand Pourpier—which in years past produced limited quantities of vetiver oil by steam distillation. These oils, therefore, resembled the higher type of vetiver oil distilled in Europe and America from imported root material.

The process applied in the two plants in St. Paul is, in reality, a combined form of direct steam, and water *and* steam distillation. The root material is charged above a false bottom, and direct steam is injected through a steam coil. The distillation water is returned warm into the still, i.e., cohobated. When the water in the still reaches a certain level above the false bottom, the direct steam is turned off, and distillation is continued by indirect steam (steam jacket). Here, too, the distillation water is automatically cohobated. The proper quantity of water in the still and a warm flow of the distillate are of great importance for successful distillation. Distillation of one batch requires 24 hr., 15 of which are for actual distillation. Due to relatively high cost of labor and fuel, the two distilleries in St. Paul in 1935 discontinued production of vetiver oil, other products, such as cane sugar and rum, being more remunerative.

The small lots of oil produced in the various distillation posts are purchased by field brokers and sold to exporters in St. Denis, who first have to filter the oil and free it of small quantities of water. Combined lots are analyzed in the official control laboratory in St. Denis and then shipped abroad.

Yield of Oil.—As was pointed out in the section on "Quality and Age of the Root," the yield of oil depends upon the age of the root material. Two-year-old root of best quality, distilled for 36 hr. in the primitive type of still used in Réunion, yields from 0.8 to 1 per cent of oil. The same root material, if processed in modern steam stills, may yield 1.5 to 2 per cent.

In general, the yield of vetiver root oil in Réunion ranges from 0.6 to 1.2 per cent.

Physicochemical Properties.—Oils distilled from young (about one year old) roots exhibit a low specific gravity, a low optical rotation (α_D +13° to +17°), and a poor solubility, a result, probably, of the predominance of terpenes and sesquiterpenes, rather than of sesquiterpene alcohols (cf. "Chemical Composition of Vetiver Oil"). The odor of the oils distilled from young roots is "green," "earthy," and slightly harsh. Prior to World War II the government of the island, in collaboration with the Chamber of Commerce in St. Denis, enacted a ruling by which such oils, when exported, must be marked "substandard in regard to specific gravity" or "substandard in regard to optical rotation."

Old root (two years old or more) yields oils exhibiting a higher specific gravity, a higher optical rotation (+19° to +23°), and a better solubility than the above-named oils. The odor is smooth, rich, and lasting.

According to Bénard,[8] the properties of vetiver oils distilled in Réunion vary within the following limits:

Specific Gravity at 15°	0.990 to 1.000
Optical Rotation	+17° 0′ to +28° 0′
Saponification Number	14 to 20

Gildemeister and Hoffmann [9] reported these properties for Réunion vetiver oils:

Specific Gravity at 15°	0.990 to 1.020
Optical Rotation	+14° 0′ to +37° 0′
Refractive Index at 20°	1.515 to 1.529
Acid Number	4.5 to 17
Ester Number	5 to 20
Ester Number after Acetylation	119 to 145
Solubility	Soluble in 1 to 2 vol. of 80% alcohol, occasionally with opalescence to turbidity

Shipments of genuine Réunion vetiver oils received and analyzed by Fritzsche Brothers, Inc., New York, had properties varying within the following limits:

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[8] Interview with Mr. René Bénard, former Government Chemist in St. Denis, Réunion.

[9] "Die Ätherischen Öle," 3d Ed., Vol. II, 329.

Specific Gravity at 15°/15°	0.990 to 1.000
Optical Rotation	+15° 12′ to +23° 20′ (shipments of vetiver oil from Réunion Island reaching the United States right after World War II exhibited optical rotations as low as +11° 48′. The quality of these oils was not up to standard)
Refractive Index at 20°	1.5202 to 1.5262
Acid Number	5.6 to 8.4
Ester Number	2.3 to 8.7
Ester Number after Acetylation	122.4 to 134.5
Solubility	Usually soluble in 1.5 vol. and more of 80% alcohol, occasionally turbid in 1.5 to 2 vol. and more of 80% alcohol. Oils with low optical rotations are usually soluble only in 90% alcohol (soluble in 0.5 vol. of 90% alcohol, opalescent in 10 vol.)

In some cases shipments of Réunion vetiver oil gave a positive test for the presence of dimethyl sulfide.

A sample of oil, distilled in Réunion under the author's supervision, had the following properties:

Specific Gravity at 15°	0.997
Optical Rotation	+23° 20′
Refractive Index at 20°	1.5241
Acid Number	8.0
Ester Number	6.0
Ester Number after Acetylation	131.6
Solubility at 20°	Soluble in 1.5 to 2 vol. of 80% alcohol; opalescent with more

Oils of vetiver distilled by the author in France from imported Java root material, and in modern steam stills, had specific gravities above 1.000 (at 15°), and optical rotations ranging from +33° to +40° which properties illustrate the superior quality of the oils produced in efficient equipment. Unfortunately the long transport of the baled root overseas increases the cost of these oils unreasonably (cf. "Oil of Vetiver Java").

As mentioned previously, Réunion vetiver oils of highest quality exhibit an optical rotation of not less than +19°.

Adulteration.—Vetiver oils imported from Réunion are usually pure, because the producers and exporters in Réunion are not familiar with the methods of "skillful" adulteration. Moreover, Réunion is a small island, and imports of any products which could be used for the purpose of essential oil adulteration would at once arouse the suspicion of the custom authorities.

Dishonest field brokers and Chinese middlemen occasionally resort to alcohol, kerosene, or fatty oils as adulterants, but such additions are readily detected in the official control laboratory in St. Denis, which examines every outgoing shipment.

Total Production.—Prior to World War II, annual production of vetiver oil in Réunion varied from 5 to 12 metric tons, depending chiefly upon the competition and the price of the Java oil. During World War II competition with Java was eliminated, and prices of the Réunion oil rose sharply. In December 1945, prices were as high as $75.00 per kg. of oil. In the same year Réunion produced about 15 tons of oil. The future development of the industry will depend upon the reappearance of the Java oil on the world market.

CHEMICAL COMPOSITION OF VETIVER OIL

The first investigations of the chemical composition of this important oil date back to the beginning of the twentieth century, when Theulier[10] fractionated vetiver oils distilled in Grasse (A. M.), France, and on the Island of Réunion, and studied the physicochemical properties of the fractions (b_{25}) thus obtained. Other investigations were carried out by Franz Fritzsche & Co.,[11] Genvresse and Langlois,[12] and Semmler, Risse and Schröter.[13] However, in the light of the latest findings mentioned below, the conclusions reached by these authors cannot be fully accepted.

Research on the chemical composition of this oil has been beset with considerable difficulties; and it is only lately that we have obtained a better, although still incomplete, insight into this complicated subject.

Up to the present the following constituents have been identified in vetiver oil:

α- and β-Vetivone (Vetiverone). According to Pfau and Plattner,[14] Java and Réunion vetiver oils contain from 7.8 to 35.1 per cent (in most cases from 15 to 27 per cent) of ketones, determined by the hydroxylamine method. By oximation, Sabetay and Trabaud[15] estimated a ketone content ranging from 12 to 13 per cent. The odor of vetiver oil is due chiefly to the ketonic sesquiterpenes $C_{15}H_{22}O$ (bicyclic and α-ethylenic), of which only α-vetivone and β-vetivone have so far been isolated.

For details pertaining to these apparently stereoisomeric substances, see Vol. II of this work, p. 454.[16]

Vetivenols (Vetiverols). The alcohols occurring in vetiver oil were investigated first by Franz Fritzsche & Co.,[17] later by Genvresse and Langlois,[18] but in both instances with inconclusive results.

According to our present knowledge, at least 60 per cent of the sesquiterpene alcohols occurring in Java vetiver oil seem to consist of a mixture of primary alcohols $C_{15}H_{24}O$, in which a tricyclic alcohol largely predominates, whereas the

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[10] *Bull. soc. chim.* [3], **25** (1901), 454.

[11] German Patent No. 142514, (1902).

[12] *Compt. rend.* **135** (1902), 1059.

[13] *Ber.* **45** (1912), 2347.

[14] *Helv. Chim. Acta* **22** (1939), 640.

[15] *Bull. soc. chim.* [5], **6** (1939), 740.

[16] The reader is also referred to the controversy, re vetivone and vetiverone, between Naves [*Helv. Chim. Acta* **25** (1942), 698], and Sabetay and Trabaud [*Helv. Chim. Acta* **25** (1942), 1187. *Bull. soc. chim.* **9** (1942), 152].

[17] German Patent No. 142416, (1902).

[18] *Compt. rend.* **135** (1902), 1059.

bicyclic alcohols amount to only about 10 per cent of the mixture of primary sesquiterpene alcohols.

The tertiary (bicyclic) sesquiterpene alcohols present in Java vetiver oil also seem to be a mixture. They amount to about one-third of the total sesquiterpene alcohol fraction of the oil.

Réunion vetiver oil contains a similar mixture of sesquiterpene alcohols $C_{15}H_{24}O$, which consists of a primary bicyclic alcohol and a tertiary tricyclic alcohol.

For details pertaining to these vetivenols see Vol. II of this work, p. 281.

Depending upon their origin and quality, vetiver oils contain from 45 to 65 per cent of free sesquiterpene alcohols (observations in the laboratories of Fritzsche Brothers, Inc., New York).

Vetivenyl Vetivenate. In the fraction $b_{0.3}$ 170°–250° of vetiver oil, Ruzicka, Capato and Huyser [19] observed an ester which, on saponification with a 10 per cent alcoholic potassium hydroxide solution, yielded the tricyclic vetivenic acid, $C_{15}H_{22}O_2$, a viscous oil, d_4^{20} 1.0748, n_D^{20} 1.5203. Treating the neutral saponification products with phthalic anhydride, these authors obtained a primary tricyclic sesquiterpene alcohol $C_{15}H_{24}O$, b_{12} 160°–162°, d_4^{15} 1.0186, n_D^{15} 1.5251.

Vetivenic acid had previously been observed in vetiver oil by Semmler, Risse and Schröter,[20] and before them by Genvresse and Langlois,[21] and by Bacon.[22] The proper empirical molecular formula $C_{15}H_{22}O_2$ was established by Semmler and collaborators. Genvresse and Langlois expressed the opinion that the characteristic odor of vetiver oil is due to the ester which vetivenic acid forms with vetivenol. The ester readily hydrolyzes, even under the influence of water.

Palmitic Acid. In a vetiver oil which for a period of time had been stored in a tin-lined vessel, Schimmel & Co.[23] observed the crystalline zinc salt of palmitic acid, which permits the conclusion that this acid is a constituent of vetiver oil.

Benzoic Acid. Bacon [24] reported the presence, in a sample of vetiver oil, of considerable quantities of benzoic acid.

Vetivene. Years ago Genvresse and Langlois [25] observed the occurrence of a sesquiterpene $C_{15}H_{24}$

b_{740}	262°–263°
b_{15}	135°
d_{20}	0.932
α_D	+18° 19′

which absorbed four atoms of bromine, thereby turning blue, without, however, solidifying.

The sesquiterpene $C_{15}H_{24}$ which Genvresse and Langlois named vetivene, was a colorless and odorless liquid.

OIL OF VETIVER HAITI

Chief producer of vetiver oil in the West Indies is the small republic of Haiti, part of the historical island of Hispaniola where Columbus established his first settlement in the New World.

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[19] *Rec. trav. chim.* **47** (1928), 370.

[20] *Ber.* **45** (1912), 2347.

[21] *Compt. rend.* **135** (1902), 1059.

[22] *Philippine J. Sci.* **4** (1909), A. 118.

[23] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 331.

[24] *Philippine J. Sci.* **4** (1908), A. 118.

[25] *Compt. rend.* **135** (1902), 1059.

Nothing is known about the introduction of vetiver to Haiti, but the root has been grown there for a long time. The plant has escaped cultivation and now grows wild and semiwild over wide areas of the island. It was formerly planted along roadsides and on the edges of fields. For generations the dried leaves (grassy part) have been used by the natives for the thatching of their huts, little attention being paid to the roots, except that occasionally they have been sold in the towns for the scenting of linen or as insect repellents. Most of the root material was allowed to remain in the ground, with the result that much of that collected today for oil distillation originates from very old plants. (As was explained in the monographs on "Oil of Vetiver Java" and "Oil of Vetiver Réunion," the age of the root material exerts a considerable influence upon the quality of the oil.) Recently the importance of vetiver for soil conservation has been recognized in Haiti, and today vetiver is planted extensively as a protection against soil erosion. It is estimated that about 4,000 acres are now under cultivation on the island. Of these, about 600 acres have been planted on large fields for the special purpose of oil production, particularly on the small island of Île à Vaches and in the Plaine des Cayes. Small peasant plantings are located in Kenscoff, Dondon, Plaisance, Limbé, La Vallée de Jacmel, Bainet, Dame-Marie, and Chambellan. At St. Michel de l'Attalaye small planting experiments are being conducted in heavy black soil.

Vetiver is planted by division of the root stocks (stools), from which three to six new plants can be obtained, depending upon the age of the old stock. The plants are set out 2 to 3 ft. apart. The most favorable time for planting is in the spring, i.e., in the rainy season.

The root material is extracted from the ground, usually in the rainy season, at which time the earth is softer than in the dry season. Harvesting of the roots is a tedious task, particularly in heavy clay. The roots are dried in the shade, sun-drying causing some loss of oil. Only the slender and fibrous parts of the root system are distilled. They are not triturated prior to distillation.

Distillation is carried out chiefly in two well-equipped distilleries, one located in Maniche, the other in Ducis (Aux Cayes, in the southern part of Haiti). Care must be exercised not to pack the charge in the stills too tightly. Distillation of one charge lasts from 36 to 72 hr. The older the root material, the longer it has to be distilled. Young roots are exhausted after 12 to 16 hr., but they yield an oil of low specific gravity and "green" or "earthy" odor. The heavy fractions of the oil are collected in large separating vats, arranged in sequence, to allow emulsified oil to separate at the bottom. After completion of the distillation, the lighter-than-water and heavier-than-water fractions are mixed and run through a centrifuge, to remove traces of water. After having been freed of water, the oil is once more centrifuged; traces of sediments are retained in the clarifying bowl.

The final limpid oil exhibits a color ranging from light amber to almost black. The color depends upon the material of which the stills are constructed, and, according to Dejoie,[26] upon the iron content of the soil in which the plants have been grown. As was pointed out in the monographs on Java and Réunion Vetiver Oils, only roots of a certain age develop the full fragrance of a high-grade vetiver oil, but such roots give a low yield of oil. Plants less than two years old should never be distilled.

As regards the yield of oil, experiments conducted by Dejoie[27] in Aux Cayes indicate that fertility of the soil is the principal factor in successful vetiver oil production. The richer the soil, the higher will be the yield of oil per ton of root material. Vetiver grown in sandy seashore land does not yield more than 0.5 per cent of oil, notwithstanding the size of the leafy over-ground part of the plant. (There is no relation between the size of the leaves and the content of oil in the roots.)

In general, the yield of oil varies from 1 to 1.5 per cent. In roots from very rich soil it may occasionally reach 2 per cent; but in Haiti such fertile soils are usually planted with sugar cane or other staple food crops. Only the poorest (and particularly the eroded) sections are planted with vetiver. In consequence, root material collected from mountainous sections usually yields less oil than root from the plains. However, the quality of the former is often better, the oil possessing a higher specific gravity and a fuller, more lasting odor.

The potential production of vetiver oil in Haiti is very large. Only the recent low prices of vetiver oil (1949) prevent the extension of the plantings. At the present time in point of fact only one distillery is in operation—and only long enough to fill orders for one or two drums of oil.

The development of Haiti's vetiver oil industry can be judged from the following figures:

Fiscal Year	*Quantity of Oil in Kilograms*
1943–1944	1,229
1944–1945	3,518
1945–1946	7,658
1946–1947	9,686
1947–1948	2,048
1948–1949	9,638

The vetiver oil produced in Haiti differs from those produced in Java and Réunion in regard to odor, physicochemical properties, and chemical composition. The Haitian oil is of very good quality; it has a high content of vetiverol, the principal constituent of all vetiver oils. For this reason the

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[26] Private communication of Senator Louis Dejoie, Port-au-Prince, Haiti, 1949.

[27] *Ibid.*

oil seems to be particularly useful as a starting material for the isolation of vetiverol and its conversion to vetiveryl acetate. The odor of the Haitian oil is rich, full, and lasting; its color usually dark. The properties characteristic of the Haitian oil are probably attributable to the unusual length of time the root has been permitted to remain in the ground (see above).

The odor of the Haitian oil being somewhat different from that of the other types, the Haitian product cannot always replace the Java and Réunion oils in established perfume formulas. Preliminary experiments ought to be made whenever such a change is contemplated. In the author's opinion the Haiti oil should be marketed as a separate and distinct type of vetiver oil, the label indicating its origin.

Several lots of Haiti vetiver oil examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.999 to 1.014
Optical Rotation	+22° 0′ to +31° 44′
Refractive Index at 20°	1.5198 to 1.5250
Acid Number	7.5 to 16.8
Ester Number	8.4 to 52.3
Ester Number after Acetylation	124.0 to 164.0
Solubility	Soluble in 0.5 vol. of 90% alcohol, sometimes cloudy upon further dilution. Occasionally soluble in 1 vol. of 80% alcohol

The physicochemical properties given above must be accepted tentatively because they are based on a limited number of analyses.

OIL OF VETIVER HONDURAS

During World War II, Honduras (C. A.) started to produce limited quantities of vetiver oil. Two samples examined by Fritzsche Brothers, Inc., New York, had the following properties:

	I	*II*
Specific Gravity at 15°/15°	1.002	1.058
Optical Rotation	Too dark	...
Refractive Index at 20°	1.5242	1.5270
Acid Number	8.1	39.2
Ester Number	9.4	17.2
Ester Number after Acetylation	133.2	162.3
Solubility	Soluble in 0.5 and more volumes of 90% alcohol	

OIL OF VETIVER DOMINICA (B. W. I.)

Since the beginning of World War II, small quantities of vetiver oil have been produced on the island of Dominica in the British West Indies. A sample examined by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°/15°	0.998
Optical Rotation	+20° 24′
Refractive Index	1.5196
Acid Number	11.2
Ester Number	11.4
Ester Number after Acetylation	136.2
Solubility	Soluble in 0.5 vol. of 90% alcohol; turbid in 2 vol. and more

OIL OF VETIVER BRAZIL [28]

The development of the Brazilian vetiver oil industry resembles that of Brazilian lemongrass oil (cf. the monograph on "Oil of Lemongrass Brazilian"). The oil is produced on the same large estate [29] in the State of São Paulo, and by similar modern methods. In the course of World War II the plantings were increased to several hundred acres, and the oil found a ready market in Brazil, Argentina, and other South American countries. The future development of the Brazilian vetiver oil industry will depend upon the demand for the oil as well as upon its price on the world market. The latter, of course, is influenced chiefly by the quantity of Java oil available, and to a lesser degree of the Réunion oil.

In the Araraquara region of São Paulo, soil and climatic conditions favor the growth of vetiver. Plants grown in light sandy soil yield a much larger proportion of fine roots than those grown in heavy "terra rocha" (red laterite). In the latter case a good part of the fibrous root will remain in the ground when the stocks are pulled out. Moreover, more water is required for the washing of the harvested root material when the root originates from a heavy soil. Only roots at least sixteen months old are dug up, which precaution, combined with the use of modern distilling equipment, assures the production of a high-grade oil.

Vetiver may be planted at any time of the year provided there is rain, but the most favorable months are November to February, when rainfall is assured. Furthermore, if set out during these months the plants will usually flower in the same season. Since the fine, hairy, oil-bearing rootlets develop only after the flowering period, some time will be saved by planting early in the rainy season; otherwise the plants tend to lie dormant or, at best, to produce only coarse roots which yield an inferior oil.

Planting is done by subdivision of the root stocks. Most of the fine, hairy root system is separated and set aside for distillation, but some of the fine

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[28] The author is greatly obliged to Mr. Charles Henderson, of Cochabamba, Bolivia, for much of the information contained in this monograph.

[29] Other plantations are located near the city of São Paulo.

roots must be left on the stock for replanting. Planting stock may be stored in the shade until the root divisions can be set out in the fields, but exposure to the sunlight for a few days will do no harm as the plants are actually quite hardy. Since the grass tops have to be cut off, prior to planting, in any case, they can be used as cover and shade for the piles of root awaiting planting.

The methods of planting resemble those employed with lemongrass. The grassy tops are cut off to within 6 or 9 in. of the root, the clumps are then split with a machete into divisions of 3 to 4 shoots each, after which the latter are set into holes previously dug with a crowbar or other implements. The distance between the plants is 0.5 m., that between the rows 1 m. The root divisions are firmed into the earth with a pole, or by treading with the feet.

Scarcity of agricultural labor in Brazil has made it necessary to mechanize the production of vetiver as much as possible. The primitive methods used in some parts of the world would not allow for a large acreage to be harvested within a few months.

In Brazil vetiver producers follow this procedure: when about sixteen months old and 2 to 3 m. high, the grass is cut roughly with scythes, left in the field to dry for a few days, and then burned off. By this method, both the cut grass and that left protruding from the ground are disposed of. The ash serves as fertilizer. In dry weather the burning takes place so quickly that the flames have no time to heat up more than, say, 1 cm. of the surface earth, with the result that the roots are not damaged by heat. After the fire has died out, the hard cores protruding from the ground are chopped off level with the ground by means of mattocks, and cleaned away. The plantation, now clear of surface vegetation and trash, is plowed with a disc plow, tractor-drawn. The earth is turned over to a depth of about 35 cm.; it contains all the root material, with the exception of a few coarse taproots. Deeper plowing would not compensate for the very small extra yield obtainable at, say, 40 cm. depth.

Once the plowing is finished, the loosened earth and freed root material are treated in batteries of shaking machines provided with screens. Mixed soil and earth are shoveled on top of the screens. The roots stay on the shaker screens, while the soil falls through the meshes and piles up beneath the machine. At intervals the root material is cleaned off the screens and collected in heaps. Being of light weight, the shaker machines are moved along the rows to continue operation. Four men accompany each machine, and about one dozen machines operate in a row. At the end of the day the collected roots are carted away, while the piles of sifted earth are leveled by tractors. All the work is done on a contract basis, and paid for per weight of dry, uncleaned root, as it comes from the field. Thus each day's harvest is weighed before further treatment.

On poor, highly acid soil the yield of root per alqueira paulista (1 alqueira paulista equals roughly 2½ hectares or 6 acres) averages 700 kg., whereas on well-fertilized and irrigated soil it may be as high as 1,300 kg.

The uncleaned root material is hauled from the fields to large concrete washing tanks, cleaned of adhering earth by washing, and spread on extensive "terreiros" or drying grounds made of bricks (such as are used for washing and drying of coffee). Here the root is turned over at regular intervals until dry, and any foreign matter is removed. The cleaned and dried roots are finally sacked for transportation to the distillery or storage shed, where they are allowed to mature (age).

Courtesy of Mr. Charles E. Henderson, Cochabamba, Bolivia.

FIG. 18. Production of vetiver oil in Brazil. Drying of vetiver root in Cambuhy, São Paulo.

Before distillation, the root is again weighed and passed through a motor-driven cutter which reduces the length of fiber to about 1 in. The stills, which hold about 600 kg. of dried root, are loaded, and the charge is tramped down evenly, during which time a stream of water plays on the material. After the charge has been soaked for a period, distillation is started, first with direct steam and later with indirect steam (by means of pressure steam coils), the pressure being varied and regulated as dictated by the progress of distillation. All the condensed water is cohobated and the oil collected in separating tanks. Distillation of one charge (600 kg. of dried root) requires about 36 hr. The lighter-than-water and heavier-than-water oil fractions are mixed and transferred, together with some water in emulsion form, to the separating room, where the oil is freed of water by centrifuging. The clear oil is then placed into cans of 5 or 18 kg. capacity and, whenever possible, left to age and mature.

It should be noted that aging for a period of six months improves the odor of the oil substantially; the harsh, "green" and earthy odor characteristic of the freshly distilled oil will disappear and develop into a fuller, heavier, and sweeter odor.

Young plants do not possess the same proportion of fine, hairy roots as do plants which have been in the ground more than sixteen months; on distillation roots from young plants give a low yield of oil. The color of such an oil is green, the odor harsh, the specific gravity subnormal (low).

The yield of oil from roots older than sixteen months ranges from 1.5 to 2.0 per cent; that from young roots is only about 1.0 per cent.

The quality of the vetiver oil produced on the above-mentioned estate in the State of São Paulo has been very good. A sample examined by the author had these properties:

Specific Gravity at 15°	1.002
Optical Rotation	Too dark
Refractive Index at 20°	1.5244
Saponification Number	34.4
Ester Number after Acetylation	166.2
Solubility	Soluble in 0.5 vol. and more of 90% alcohol

In odor, the Brazilian oil resembles the West Indian type of vetiver oil. What was said in the monograph on "Oil of Vetiver Haiti" therefore also applies to the Brazilian oil.

In the course of the last few years the above-mentioned estate in Mattão, State of São Paulo, produced the following quantities of vetiver oil:[30]

	Kilograms
1946	1,053
1947	1,223
1948	404

Oil of Vetiver India

In the Central Indian State of Bharatpur (perhaps the most important area for vetiver oil production in the whole of India) no attempt is made to cultivate the roots. Roots growing wild in the extensive forest areas of the state are dug out and distilled *in situ*. Although these roots are said to yield only 0.2 to 0.3 per cent of oil, the industry has been able to operate profitably because there are few cultivation expenses beyond payment of a

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[30] Courtesy of Mr. Dan Haggard, General Manager, Companhia Agricola Fazendas Paulistas, Fazendas do Cambuhy, Mattão.

royalty to the state. Fuel is freely available on the spot for distillation at a low cost.

The production of vetiver oil in India increased during World War II, due to the steep rise in price—a result of the complete stoppage of imports from Java. This condition stimulated several private and state efforts toward a scientific study of the cultivation and distillation of this valuable and neglected crop. The most important work along these lines is that sanctioned by the Government of Madras, and carried out by the Kerala Soap Institute, Calicut.

According to Murti and Moosad,[31] the white sandy soils on the west coast of southern India were first considered to be best suited to the cultivation of this crop. Cultivation and distillation experiments carried out by Murti and Moosad, however, proved that pure (white) sandy soil is not suited to the growing of vetiver. The root, on distillation (for 16 hr.), yielded only 0.18 to 0.22 per cent of oil. Root grown in red laterite loam, on the other hand, yielded from 0.76 to 0.94 per cent of oil. Root grown on red laterite with very little sand yielded 1.02 per cent of oil. In all experiments root of eighteen months' maturity was used. In two years of experimentation the roots produced in loamy soils were found to be thick and wiry, with only a small proportion of hairy rootlets, whereas the roots grown in sandy soils were thin and hairy.

So far as the maturity of the roots at harvest time is concerned, Murti and Moosad[32] found by systematic experiments that the oil content increases progressively up to twenty-one months (yield 0.87 per cent); at ten months it is 0.10 per cent, at fifteen months 0.56 per cent, at seventeen months 0.79 per cent. It is definitely uneconomical to harvest before a minimum maturity of fifteen months, while a period of twenty-one or twenty-four months will also be uneconomical. A period of maturity of fifteen to eighteen months for the roots in the soil may be considered the optimum. In these experiments Murti and Moosad harvested the root during the dry period.

The same authors also found that at twenty-four and twenty-five months' maturity the roots yielded only 0.25 and 0.20 per cent of oil, respectively. However, in these two cases the root was dug up during the rainy season. It may well be that the drop in oil content of the root, twenty-four and twenty-five months old, was due to washing out of a part of the oil from the underground roots during heavy rains.

Data on manuring showed that fertilizing with ammonium sulfate, brine manure, and groundnut cake increases the oil content of the roots to some extent, but the increase is far less than that of roots cultivated in a good

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[31] *Am. Perfumer* **54** (August 1949), 113.

[32] *Ibid.*

soil—red laterite, for example. In other words, natural soil fertility is more important than fertility created by manuring.

USE OF VETIVER OIL

Oil of vetiver is one of the most valuable and most important perfumers' raw materials, widely used in perfumes, cosmetics and for the scenting of soaps. It is indispensable in odors of the heavier, oriental type. The oil imparts pleasant, strong, and very lasting notes to perfume compositions, acting, at the same time, as a natural fixative. Because of its odor strength, the oil has to be dosed with care and discretion, as an overdose may result in a pronounced "woody" note. Oil of vetiver blends particularly well with those of sandalwood, patchouly, and rose. The usually lower priced (in normal times) Java type is employed chiefly in soap work, the higher priced Réunion type in fine perfumes.

Substantial quantities of vetiver oil are used for the isolation of the sesquiterpene alcohols ("Vetiverol" and similar commercial brands) which possess an even softer and smoother odor than the original oil and represent natural fixatives *par excellence.* The same is true of the acetates of these sesquiterpene alcohols which are prepared by acetylation of the alcohols.

SUGGESTED ADDITIONAL LITERATURE

Harold A. Levey, "American Vetiver and Its Production," *Drug Cosmetic Ind.* **47** (1940), 534, 538.

B. K. Bhattacharyya, "Synthetic Experiments in the Degradation Products of Vetivone," *Science and Culture* **8** (1943), 426. *Chem. Abstracts* **37** (1943), 5031.

B. K. Bhattacharyya, "Synthesis of the Diethyl Ester of an Isomer of the Dicarboxylic Acid ($C_{12}H_{20}O_4$). A Degradation Product of β-Vetivone," *J. Indian Chem. Soc.* **22** (1945), 214. *Chem. Abstracts* **40** (1946), 4680.

J. N. Rakshit and K. B. Dutt, "Khas Khas (Vetiver) Oil," *Indian Soap J.* **13** (1948), 138. *Chem. Abstracts* **42** (1948), 5170.

R. Saheb A. K. Menon and C. T. Ittyachan, "Survey of Indian Vetiver (*Khus*) and Its Oil," *India Council Sci. Ind. Research, Essential Oil Advisory Committee* (1945).

CHAPTER II

ESSENTIAL OILS OF THE PLANT FAMILY *LAURACEAE*

OIL OF BOIS DE ROSE

(Oil of Rosewood)

Essence de Bois de Rose *Aceite Esencial Bois de Rose* (*Palo de Rosa*)
Rosenholzöl

Introduction.—There are two types of commercial bois de rose oil, viz., the so-called Cayenne oil, produced in French Guiana, and the much more important Brazilian oil, produced in the lower Amazon Basin. Until about 1927 the Cayenne oil was the only type available, but in the intervening years the Brazilian oil has come by far to outrank it. At present French Guiana produces yearly only a few tons of oil, whereas Brazil could produce several hundred tons, provided prices and general conditions should warrant such a large output.

The two oils are distilled from the wood of trees belonging to closely related varieties. Their chemical composition is similar, the chief constituent of both oils being linaloöl. The Guiana oil, however, usually contains a higher percentage of linaloöl (90–97 per cent) than the Brazilian (80–90 per cent). The linaloöl present in the Guiana oil is usually laevorotatory, whereas the linaloöl in the Brazilian oil seems to consist of a mixture of dextro- and laevorotatory isomers.

The two oils will now be described in order.

Oil of Bois de Rose Cayenne

(Cayenne Rosewood Oil)

Essence de Bois de Rose Cayenne
Aceite Esencial Bois de Rose Cayenne (*Palo de Rosa*)
Cayenne Rosenholzöl

Botanical Origin.—There has been much confusion regarding the taxonomy of the tree from the wood of which this oil is distilled. In French Guiana there appear to exist several species or varieties, locally called "likari kanali," "bois de rose femelle," and "bois de rose mâle" which serve for distillation of the oil. Moeller[1] classified the parent plant as (probably) *Ocotea caudata* Mez. (fam. *Lauraceae*), whereas Holmes[2] suggested *Protium*

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[1] *Pharm. Post* **29** (1896), Heft 46–48. *Jahrbuch des Kgl. bot. Gartens zu Berlin* (1889), 378. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 699.

[2] *Perfumery Essential Oil Record* **1** (1910), 32.

(*Icica*) *altissimum* March (fam. *Burseraceae*). More recently, Freise[3] introduced the term *Aniba rosaeodora* Ducke (fam. *Lauraceae*), which would seem most appropriate in view of the fact that he classified the related Brazilian tree (growing in the Amazon Basin) as *Aniba rosaeodora* var. *amazonica* Ducke.

The wood is hard and heavy, resembling mahogany; it is yellow-reddish in color, and possesses a very pleasant odor.

Regions of Production.—The tree, an evergreen, grows wild in the vast forests and jungles of French Guiana (in the northeastern part of South America), between the Maroni and Oyapock Rivers.

The term "bois de rose Cayenne" originates from the fact that prior to World War I large quantities of logs were shipped from Cayenne, capital of French Guiana, chiefly to Europe, where the wood was processed for essential oil recovery in the well-equipped distilleries of Germany, France, and England.

Shortage of shipping space during the war, increased freight rates, and the fact that during the long transport of the logs overseas substantial quantities of oil were lost by evaporation, induced a number of producers to distill the wood locally, and distilleries were installed in the interior of French Guiana. Some of these distillation posts were provided with efficient stills, with the result that the oil was of good quality, and readily accepted in Europe and North America, particularly for the isolation of a high grade linaloöl, one of the most important aromatic isolates. In 1929 almost 50 field distilleries operated in the interior of the colony (a few of them in the adjacent sections of Brazil), and about 190,000 lb. of oil were exported from Cayenne in that year. The demand for wood became so great that the trees were exploited recklessly, and, since no provisions had been made for replanting, the wood cutters (and the stills) had to move to ever more remote and less accessible sections, thrusting finally across the border river Oyapock into the contiguous areas of Brazil, where a similar variety of trees also grows wild. The trees ultimately became so scarce that by 1932 only three distilleries were able to continue operation. Today the total annual production of oil of bois de rose, Cayenne type, amounts to only a few tons.

While the production of Cayenne oil was declining rapidly, another variety of bois de rose, growing wild in parts of the Amazon Basin of Brazil (more than 1,000 miles distant from Guiana), was found to yield an essential oil similar to, but not quite as good as, the Cayenne type. Soon the Brazilian oil became an important article of export, and now it far exceeds the Cayenne oil in production. (See the monograph on "Oil of Bois de Rose Brazilian.")

Distillation.—The difficulties connected with distillation, and the primitive conditions prevailing in the hardly accessible interior of Cayenne,

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[3] *Ibid.* **24** (1933), 307.

leave much to be desired in regard to efficient working methods. It appears, for instance, that at certain periods of the year the trees contain substantially more oil than at other periods; but it is not always possible to cut the trees at the proper time. On the other hand, felled trunks left lying in the woods, and exposed for months to sun and rain, lose some of their essential oil.

Prior to distillation, the wood is reduced to chips. It is distilled in stills of about 1,000 liters capacity. Distillation of one charge lasts 2 to 3 hr., the steam being generated usually in a separate steam boiler. More primitive stills are heated directly with fire. The crude oil is transported, generally via canoes, to Cayenne, where it is filtered, bulked, and shipped abroad.

Physicochemical Properties.—Gildemeister and Hoffmann[4] reported the following properties for Cayenne rosewood oils (which these authors call Cayenne linaloe oil):

Specific Gravity at 15°	0.870 to 0.880
Optical Rotation	−9° 0′ to −19° 0′
Refractive Index at 20°	1.461 to 1.465
Acid Number	Up to 1.5
Ester Number	Up to 6.3
Alcohol Content, Calculated as Linaloöl [Determined by Acetylation in a Xylene Solution (1:5) for Seven Hours]	90 to 97%
Solubility	Soluble in 1.5 to 2 vol. of 70% alcohol; soluble in 4 vol. and more of 60% alcohol

Commercial shipments of Cayenne rosewood oil received and analyzed by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.872 to 0.878
Optical Rotation	−12° 30′ to −16° 24′
Refractive Index at 20°	1.4602 to 1.4628
Ester Content, Calculated as Linalyl Acetate	0.3 to 1.5%
Solubility	Soluble in 3 to 4.5 vol. and more of 60% alcohol

The Cayenne type of bois de rose oil differs from the Amazon (Brazilian) type in its pronounced laevorotation, which is due to the presence of *l*-linaloöl in the oil. For example, a sample of pure linaloöl, isolated by the author from Cayenne oil, had a rotation of α_D −15° 30′.

Moreover, the content of linaloöl in the Cayenne oil is usually higher than that in the Amazon (Brazilian) type. The Cayenne oil possesses a finer, less camphoraceous odor.

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[4] "Die Ätherischen Öle," 3d Ed., Vol. II, 702.

For these reasons the Cayenne oil has always been highly esteemed, particularly for use in perfumes. It possesses a suave odor reminiscent of lily of the valley.

Chemical Composition.—The following substances (listed approximately in order of their boiling points) have been identified in oil of bois de rose derived from the tree growing in French Guiana. The oil from the variety occurring in the Amazon Basin of Brazil, although produced and used on a much larger scale, does not seem to have been investigated as thoroughly as the so-called Cayenne variety (see also the section on "Physicochemical Properties").

An Aliphatic Terpene(?). According to Schimmel & Co.,[5] the forerun of the oil, b. 168°–170°, probably contains an aliphatic terpene which, on hydration with glacial acetic acid-sulfuric acid and on saponification, yielded an alcohol b. 210°–215°, d_{15} 0.915 with an odor reminiscent of linaloöl and terpineol. The terpene in question is perhaps aliphatic as the fraction investigated did not contain any sabinene, camphene, fenchene, or pinene.

Dipentene. Identified by the same workers through the preparation of the tetrabromide m. 124°–125°, and of the dihydrochloride m. 47°–48°.

Cineole (Eucalyptol). Characterized by preparation of its iodol compound m. 110°–111° in the course of the same investigation.

Methyl Heptenone. Observed by Roure-Bertrand Fils.[6]

Methyl Heptenol. Schimmel & Co.[7] isolated small quantities of this alcohol from the fraction d_{15} 0.8655, α_D $-11° 40'$ by means of the acid phthalate. Oxidation of the regenerated alcohol led to methyl heptenone which could be characterized through the preparation of its semicarbazone m. 137°–138°.

Linaloöl. This, the main constituent of oil of bois de rose, was first observed by Morin[8] and named licareol. Barbier[9] originally believed licareol and linaloöl to be different substances, but later agreed that they are identical (cf. "Oil of Linaloe Mexican").

Cayenne oils of bois de rose contain more than 80 per cent (usually 85 to 95 per cent) of linaloöl, in laevorotatory form (cf. "Physicochemical Properties").

Terpineol. Schimmel & Co.[10] isolated 5 per cent of terpineol from Cayenne oil of bois de rose.

Nerol. According to Roure-Bertrand Fils[11] the oil contains about 1.2 per cent of nerol.

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[5] *Ber. Schimmel & Co.*, April (1912), 85.

[6] *Repts. Roure-Bertrand Fils*, October (1909), 45.

[7] *Ber. Schimmel & Co.*, October (1911), 60.

[8] *Compt. rend.* **92** (1881), 998; **94** (1882), 733. *Ann. chim. phys.* [5], **25** (1882), 427.

[9] *Compt. rend.* **114** (1892), 674; **116** (1893), 883.

[10] *Ber. Schimmel & Co.*, April (1909), 64.

[11] *Repts. Roure-Bertrand Fils*, October (1909), 45.

Geraniol. In the above-mentioned investigation of oil of bois de rose Cayenne, Schimmel & Co.[12] established the presence of about 1 per cent of geraniol through the preparation of its diphenylurethanes m. 80°–81.5°.

p-Methyl Acetophenone(?) and *l*-Tetrahydro-Δ^3-*p*-methyl Acetophenone(?). In the opinion of Naves,[13] very small quantities of these two ketones occur probably in the oil derived from bois de rose Cayenne (cf. the section on the "Chemical Composition" of "Oil Bois de Rose Brazilian").

Examining the distillation waters of oil of bois de rose Cayenne, Schimmel & Co.[14] observed *furfural* (b. 159°–161°; phenylhydrazone m. 96°–98°; semicarbazone m. 196°), and a cough-provoking aldehyde b. 90°–95°, which probably was *isovaleraldehyde.*

Use.—In the past, when it was freely available, oil of bois de rose Cayenne served chiefly as starting material for the isolation of high grade linaloöl. Even today the oil is much valued as an ingredient in fine perfumes.

Oil of Bois de Rose Brazilian

(Brazilian Rosewood Oil)

Essence de Bois de Rose Brésil
Aceite Esencial Bois de Rose Brasilero (Palo de Rosa)
Brasilianisches Rosenholzöl

Botanical Origin.—As in the case of the Cayenne type, there has been considerable confusion in regard to the taxonomy of the tree, the wood of which yields the Brazilian (Amazon) oil. Gildemeister and Hoffmann [15] mention *Aniba parviflora* Mez. = *Aydendron parviflorum* Meissn. = *Ocotea parviflora* (fam. *Lauraceae*) as parent plant. More recently Freise [16] suggested *Aniba rosaeodora* var. *amazonica* Ducke, which classification is now generally accepted in the literature of the essential oil industry.

The wood has a gray-yellow color with a somewhat silky gloss. The difference between the Amazon and the Guiana varieties is slight and involves anatomical features such as leaf nerves, size, and shape of the blossoms, etc. The wood possesses an agreeable odor, due to the presence of essential oil.

Development of the Industry.[17]—The actual beginning of rosewood oil production in the Amazon Basin around Maués and Itacoatiara dates back

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[12] *Ber. Schimmel & Co.*, April (1909), 64.

[13] *Helv. Chim. Acta* **31** (1948), 49.

[14] *Ber. Schimmel & Co.*, April (1912), 84.

[15] "Die Ätherischen Öle," 3d Ed., Vol. II, 701.

[16] *Perfumery Essential Oil Record* **24** (1933), 307.

[17] For a survey of the economic and social factors underlying this industry the reader is referred to an article which the author published in the *Am. Perfumer* **42** (May and June 1941), after a visit to the Amazon Basin.

about thirty years. Because of a marked difference between the odors of the Brazilian and the Guiana oils, the trade for a long time refused to adopt the Brazilian oil as a substitute for the Guiana oil. This attitude still prevailed when, in 1927, about 200 metric tons of oil were produced. Brazil encountered great difficulties in disposing of this large quantity, and about 80 tons remained in the hands of the producers and exporters in Manáos (Amazonas) and Belem (Pará). Overproduction and sharp competition caused such a decline in prices that they covered only part of the cost, with the result that for about two years production was discontinued.

These unfavorable conditions forced the State of Amazonas to take drastic steps toward organizing and protecting the new and promising industry. Decree No. 1455, issued on April 9, 1932, stipulated that only a limited quantity of bois de rose oil could be produced yearly, and this only by those distillers who obligated themselves to replace every cut tree with a newly planted one. Practically all producers subscribed to this obligation for the duration of five years, with the intention of renewal for another five years. A Cooperativa was thus created which, after many initial difficulties, hostilities, mistakes, and failure, finally developed into the Consorcio dos Extractores de Essencias Vegetaes which, for a time, occupied a very powerful, if not monopolistic, position in Amazonas and most of Pará State. In close collaboration with the government, the Consorcio decreed each year a maximum export figure, and the corresponding total quantity of production, and allotted a certain quota of production to each of its members. The Consorcio, acting also as a price establishing, exclusive sales and export agency, grew into a strong organization comprising nine producers in the State of Amazonas and six in the State of Pará. It installed modern distilleries in different localities, and contributed greatly to the production of a high-grade oil.

The Consorcio continued in existence until 1944, when urgent demand on the part of the United States and Allies for rubber concentrated all labor available in the Amazon Basin on the collection of natural rubber, and production of rosewood oil was abandoned. As a result of the boom in the price of natural rubber, wages in the area increased some 800 per cent,[18] and the price of rosewood advanced 1,700 per cent above the price prevailing in 1937.

Because of the chaotic conditions, which developed after World War II, and the resumption of production of rosewood oil, the Consorcio in 1947 was re-established, and of the 47 distillers in Brazil, 45 then joined the new Consorcio.

Producing Regions.—The trees grow wild, on a particular type of clay soil and at elevated altitudes, along the tributaries of the right bank of the

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[18] *Drug Cosmetic Ind.* **61** (1947), 177.

lower Amazon, in the States of Amazonas and Pará. Aside from a few smaller ones, these tributaries are the Autaz, Madeira, Andira and Maués. It seems strange that the trees do not occur on the left (northern) side of the mighty Amazon. Distilleries are located in Parintins, Barreirinhas, Maués, Itacoatiara, Manáos and in a number of other municipalities.

About 70 per cent of the total output of oil originates from the State of Amazonas, and 30 per cent from the State of Pará, exclusive of the small quantity of oil (4–5 tons annually) produced south of the Oyapock River, which forms the borderline between French Guiana and Brazil (State of Pará).

Obviously, woodcutters are inclined to cut first those trees which are most easily reached; but the more such trees are felled, the more inaccessible the remaining supply becomes, and the more the price of the wood rises. Not all the trees which, by government regulation, were required to be planted in the past fifteen years, have reached the age at which they can be cut.

Collection of the Wood.—The collection of any product from the wild and remote jungles of the Amazon Basin is beset with many difficulties. This applies particularly to the heavy logs of rosewood which in some places are cut a hundred miles away from the Amazon. The only way to transport them is by water on the rivers and creeks that feed the Amazon. Here they are loaded on barges or larger boats and shipped to the distilleries, most of which are located on the banks of the Amazon. For a long period of the year, however, the tributaries are quite dry, and it is only during the flood season, from April to July, that they contain sufficient water to permit transport of the logs. The level of the Amazon rises, at this time, about 50 ft. This high water level is required in order to reach most of the sites where the trees are located.

Not many native laborers are willing to penetrate into the jungles and stay there for months, exposed to all kinds of hardships and diseases. Teams of experienced and hardy woodsmen have, therefore, to be organized, financed, and provided with sufficient food and supplies, before they can be sent into the jungle. Most distillers do not collect their own wood. They contract with firms specializing in wood cutting, and advance them 50 per cent of the value of the contracted logs. The balance is paid on delivery of the wood. The contractors, in turn, organize crews of woodcutters and send them into the interior. Cutting may start in the dry season, continuing until the end of the flood season, when the logs can no longer be transported down the tributaries.

To prevent gradual extinction of the rosewood trees, the Brazilian Government, in collaboration with the Consorcio, some years ago enacted legislation requiring that one new tree be planted by the distillery for every 20 kg. of rosewood oil sold. The replanting must be done under the supervision of a government inspector, who signs a receipt for every planted tree. For replanting, young trees growing wild around old ones are set out in rows, on regular plantings which are laid out on virgin jungle soil, after it has been cleared of underbrush.

Trees should not be cut before they are at least ten, preferably fifteen, years old, and the trunks should have a diameter of at least 12 in.

Distillation.—At the distillery the wood is either distilled immediately or stored. Prior to distillation, the logs are cut lengthwise with axes. Subsequently they are reduced to chips in regular sawmills (such as are used in paper factories), consisting of a rapidly rotating flywheel provided with three slanting blades. The chips are then transported to the stills in wheelbarrows and distilled immediately.

The stills are quite modern, made of galvanized iron or copper, the latter being preferred because they last longer, do not wear out so easily, and the copper can always be used again after the stills have become useless. The stills hold from 200 to 500 kg. of chips, those holding 500 kg. being preferred because they are more economical. One distillery houses several stills.

Live steam of about 30 lb. pressure (measured in the separate steam boiler) is blown through the still; oil and water separate in a Florentine flask. The distillation waters are not cohobated, but simply discarded. Distillation of 500 kg. of chips lasts about 2½ hr. The exhausted plant material is discharged and sun-dried so that it may be used as fuel, together with regular firewood.

The yield of oil averages 1 per cent, but varies from 0.7 to 1.2 per cent, according to the localities from which the wood originates. The highest yields are obtained from wood cut in Barreirinhas and Parintins, the lowest from Autaz, Manáos, and Itacoatiara wood. Under normal conditions a distillery carries out two distillation operations a day; but this number could be doubled or tripled if a higher quota of oil were assigned to it by the Consorcio.

Total Production.—Total production of Brazilian rosewood oil has fluctuated greatly. In the years before World War II the following quantities of oil were exported:

	Kilograms
1937	130,706
1938	92,789
1939	185,177

Of the latter quantity 127,693 kg. came from the State of Amazonas and 57,484 kg. from the State of Pará.

With a view to keeping demand, production, and prices in line, the Government permitted production of 100 metric tons of oil, or more, per year, provided 80 tons could be sold in that particular year by the Consorcio, in the form of actual shipments, or in the form of contracts entered before the end of the year.

During World War II production and exports were very irregular. In 1947 about 110 tons of oil were produced, about half of which went to Europe, half to the United States.

The average annual production, taken over the last fifteen years, is approximately 80 tons of oil.

Physicochemical Properties.—The Brazilian rosewood oil differs from the Cayenne oil in respect to both specific gravity (slightly higher in the case of the Brazilian oil) and optical rotation. Whereas the Cayenne oils exhibit a pronounced laevorotation, the Brazilian oils are either slightly laevo- or slightly dextrorotatory, owing to the fact that in the Brazilian oils linaloöl, the chief constituent, occurs as a mixture of *d*- and *l*- isomers. Commercial lots of linaloöl, isolated by Fritzsche Brothers, Inc., New York, from Brazilian rosewood oils had rotations ranging from α_D $-0° 23'$ to $+0° 30'$.

Owing to the higher percentage of cineole present, the odor of the Brazilian oil is very slightly camphoraceous, and therefore somewhat harsher than that of the Cayenne oil. Rectification of the oil and elimination of the cineole fractions improve the odor considerably.

Shipments of genuine Brazilian rosewood oils received and analyzed by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.875 to 0.895
Optical Rotation	$-4° 0'$ to $+5° 0'$
Refractive Index at 20°	1.4620 to 1.4685
Total Alcohol Content, Calculated as Linaloöl (Acetyl Chloride-Dimethyl Aniline Method[19])	84 to 92%
Solubility	Soluble in 2 vol. and more of 70% alcohol

Simmons[20] suggested determining the linaloöl content of Brazilian rosewood oil by fractionation at atmospheric pressure, setting aside and weighing the fraction b. 194°–205°. Oils of best quality contain 88 to 89 per cent of this fraction, oils of medium quality about 85 per cent, and oils of lower quality less than 80 per cent. The analytical control laboratory of the Consorcio in Manáos made it a policy to reject lots of oil containing less than 85 per cent of this fraction.

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[19] See Vol. I of this work, p. 277.

[20] *Perfumery Essential Oil Record* **24** (1933), 338.

Fractionation (at atmospheric pressure) of a normal Brazilian rosewood oil yields approximately these fractions:

		Per Cent
I.	b. up to 100°	1.2
II.	b. 100°–194°	4.3
III.	b. 194°–205° (linaloöl fraction)	85.8
IV.	Residue	8.7
		100.0

Refractionation of fraction III will yield 70 per cent (= ca. 60 per cent, calculated upon the total, original oil) of a pure linaloöl fraction.

Simmons[21] advises against the determination of linaloöl by the well-known formylation method, because too high values will be obtained, owing to the presence of geraniol, nerol, and terpineol in the oil.

Today the essential oil industry uses the method of Fiore for the assaying of linaloöl; it gives very satisfactory results (for details see Vol. I of this work, p. 277).

Oyapock Oils.—At this point brief mention should be made of the so-called Oyapock type of Brazilian rosewood oil. This oil is produced in small quantities (4 to 5 tons per year) in the Brazilian State of Pará, south of the Oyapock River, which represents the border between Brazil and French Guiana. Compared with the Amazon oils, which form the bulk of the Brazilian production, the Oyapock oil is not important. However, it is interesting because of its physicochemical properties which lie between those of the Amazon and the Cayenne oils (cf. the monograph on "Oil of Bois de Rose Cayenne"). The optical rotation of the Oyapock oils is usually slightly laevo-, up to −2° 40′.

The trees growing in the Oyapock region probably belong to a variety similar to that occurring in French Guiana.

The odor of the oil also resembles that of the Cayenne oil, and therefore the Oyapock oil usually fetches a slightly higher price than the Amazon oil. Prior to World War II the small quantities of Oyapock oil were sold chiefly to Germany, probably for the isolation of a high-grade linaloöl.

Adulteration.—The control exercised in the analytical laboratories of the Consorcio in Manáos prevents shipment of any adulterated lots abroad.

Chemical Composition.—To the author's knowledge, no exhaustive investigation of oil of bois de rose Brazilian has been carried out, or else the results have not been published, perhaps because it is generally assumed that the composition of the Brazilian oil closely resembles that of the Cayenne oil (cf. the monograph on "Oil of Bois de Rose Cayenne").

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[21] *Ibid.*

It is known that the Brazilian oil contains *linaloöl* as chief constituent, and as a mixture of the *d*- and *l*- isomers.

It was only recently that Naves,[22] by means of Girard and Sandulesco's reagent P, isolated a mixture of 10.3 g. of ketones from 85 kg. of Brazilian bois de rose oil. The mixture was found to contain *p-methyl acetophenone* (semicarbazone m. 208°–209°), and *l-tetrahydro-*Δ^3*-p-methyl acetophenone* $b_{3.3}$ 61°, d_4^{20} 0.9371, $[\alpha]_D^{20}$ $-35°\,6'$, n_D^{20} 1.47110; semicarbazone m. 157°–157.5°.

In the opinion of Naves, these two ketones occur also in the Cayenne type of bois de rose oil.

According to Louveau,[23] the slightly camphoraceous odor of the Brazilian bois de rose oil is caused by the presence of 6 to 10 per cent of *cineole*.

Use.—Brazilian rosewood oil is used largely for the isolation of linaloöl, one of the most important aromatic isolates. Substantial quantities of the oil as such are employed for the scenting of soaps and all kinds of technical preparations.

OIL OF SASSAFRAS

Essence de Sassafras *Aceite Esencial Sasafrás* *Sassafrasöl*
Oleum Sassafras

Oil of Sassafras North American

History.—One of the oldest and best known American essential oils is that of sassafras. Since early colonial days tea made from the bark of the root has been a popular domestic remedy as a sudorific for colds and as a spring tonic to "thin the blood," as the natives claim, or to "get the winter sluggishness out of the blood." Old country doctors still prescribe the oil in cases of muscular aches and as a general liniment. The oil is also said to reduce high blood pressure.

Range and Habitat.—*Sassafras albidum* (Nutt.) Nees (fam. *Lauraceae*) is an indigenous tree, growing wild from Maine to Florida, and from the Atlantic Coast to the Mississippi; it is not common in the Far West. The producing regions lie in Virginia, Kentucky, North Carolina, Tennessee, and southern Ohio, largely in the Appalachian Mountain regions.

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[22] *Helv. Chim. Acta* **31** (1948), 44.

[23] *Rev. Marques Parfumerie Savonnerie* **15** (1937), 186.

Sassafras thrives on poor soil, on exhausted farm land for example. It grows so rank that it becomes an agricultural nuisance, crowding out good timber. Usually the trees spring up along the fences first, and then spread out into the fields in a belt as wide as 40 ft. Landowners and farmers are only too glad to have someone cut these trees and pull the stumps. Sassafras grows spontaneously and rapidly for the first four or five years, almost like a weed; but then the rate of growth slows up like that of any other tree.

Description.—The sassafras tree is of medium size, reaching a height of 35 ft. under favorable conditions, and with old age even 45 ft. Some trees are eighty to eighty-five years old, but the average tree felled for the pulling of its root is thirty-two to forty years old. Such trees are 12 to 16 in. in diameter at the base.

The bark of the trunk is rough, furrowed and grayish, that of the extreme branches smooth and very green. The leaves vary in form and size, even on the same tree; some are oval and entire, others have a lobe on one side, but the greater number are three-lobed. The wood of the trunks is grainy and soft, and therefore useless. It splits and splinters easily and cannot be employed for cabinet making. The only possible use for it is in railroad ties.

The living root bark is almost white, but when collected and exposed it darkens. Deprived of the outer cork and dried, it is marketed as sassafras. The National Formulary, Eighth Edition, specifies that sassafras contain not more than 4 per cent of adhering wood, outer corky tissue, or other foreign organic matter, and yield not more than 5 per cent of acid-insoluble ash.

The essential oil occurs in the underground parts of the tree, especially in the bark of the root, which yields 6 to 9 per cent of oil. The wood of the root yields less than 1 per cent of oil. The trunk, branches, and leaves, although slightly aromatic, do not contain sufficient oil to make distillation worth-while.

Collection.—During the winter months it is much more difficult to pull the stumps, because the earth is partly frozen. The bark is then easily torn off and may be lost in the ground. In spring, the sap develops in the tree, which causes the bark of the root to slip during pulling. Hence, the best period for economical operation is in the summer and fall.

Organized crews of woodsmen go through the forests felling the sassafras trees with axes. A tractor follows the men, and with a strong cable pulls stumps and roots from the ground, a very simple procedure. The pulling of the root is possible only when the trees are about ten years old; the type of soil, too, is a factor. Stumps of too young and, therefore, fragile trees, when pulled, easily break at ground level, and their roots stay in the ground.

Other workers, following the tractor, clean the stumps and roots with hoes to remove adhering soil and dirt. Subsequently, the stumps are loaded on tractor-drawn trailers and hauled to storage piles in the forests, from where they are trucked to the distilleries.

Supply of Raw Material.—Most of the root material is supplied by farmers who pull the stumps on their property and sell them to the distilleries at a stipulated price, which, of course, varies with economic conditions. A serious problem for the distillers is the fact that it is becoming increasingly difficult to obtain root material; also since the outbreak of World War II wages have risen substantially.

Unfortunately, individual farmers cannot always be relied upon as regards prompt delivery; they usually pull the stumps when they have nothing else to do and when in need of cash. The larger distillers, therefore, procure the necessary root material through their own organization which consists of pulling equipment, tractors, trucks, and hired labor.

Comminution of the Root Material.—The root system of the sassafras tree consists of a large bole from which many small roots radiate. In order to comminute the large stumps and roots into chips which can be distilled, the side roots are hacked off close to the bole, and the latter is split. The principal producer of sassafras oil in Elizabethtown, Kentucky,[1] employs for this purpose a specially constructed hydraulic splitting machine. The split boles and the hacked-off side roots are then placed in so-called "wooden hogs" (such as are used in lumber mills) and reduced to chips. The chips are blown through a system of pipes into a storage bin above the still, and from there charged into the still.

Distillation.—There exist in the producing regions a number of rather primitive distilleries which work according to old-fashioned methods. The stills are constructed of wood. Oil of sassafras is obtained by direct steam distillation. Steam generated in a separate boiler is injected into the chip material in the still, liberating and vaporizing the essential oil. Steam and oil vapors are reliquefied in a condenser, and the oil and water separated in a Florentine flask. The above mentioned principal producer of sassafras oil in Elizabethtown operates several large stills holding about 1¾ tons of chips each. The number of hours required for distilling the oil depends upon the steam pressure in the boiler and upon the temperature of the sassafras wood. Because of the difference in temperature, it is necessary to distill 4 hr. in winter, whereas during the summer 3 hr. is sufficient.

The yield of oil averages 1.8 per cent; it undergoes fluctuations with the various seasons of the year, rising after the leaves have fallen and increasing considerably whenever the stumps or chips have been attacked by frost. Since the distillation water contains some essential oil in suspension, it is

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[1] The author wishes to express sincere thanks to Mr. Geo. J. Glaub of Elizabethtown for assistance given him during his visit to the sassafras producing regions.

advisable to store it in a settling tank connected with the Florentine flask. Some additional oil is obtained in this way.

Physicochemical Properties.—Sassafras oil is a yellow or reddish-yellow liquid having the characteristic odor and taste of sassafras. If the oil has solidified in whole or in part, it should be warmed carefully at low temperature until it liquefies; then it should be thoroughly mixed before dispensing. The oil must be preserved in tight containers. It must not contain any heavy metals.

Genuine North American sassafras oils examined in the laboratories of Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 25°/25°	1.065 to 1.076 (in oils distilled at certain periods of the year as low as 1.061)
Optical Rotation at 25°	+2° 0′ to +3° 38′
Refractive Index at 20°	1.5270 to 1.5311 (at certain periods of the year, the refractive index may be slightly lower)
Congealing Point	4.5° to 6.9° (congealing points as low as 4.1° have been observed at certain periods of the year)
Solubility	Soluble in 1 to 2 vol. and more of 90% alcohol

Gildemeister and Hoffmann[2] reported the following properties for North American sassafras oil:

Specific Gravity at 15°	1.070 to 1.080
Optical Rotation	+2° 0′ to +4° 0′
Refractive Index at 20°	About 1.530
Acid Number	Up to 1
Ester Number	0.5 to 5
Solubility	Soluble in 95% alcohol; soluble in 1 to 2 vol. of 90% alcohol

Regarding the determination of the safrole content in sassafras oil, see Vol. I of the present work, p. 329.

It might be interesting to mention that the specific gravity of sassafras root oil produced in late July and during most of the month of August is low. The gravity of the oils distilled in this period may even fall beneath the limits of the United States Pharmacopoeia. The lowering of the specific gravity seems to coincide with the change in leaf coloring from green to brilliant red, which occurs much earlier in sassafras than in most trees. Very probably some biochemical change takes place, the nature of which is unknown. The specific gravity of the oil in the roots rises again when the leaves begin to fall.

Adulteration.—North American sassafras oil is occasionally adulterated with the so-called "artificial sassafras oil." The latter consists of certain

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[2] "Die Ätherischen Öle," 3d Ed., Vol. II, 720.

fractions of camphor oil, produced in very large quantities and at very low prices in Formosa and Japan. These fractions possess a chemical constitution similar to that of true sassafras oil; their physical and chemical constants, too, are so similar that it is very difficult to detect, by chemical means, moderate additions of this product to sassafras oil. Large quantities of artificial sassafras oil used to be imported to the United States before the outbreak of World War II.

Genuine sassafras oil has a much finer and more delicate flavor than the artificial oil, which possesses a camphoraceous by-note.

Another possible adulterant of the North American (true) sassafras oil is the Brazilian sassafras oil, which has an odor and composition similar to the American. It contains more than 90 per cent of safrole (see "Oil of Sassafras Brazilian"). However, the physicochemical properties of the two types of oil differ sufficiently to permit the detection of substantial quantities of the Brazilian oil in the North American oil.

Chemical Composition.—The first investigations of North American sassafras oil (*Sassafras albidum* [Nutt.] Nees) date back more than a century, when Binder[3] observed that a constituent, later identified as safrole, separated from the oil in crystalline form. Subsequently, Faltin[4] reported camphor as another component of sassafras oil. Grimaux and Ruotte[5] introduced the designation safrole (a phenol ether $C_{10}H_{10}O_2$) for the chief constituent of sassafras oil and isolated from the oil a hydrocarbon $C_{10}H_{16}$ which they named safrene, but which was later found to be α-pinene (see below). The same workers observed in the oil a phenol which Pomeranz[6] recognized as eugenol.

The most thorough investigation of North American sassafras oil was carried out by Power and Kleber[7] who identified the following constituents:

α-Pinene. Identified by preparation of its nitrolbenzylamine m. 123°.

Phellandrene. Characterized by means of its nitrite.

Safrole. The chief constituent, amounting to about 80 per cent of the oil.

Eugenol. Characterized by means of its benzoyl compound m. 69°.

d-Camphor. Oxime m. 115°.

A Sesquiterpene(?). The fraction b. 260°–270° very probably contained a sesquiterpene.

According to Power and Kleber,[8] North American sassafras oil has the following composition, quantitatively:

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[3] *Buchners Repert. f. d. Pharm.* **11** (1821), 346.

[4] *Liebigs Ann.* **87** (1853), 376.

[5] *Compt. rend.* **68** (1869), 928.

[6] *Monatsh.* **11** (1890), 101.

[7] *Pharm. Rev.* **14** (1896), 101.

[8] *Ibid.*

	Per Cent
Safrole	80.0
α-Pinene and Phellandrene	10.0
d-Camphor	6.8
Eugenol	0.5
High Boiling Constituents, a Sesquiterpene, and Residue	3.0
	100.3

Use.—Sassafras bark owes its therapeutic qualities chiefly to the volatile oil, which possesses antiseptic properties. It is much less irritating to mucous membranes than many other essential oils. The oil has been recommended in dentistry as a disinfectant for root canals. In the form of a 1 per cent solution in petrolatum it is employed in the treatment of nasal catarrhs.

The most important use of sassafras oil, however, is in flavors. Its taste is aromatic and slightly astringent. Some of the most typical American soft drinks—root beer and sarsaparilla, for example—owe their characteristic flavor largely to sassafras oil. Some types of candies and chewing gums are also flavored with sassafras oil. Another application is in semipharmaceuticals (such as mouth wash and tooth paste) and, finally, for the scenting of soaps.

OIL OF SASSAFRAS LEAVES

The leaves of the North American sassafras tree, *Sassafras albidum* (Nutt.) Nees, contain a small amount of an essential oil which possesses an agreeable, lemon-like odor. The oil is not produced on a commercial scale, however. It differs from the oil present in the root chiefly in containing no safrole.

Distilling fresh leaves of the North American sassafras tree experimentally, Power and Kleber[9] obtained 0.028 per cent of a volatile oil, d_{15} 0.872, α_D +6° 25′.

The oil contained:

α-Pinene.

Myrcene.

Phellandrene.

Citral.

Linaloöl and Geraniol (both free and as acetic and valeric esters).

A Sesquiterpene (cadinene?).

A Paraffin m. 58°.

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[9] *Ibid.*, 103.

Oil of Ocotea Cymbarum H.B.K.

(*Oil of Sassafras Brazilian*)

Development.—In the course of World War II, while the Western Hemisphere was cut off from sources of supply in Europe and Asia, Brazil developed the production of certain essential oils which were eagerly absorbed by the American pharmaceutical, food, beverage, soap and cosmetic industries. The development of the Brazilian industry, spectacular in some of its aspects, was the result, in part, of the country's immense and largely untapped natural resources, its varied climatic and soil conditions, and its comparatively low-priced labor. The vast forests and plains of Brazil, not yet completely explored, abound with little known plants and trees, some of which could probably be exploited commercially for their essential oils, gums, resins, waxes, and drugs.

One of the most remarkable examples of the developments we have just mentioned is that of the so-called Brazilian sassafras oil industry. This oil was practically unknown some years ago, but its production has now reached the astounding figure of several hundred metric tons per year. The first distilling experiments were undertaken in 1938 by a German immigrant, Otto Grimm, who came to Brazil in 1930. His firm alone is said to have produced in 1942 more than 30 tons of the oil, while many other newer firms commenced or expanded distillation.

When the first shipments of the so-called Brazilian sassafras oil reached our ports, the U. S. Customs officials hesitated to admit it as a natural and genuine oil, since nothing was known about its botanical origin. More recently its import has been permitted under the label oil of *Ocotea cymbarum.*

Botany and Geographical Distribution.—The taxonomy of the tree from the wood of which the Brazilian oil is derived has not yet been fully elucidated. It has been classified variously as *Ocotea pretiosa* Benth. or *O. cymbarum* (fam. *Lauraceae*), locally called "Canela Sassafraz," a tall, beautiful tree, 10 to 15 m. high, with a trunk 30 to 50 cm. in diameter. It grows feral and abundant in the vast forests of the State of Santa Catharina, along the River Itajai, chiefly in the provinces of Rio do Sul, Blumenau, Itajai, Camboriu, and Grão Pará. These temperate sections are among the wealthiest, most prosperous, and picturesque farming areas of Brazil, in many ways recalling the Black Forest on the upper Rhine in Germany. The population consists chiefly of descendants of German and Swiss settlers (who also dominate the newly established sassafras oil industry).

Ocotea cymbarum occurs in other parts of Brazil and South America also, for example, in the forests of temperate Colombia. It has never, however, been exploited commercially outside of the Brazilian State of Santa Catharina.

Some vague references to Brazilian sassafras oil are given by Gildemeister and Hoffmann[10] under *Ocotea sassafras* (syn. *Mespilodaphne sassafras* Meissn.), which may be a related species or even identical with *Ocotea cymbarum*. Distilling fresh leaves of *Ocotea sassafras* years ago, Peckolt[11] obtained a yield of 0.0055 per cent, from the fresh flowers 0.009 per cent, from the ground bark 0.2 per cent, and from the air-dried chips 0.9 per cent of oil. The present commercial distillers employ only the wood of the tree.

The wood of *Ocotea cymbarum,* hard and resistant, is grainy and full of fissures; it splits easily, especially in the drier highlands. Hence it is utilizable only for certain purposes—railroad ties, for instance. It cannot be used for the manufacture of furniture, except in the humid, warm coastal regions. But even for this purpose its use is limited, since its marked odor confines its utilization to cheap furniture.

Cutting of the Wood.—When the first settlers of Santa Catharina cut clearings in the virgin forests of cedars and sassafras, they simply left a great many of the hard and heavy sassafras trunks lying on the ground, the lack of roads making it impossible to haul such big logs away. Without tractors it is extremely difficult to remove these felled giants from the woods. Many of these old logs are now sawed into blocks and used for distillation. The main supply of wood, however, originates today from newly cut trees. For this purpose the wood cutters must now penetrate even further into virgin woods to find sufficiently old trees (forty to fifty years old), which alone give a good yield of oil. This, obviously, increases the cost of transportation to the distilleries. Oxcarts are often employed. During the period of heavy rains from December to May the hauling of the wood from the interior becomes almost impossible. As a result, actual oil production lasts only about seven months per year, unless the distilleries process stored wood.

The trees are cut close to the ground, the roots being left in the soil, as they cannot be extracted without heavy tractors. The great demand for oil during the past years has resulted in a rather reckless exploitation of the sassafras stands, with no adequate plans or laws for preservation or reforestation. The forests in Santa Catharina are, however, of such vastness that there need be no fear (at least for the next few years) of a shortage of sassafras wood for distilling purposes. On the other hand, higher prices may be expected in the future because of longer haulage.

Distillation.—In many cases the production of oil of *Ocotea cymbarum* constitutes a side industry in the operation of the sawmills (very much like

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[10] "Die Ätherischen Öle," 3d Ed., Vol. II, 708.

[11] *Pharm. Rev.* **15** (1897), 45.

the distillation of cedar wood oil in the southeast United States). There exist in Santa Catharina quite a number of sassafras distilleries, including several large ones, about a dozen middle-sized ones, and many small ones operating on a more primitive basis. The larger ones are equipped with good sized stills, for example, 3 m. high, 1.8 m. wide at the base, and 1.6 m. wide at the top. Some stills are constructed of sassafras wood, which serves very well for the purpose. A still with a capacity of about 8 cu. m. yields on the average about 25 kg. of oil per charge.

The logs are first sawed into blocks, then chipped and reduced to sawdust by the usual mechanical means. Direct steam from a separate steam generator (operating at about 8 atmospheres pressure) is injected into the stills charged with chips and sawdust. Distillation of one charge lasts 24 hr. The oil is collected in Florentine flasks constructed for the separation of oil heavier than water. The oil is then filtered through flannel, cotton, and filter paper, the better equipped distilleries using centrifuges instead of filters.

There seem to exist several varieties of *Ocotea cymbarum* trees, distinguished by the color of their wood and giving different yields of oil. This question, however, requires further botanical study. It is also possible that the variation in the color of the wood may be due to its age.

Dark sassafras wood is said to yield about 1.5 per cent of oil, brown wood 1.2 per cent, and yellow wood about 0.9 per cent of oil.

Not all distilleries are in a position to supply oil of high safrole content, probably because they do not possess adequate distilling equipment. People in the State of Santa Catharina are known for their thrift, and hesitate to invest money in costly new equipment, especially in view of the low prices of the oil.

Most of the larger and better equipped distilleries are able to produce oils of high safrole content, but not infrequently it happens that the safrole content varies in the course of a year, although distillation is carried out by the same method. Quite likely, the safrole content depends upon the place of origin, the exposure and age of the tree, the period of cutting, etc., a question not yet clarified and requiring systematic study.

Total Production.—Various estimates, up to 300 metric tons of oil per year, have been given, but very probably actual production amounts to not more than 20 tons of oil per month, or about 240–250 tons a year. An exact estimate is difficult to obtain, because each producer seems inclined to include in his own output also that of his neighbors and relatives (and many of the distillers are related).

Physicochemical Properties.—Genuine Brazilian oils of *Ocotea cymbarum* examined in the New York laboratories of Fritzsche Brothers, Inc., had properties varying within the following limits:

Specific Gravity at 25°/25°	1.076 to 1.092
Optical Rotation at 25°	−0° 30′ to −2° 27′
Refractive Index at 20°	1.5327 to 1.5363
Congealing Point	+7.4° to +9.3°, in exceptional cases as low as +6.2°
Solubility at 25°	Soluble in 8 to 10 vol. of 80% alcohol, often with faint haziness

The safrole content of a high-grade *Ocotea cymbarum* oil should not be lower than 90 per cent. For standard methods of assay, see Vol. I of this work, p. 329. A new method has recently been suggested by Shukis and Wachs.[12]

Machado[13] reported these properties of Brazilian sassafras oil:

Specific Gravity at 25°/25°	1.0760 to 1.091
Optical Rotation at 25°	−0° 55′ to −2° 24′
Refractive Index at 20°	1.5251 to 1.5363
Congealing Point	+8.0 to +9.3°
Safrole Content	84 to 90%

Chemical Composition.—Investigating the chemical composition of oil of *Ocotea cymbarum,*[14] Hickey[15] noted that the identified optically active compounds in the Brazilian oil are laevorotatory, whereas those in the oil of *Sassafras albidum* (Nutt.) Nees, the North American (official) sassafras oil, are dextrorotatory. Hickey observed the presence of the following substances in oil of *Ocotea cymbarum:*

Valeraldehyde. In the fraction b. 101°–103°. Identified by means of its 2,4-dinitrophenylhydrazone m. 97°–98°.

l-α-Pinene. In the fraction b. 155°–160°. Oxidation yielded *l*-pinonic acid, the semicarbazone of which melted at 203.5°–204.5°.

Furfural. In the fraction b_{759} 160°–165°. Identified by means of its *p*-nitrophenylhydrazone m. 153°–154°.

Cineole. In the fraction b. 170°–180°. Characterized by the preparation of the *o*-cresol addition product m. 55.5°–56.5°.

Benzaldehyde. 2,4-Dinitrophenylhydrazone m. 237°.

A Compound(?). The fraction b_{758} 215°–225° had a camphoraceous odor and consisted of a compound which was not further characterized.

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[12] *Anal. Chem.* **20** (1948), 248. Cf. Littlejohn, *Perfumery Essential Oil Record* **40** (1949), 422. Littlejohn highly recommends this new method.

[13] *Bol. divulgacão inst. óleos* (1945), No. 3, 21. *Chem. Abstracts* **41** (1947), 7058.

[14] In his publication Hickey uses the term *Ocotea pretiosa.* To prevent confusion we shall refer to the oil as *Ocotea cymbarum,* the term by which the oil is admitted to the United States.

[15] *J. Org. Chem.* **13,** No. 3 (1948), 443.

Safrole. The chief constituent, amounting to almost 93 per cent of the oil, was identified by means of its picrate m. 104°–105.2°.

Eugenol. In the fraction b_6 118°–120°. Characterized by means of its benzoate m. 68.5°–69.5°.

A Sesquiterpene(?). The fraction b_1 110°–114° contained a hydrocarbon, probably a sesquiterpene.

Hickey,[16] as a result of his investigation, reported that the quantitative composition of Brazilian sassafras oil (*Ocotea cymbarum*) compared with that of North American (official) sassafras oil (*Sassafras albidum* [Nutt.] Nees) is as follows:

Components	*Ocotea cymbarum* (*Per Cent*)	*Sassafras albidum*[17] (*Per Cent*)
Safrole	92.9	80.0
α-Pinene	0.7	Less than 10.0
Phellandrene		Less than 10.0
d-Camphor	.	6.8
Eugenol	0.6	0.5
n-Valeraldehyde	0.001	
Furfural	0.17	
Cineole	0.21	
Benzaldehyde	0.03	
Sesquiterpenes, high boiling constituents and residue	ca. 5.1	3.0

Use.—Oil of *Ocotea cymbarum* is employed largely for the isolation of safrole and its conversion into heliotropin. In many technical preparations, soaps, sprays, disinfectants, and deodorants, for example, Brazilian sassafras oil also replaces the Japanese artificial sassafras oil, which is a certain fraction of camphor oil.

Brazilian sassafras oil, however, cannot be substituted for the North American official sassafras oil, *Sassafras albidum* (Nutt.) Nees, as the Brazilian oil is distilled from a different plant and has not been recognized by the U. S. Pharmacopoeia.

Suggested Additional Literature

Paulo Agostinho de Matos Araujo, "Sassafras Oil in the State of Santa Catharina," *Bol. divulgacão inst. óleos* (1945), No. 3, 31 (in Portuguese). *Chem. Abstracts* **41** (1947), 7058

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[16] *Ibid.*

[17] According to Power and Kleber, *Pharm. Rev.* **14** (1896), 101.

OIL OF LAUREL LEAVES

Essence de Laurier *Aceite Esencial de Laurel de las Hojas*
Loorbeerblätteröl *Oleum Lauri Foliorum*

Botanical Origin and Producing Regions.—*Laurus nobilis* L., an evergreen tree or shrub, is cultivated in many temperate and warm parts of the world, particularly in the countries bordering the Mediterranean. In ancient Greece and Rome its leaves and branchlets were used as garlands to be bestowed upon heroes on festive occasions. The dried leaves, also called "sweet bay" are esteemed as a flavoring material in culinary preparations (soups, fish, ragouts), especially in the French type of cuisine. They contain an essential oil of aromatic, spicy odor and flavor, which can be isolated by steam distillation.

The leaves of the true *Laurus nobilis* L. must not be confused with those of the West Indian bay tree (*Pimenta racemosa* [Mill.] J. W. Moore), the Californian bay laurel (*Umbellularia californica* Nutt.) or the cherry laurel (*Prunus laurocerasus* L.). The leaves of the last named species are poisonous because of their content of prussic acid.

Small quantities of laurel leaf oil are produced in several Mediterranean countries, among them Algeria, Morocco, Spain, Southern France, Italy, Palestine, and the island of Cyprus.

Prior to World War II the commercially most important lots came from Dalmatia, where the oil was distilled on the island of San Martino di Cherso. There the laurel trees are pruned from September to March. The fresh terminal branchlets and leaves yield about 0.5 per cent of volatile oil, the dried material about 0.8 per cent.[1] Before the last war much of the oil produced in Dalmatia was exported to Germany, and from there re-exported.

Gildemeister and Hoffmann [2] report yields of oil ranging from 1 to 3 per cent.

Physicochemical Properties.—Oil of laurel leaves possesses a characteristic sweet and spicy odor, somewhat reminiscent of cajuput. According to Gildemeister and Hoffmann [3] the properties of the oil vary within the following limits:

Specific Gravity at 15°	0.910 to 0.944
Optical Rotation	−4° 40′ to −21° 40′
Refractive Index at 20°	1.460 to 1.477
Acid Number	Up to 3

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[1] Personal observation by the author.

[2] "Die Ätherischen Öle," 3d Ed., Vol. II, 732.

[3] *Ibid.*

Ester Number	21 to 55
Ester Number after Acetylation	36 to 96
Solubility	Soluble in 1 to 3 vol. of 80% alcohol; in some cases soluble in 3 to 10 vol. of 70% alcohol

Genuine laurel leaf oils examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.912 to 0.926
Optical Rotation	−16° 16′ to −18° 11′
Refractive Index at 20°	1.4669 to 1.4695
Saponification Number	13.0 to 36.6
Solubility	Soluble in 1 vol. and more of 80% alcohol

Chemical Composition.—The chemical composition of laurel leaf oil (*Laurus nobilis* L.) has been investigated by Wallach,[4] Schimmel & Co.,[5] Thoms and Molle,[6] Haensel,[7] Morani,[8] and Rutovski and Semlyanskaya,[9] who identified the following constituents:

Pinene. In the lowest boiling fraction of the oil Wallach observed α-pinene, which he identified by the preparation of its nitrolpiperidine m. 118°. According to Haensel, α-pinene is present in the laevorotatory form.

Morani found that the Italian oil contains β-pinene, which he characterized by oxidation to nopinic acid m. 126°–128°.

α-Phellandrene. Identified by Haensel, and by Morani.

Cineole. Observed by Wallach.

l-Linaloöl. Schimmel & Co. identified *l*-linaloöl by preparation of its phenylurethane m. 65°, and by oxidation to citral.

l-α-Terpineol. Morani first identified *l*-α-terpineol by means of its phenylurethane m. 113°. Somewhat later, Rutovski and Semlyanskaya observed the presence of this terpene alcohol in a laurel leaf oil originating from the Caucasus. These authors prepared the phenylurethane m. 110°, the nitrosochloride m. 99°, and the nitrolpiperidine m. 151°.

Geraniol. Identified by means of the diphenylurethane m. 83°, and by oxidation to citral. The latter yielded the β-naphthocinchoninic acid compound m. 197° (Thoms and Molle).

Eugenol. Characterized by preparation of benzoyl eugenol m. 70° (Schimmel & Co.).

Eugenol Acetate. Observed in the Italian oil by Morani, and in the above-mentioned Caucasian oil by Rutovski and Semlyanskaya.

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[4] *Liebigs Ann.* **252** (1889), 96.

[5] *Ber. Schimmel & Co.,* April (1899), 31; April (1906), 45.

[6] *Arch. Pharm.* **242** (1904), 161.

[7] *Chem. Zentr.* (1908), I, 1837.

[8] *Ann. chim. applicata* **16** (1926), 21.

[9] *Trans. Sci. Chem. Pharm. Inst. Moscow,* No. 19 (1928), 157. *Chem. Abstracts* **24** (1930), 3603.

Methyl Eugenol. Identified by Schimmel & Co. Later Morani found this constituent in an Italian oil. Oxidation yielded veratric acid m. 178°–180°.

A Sesquiterpene(?). In the highest boiling fractions of their Caucasian oil, Rutovski and Semlyanskaya observed a sesquiterpene: b_{12} 118°–122°, d_{20}^{20} 0.9335, α_D $-16° 48'$, n_D^{20} 1.4902.

This sesquiterpene, which yielded a nitrosochloride m. 113°, was not identified.

Acetic Acid, Isobutyric Acid, Valeric (Isovaleric?) Acid. So far as the acid constituents of the oil are concerned, Thoms and Molle observed acetic acid, isobutyric acid, and valeric (isovaleric?) acid.

Esters. The esters present in the oil are composed of linaloöl, terpineol, geraniol, and eugenol, combined with several acids of which Thoms and Molle identified acetic-, valeric-, caproic-, and an acid $C_{10}H_{14}O_2$, m. 146°–147°.

Thoms and Molle suggested the following quantitative composition of laurel leaf oil:

	Per Cent
Eugenol, in free form	1.7
Eugenol, in ester form	0.4
Cineole	50.0
Acid $C_{10}H_{14}O_2$	0.07

The ratio of valeric acid to caproic acid in the mixture of higher fatty acids was 4:6.

According to an anonymous writer,[10] two laurel leaf oils from the island of Cyprus contained 66 per cent and 71 per cent, respectively, of cineole.

The above-mentioned Italian laurel leaf oil investigated by Morani had the following composition:

	Per Cent
Terpenes	12.0
Cineole	45.0
Alcohols, free	18.0
Esters, mainly acetates	13.0
Eugenol	0.53
Eugenol Acetate	1.1
Methyl Eugenol	3.0
Sesquiterpenes	3.0–4.0

Use.—Oil of laurel leaves is a valuable adjunct in the flavoring of all kinds of food products, particularly meats, sausages, canned soups, baked goods, confectionery, etc. The oil replaces the dried leaves to great advantage, because it can be dosed more exactly and therefore give more uniform results than the dried leaves.

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[10] *Bull. Imp. Inst.* **11** (1913), 430.

SUGGESTED ADDITIONAL LITERATURE

M. G. Cancer, "Results of Distillation of Wild Plants from Calabria," *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **14** (1939), 147. *Chem. Zentr.* (1940), II, 2825. *Chem. Abstracts* **36** (1942), 5955.

G. Rovesti, "Laurel (*Laurus nobilis* L.) and Its Utilization," *Rivista ital. essenze profumi, piante offic., olii vegetali, saponi* **23** (1941), 220. *Chem. Abstracts* **35** (1941), 8332.

OIL OF CALIFORNIA BAY LAUREL

(Oil of Mountain Laurel)

The leaves of the California laurel or bay tree *Umbellularia californica* Nutt. have been used locally for a long time. Indians and early Spanish settlers employed them as a condiment, and as ingredients in counterirritants and insecticides. According to Swancc,[1] the possibility of fly-blow in meat will be eliminated, if the crushed leaves are packed in and around game immediately after killing. The meat will then assume a pleasant spiced character.

When gathering large amounts of leaves and twigs, caution must be exercised to prevent irritation of the pulmonary passages, irritation of nose and eyes, and superficial dermatitis.

Occurrence and Description of the Tree.—According to Aries and Kidder,[2] the California bay or laurel tree, an evergreen, grows throughout almost all of the state of California, as well as in southwest Oregon. In Oregon it is found as a straight tree, 60 to 80 ft. high, with a clean, straight trunk from 30 to 40 ft. long and a narrow crown of close, small upright branches. The height of the branches from the ground makes it impractical to harvest the leaves from such a tree. However, in California, the tree appears in a many-stemmed shrubby form, in clumps and thickets, from 10 to 15 ft. high. The harvesting of leaves under these conditions is a much simpler matter. New leaves are produced on the stems throughout the summer, the stems growing constantly in height and the branches being heavily foliaged. The leaves of

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[1] Conference on the Cultivation of Drug and Associated Economic Plants in California, Proceedings (1944), 82. (California State Department of Education and California Polytechnic School, San Luis Obispo, Calif.)

[2] *Ibid.*, December (1947), 218.

a season's growth usually persist on the branches for about two years, but some may be retained for five or six years.

To collect the leaf and branch material, long-arm pruning clippers capable of clipping branches more than an inch thick should be used. By this method most of the trees of average height growing in California can be pruned. Packing of stills with branches over 15 mm. thick is inconvenient.

Yield of Oil.—According to Swance,[3] the yield of oil varies and depends on the season and location. The yield was found to be greatest in summer and fall. The leaves and stems (stems not over 5 mm. thick) yield as high as 4.1 per cent of oil. The stems alone yield from 0.56 to 1.13 per cent; the leaves alone as much as 4.69 per cent of oil. The average of seven distillations of leaves and stems was 2.87 per cent.

Physicochemical Properties.—The oil possesses an extremely pungent odor and is strongly lachrymose, causing severe headache on inhalation. The oil has, therefore, to be handled with great care. The flavor is warm and camphoraceous.

Gildemeister and Hoffmann [4] reported the following physicochemical properties for several California bay oils:

Specific Gravity at 15°	0.916 to 0.948
Optical Rotation	−22° 0′ to −24° 0′
Refractive Index at 20°	1.47210
Acid Number	0.4 and 4.7
Ester Number	5.5 and 5.6
Ester Number after Acetylation	29.9 and 50.8
Solubility	Soluble in 1.5 to 2.2 vol. of 70% alcohol; soluble in 1 vol. and more of 80% alcohol. The diluted solutions are occasionally opalescent

Shipments of genuine California bay oils received and examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.927 to 0.934
Optical Rotation	−26° 13′ to −28° 20′
Refractive Index at 20°	1.4750 to 1.4769
Ketone Content, Calculated as Umbellulone (Sodium Sulfite Method)	40 to 43%
Solubility	Soluble in 1.5 to 2 vol. and more of 70% alcohol

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[3] *Ibid.*, December (1944), 82.

[4] "Die Ätherischen Öle," 3d Ed., Vol. II, 710.

Eliminating the first fractions (b. up to 155°, or about 8 to 10 per cent of the oil), Swanee[5] found that the remaining oil had a pleasant odor.

Chemical Composition.—The first investigations of the chemical composition of the volatile oil derived from the California bay tree were carried out by Heaney,[6] and by Stillmann,[7] but were rather inconclusive. Later, Power and Lees,[8] Schimmel & Co.,[9] Semmler,[10] and Lees[11] and Tutin[12] succeeded in elucidating not only the chemical composition of the oil, but also the structure of its chief constituent, viz., umbellulone, a ketone, $C_{10}H_{14}O$, of very pungent, mint-like odor.

According to Power and Lees,[13] the oil contains the following compounds:

Eugenol. In small quantities; identified by means of its benzoyl compound m. 69°–70°.

l-α-Pinene. Identified by preparation of its nitrolpiperidine m. 119°–120°, and nitrolbenzylamine m. 124°–125°.

Cineole. Iodol compound m. 115° (Schimmel & Co.[14]).

Safrole. Very small quantities. Characterized by oxidation to piperonal m. 35° (Power and Lees).

Methyl Eugenol. Identified by means of the bromoeugenol methyl ether dibromide m. 78°–79°, and by oxidation to veratric acid m. 177° (Power and Lees).

Formic Acid and Higher Fatty Acids. The oil contains traces of formic acid and higher fatty acids in free form (Power and Lees).

Umbellulone. The chief component of the oil, umbellulone, is present in amounts ranging from 40 to 60 per cent (Power and Lees).

Regenerating the substance from its semicarbazido-semicarbazone m. above 200°, Semmler[15] obtained the pure ketone $C_{10}H_{14}O$, which had these properties: b_{10} 92.5°–93°, d_{20} 0.950, α_D $-36° 30'$, n_D 1.48325. Power and Lees[16] reported b_{749} 219°–220°.

For further details and the structural formula, the reader is referred to Vol. II, p. 440, of this work.

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[5] Conference on the Cultivation of Drug and Associated Economic Plants in California, Proceedings (1944), 82. (California State Department of Education and California Polytechnic School, San Luis Obispo, Calif.)

[6] *Am. J. Pharm.* **47** (1875), 105. *Pharm. J.* [3] **5** (1875), 791.

[7] *Ber.* **13** (1880), 630.

[8] *J. Chem. Soc.* **85** (1904), 629.

[9] *Ber. Schimmel & Co.*, October (1893), Table in Appendix, 27.

[10] *Ber.* **40** (1907), 5017; **41** (1908), 3988.

[11] *J. Chem. Soc.* **85** (1904), 644.

[12] *Ibid.* **89** (1906), 1104; **91** (1907), 271, 275; **93** (1908), 252.

[13] *Ibid.* **85** (1904), 629.

[14] *Ber. Schimmel & Co.*, October (1893), Table in Appendix, 27.

[15] *Ber.* **40** (1907), 5017; **41** (1908), 3988.

[16] *J. Chem. Soc.* **85** (1904), 629.

As a result of their investigation, Power and Lees [17] suggested the following quantitative composition for California bay oil:

Mixture of fatty acids containing formic acid	Traces
Safrole	Small quantities
Eugenol	1.7%
l-α-Pinene	6.0%
Eugenol Methyl Ether	10.0%
Cineole	20.0%
Umbellulone	60.0%
	100.0%

More recently Haagen-Smit [18] arrived at a somewhat different composition of California bay oil:

Eugenol	About 1.4%
Eugenol Methyl Ether	2.5%
Pinene	6.0%
Cineole	15.0%
Umbellulone	52.0%
Sesquiterpenes	Small amounts

Use.—Since it irritates the mucous membranes of the eyes and nose, and causes severe headache and irregular respiration at times, the oil must be used with the greatest of care, and only in minute quantities. Due to the presence of umbellulone, inhalation of the oil raises the blood pressure.

Because of its physiological effects, the oil is now rarely used.

The possibility has been suggested of using California bay oil as a source of thymol, by conversion of umbellulone into this phenol. However, considering the high cost of labor in the United States and the difficulty of collecting the plant material from the scattered trees, it would appear that under normal conditions thymol prepared from umbellulone cannot compete with the synthetic product, or with thymol derived from certain varieties of oil of *Eucalyptus dives,* or from Spanish thyme oil.

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[17] *Ibid.*

[18] Conference on the Cultivation of Drug and Associated Economic Plants in California, Proceedings (1944), 82. (California State Department of Education and California Polytechnic School, San Luis Obispo, Calif.)

OIL OF MASSOI BARK

There has been a great deal of confusion regarding the taxonomy of the plant, the bark of which, on steam distillation, yields oil of massoi. It was only in 1937 that Abe[1] succeeded in clarifying the problem of the origin and the properties of true massoi bark oil. The most recent and thorough investigation has been carried out by Meijer.[2]

Meijer showed that in a number of cases where oil of massoi bark has been described in literature, the description actually refers to the oil of lawang bark. Oil of massoi bark does not contain eugenol, whereas oil of lawang bark contains a considerable amount. The chief constituent of massoi bark oil, massoilactone, was first isolated by Abe, but its correct structure was established by Meijer[3] as a lactone $C_{10}H_{16}O_2$, details of which will be found in Vol. II of this work, p. 688.

According to Meijer, the principal oil-containing barks of Netherlands New Guinea are those of massoi and lawang. Massoi bark has been collected for centuries. Trade in the bark was once of such importance that, in the seventeenth century, the East India Company organized special expeditions to New Guinea to procure the bark.

The latter, handled in bundles weighing about 10 kg., consists of pieces about 100 cm. in length and 5 cm. in width. It has some medicinal value and forms an ingredient of Javanese medicines, called obat or djamoe, which consist of a mixture of various herbs.

The botanical name of the plant from which true massoi bark is derived had been a matter of much controversy until Salverda[4] made an expedition to New Guinea and collected several authentic specimens of the bark. These were identified as *Cryptocaria massoia* (fam. *Lauraceae*) at the government station in Buitenzorg. Previously Gildemeister and Hoffmann[5] had reported several names for the plant, viz., *Massoia aromatica* Beccari, *Cinnamomum xanthoneuron* Blume, and *Cinnamomum culilawan* Blume.

A great deal of misunderstanding has occurred in the description of lawang and massoi oils. Very often literature refers to a massoi oil where, according to physicochemical properties and constituents, the reference should be

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[1] *J. Chem. Soc. Japan* **58** (1937), 246.

[2] *Rec. trav. chim.* **59** (1940), 191.

[3] *Ibid.*

[4] *Rapport van een oriënteerende exploratie in Z. W. Nw. Guinea* van Nov. 1937 tot Mei 1938, 93. See also *De Bergcultures* **13** (1939), 1265. Cf. Meijer, *Rec. trav. chim.* **59** (1940), 192.

[5] "Die Ätherischen Öle," 3d Ed., Vol. II, 714.

to lawang oil. Woy[6] described, as the essential oil of massoi bark, an oil that contained 80 per cent of eugenol, and 6 per cent of terpenes and safrole. Eugenol gives a greenish color with aqueous ferric chloride in alcoholic solution. Meijer,[7] however, definitely proved that the essential oil of massoi bark does not contain substances which give a color reaction on treatment with ferric chloride, a very simple test to distinguish between massoi oil and lawang oil. The error of mistaking lawang oil for massoi oil has been made by several other authors, for example, Schimmel & Co.,[8] Burger,[9] and Parry.[10] An article by an anonymous writer [*Bull. Imp. Inst.* **23** (1925), 423] on massoi bark from Papua also contains details on the essential oil of these barks; according to this article massoi oil should contain from 60 to 75 per cent of eugenol. A West Australian firm regularly advertises "massoi bark oil" with 70 to 75 per cent of eugenol. The first author to give a correct description and who investigated genuine massoi bark oil was Abe.[11] This oil (yield 1.8 to 2.4 per cent) had the following properties:

Specific Gravity at 20°/20°	0.9822
Optical Rotation	−87° 6′
Refractive Index at 20°	1.4721

Meijer[12] obtained from Salverda (see above) a few authentic specimens of massoi bark, which on steam distillation yielded 1.7 to 2.4 per cent of volatile oil with these properties:

	I	*II*	*III*	*IV*
Specific Gravity at 27.5°/4°	0.9821	0.9643	0.9695	0.9782
Optical Rotation	−94° 0′	−64° 0′	−74° 0′	−106° 0′
Refractive Index at 20°	1.4770	1.4726	1.4717	1.4749

In all cases the ferric chloride test for eugenol was negative. Massoi oil has a peculiar, sweetish smell; it burns the skin. Viewing the figures given above, it appears that the properties of massoi oils show some differences. According to Salverda,[13] the massoi tree occurs in a few varieties; the natives distinguish a variety with a thin bark, and one with a thick bark.

If we compare these properties with those of lawang oil, it is quite obvious

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[6] *Arch. Pharm.* **228** (1890), 22, 687.

[7] *Rec. trav. chim.* **59** (1940), 191.

[8] *Ber. Schimmel & Co.* (1917), 33.

[9] *Riechstoff Ind.* **4** (1929), 121.

[10] "Chemistry of Essential Oils," 4th Ed., Vol. I, D. Van Nostrand Co., Inc., New York (1921), 150.

[11] *J. Chem. Soc. Japan* **58** (1937), 246.

[12] *Rec. trav. chim.* **59** (1940), 191.

[13] *Rapport van een oriënteerende exploratie in Z. W. Nw. Guinea* van November 1937 tot Mei 1938, 93. See also *De Bergcultures* **13** (1939), 1265. Cf. Meijer, *Rec. trav. chim.* **59** (1940), 192.

that these two oils are entirely different. Meijer[14] reported the following properties of two samples of genuine lawang oil:

	I	II
Specific Gravity at 15°/15°	1.060	1.0559
Optical Rotation	−0° 54′	−0° 48′
Refractive Index at 20°	1.534	1.5350
Eugenol Content	60%	94%

Lawang oil has a characteristic odor of cloves and nutmeg, and undoubtedly originates from the bark of several species of *Cinnamomum,* which is the reason for the great variation in eugenol content.

Abe[15] found that the essential oil of massoi bark contains a substantial amount of a lactone $C_{10}H_{16}O_2$, which he named massoilactone. Since this lactone also passes into solution when the essential oil is treated with a solution of potassium hydroxide, as in the treatment of eugenol, it is quite obvious that a mistake may arise, if the amount of essential oil taken up by the potassium hydroxide solution is considered as eugenol.

The correct structural formula of massoilactone was established by Meijer,[16] details of which will be found in Vol. II of this work, p. 688.

True massoi bark oil is not an article of commerce, but oil of lawang is used in perfumes and flavors in conjunction with oil of clove and nutmeg.

OIL OF CINNAMON

Essence de Canelle de Ceylan
Aceite Esencial Cinamon (Canela) de Ceilan   *Ceylon Zimtöl*
Oleum Cinnamomi Zeylanici

History.—The story of cinnamon reaches back into antiquity. Flotillas of sturdy vessels, their sails bulging in the steady monsoon winds, winged their way across the Indian Ocean's blue billows and along Arabia's barren shores toward Egypt where the precious spice could be conveyed to sharp faced dealers from Phoenicia who supplied the Greek and Roman trade. Or the spice was carried on camel back across Mesopotamia's timeless caravan trails, now buried in sand and forgotten, from the Persian Gulf to Babylon, and finally to Sidon and Tyre on the Mediterranean.

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[14] *Rec. trav. chim.* **59** (1940), 191.

[15] *J. Chem. Soc. Japan* **58** (1937), 246.

[16] *Rec. trav. chim.* **59** (1940), 191.

In their quest for spices, early Portuguese explorers rounded the Cape of Good Hope and, conquering Ceylon, forced the Singhalese kings to pay tribute in the form of cinnamon bark collected from wild-growing trees. About 1770, during their rule over the island, the Hollanders started to plant cinnamon and established a strict control over the spice by regulating production and destroying any surplus in order to keep prices high. Taking advantage of Holland's embroilment in the Napoleonic wars, England took over Ceylon in 1796, and its cinnamon industry became a monopoly of the powerful East India Company which lasted until 1833.

Botanical Origin.—There has been much confusion, in the trade as well as in official standard texts, in regard to the botanical origin of cinnamon bark, and the oil distilled from it. In fact, in some cases it is almost impossible to establish to what particular botanical species or varieties certain types of cinnamon bark belong. Climatic and soil conditions affect the Ceylon cinnamon plant so profoundly that the bush or tree, when grown in other countries, produces a bark quite different from that of the Ceylon-grown bush. Moreover, the appearance and quality of the bark depend upon the age of the tree, the method of collection and preparation. For example, the dried *inner* bark of the shoots of *coppiced bushes* (true Ceylon cinnamon) differs substantially from the dried *whole* bark of *semiwild trees* (Madagascar cinnamon), although the Madagascar cinnamon plant was originally introduced from Ceylon. Similar conditions apply to the Seychelles cinnamon.

Official standard works describe three principal types of cinnamon, but in regard to the volatile oils do not always clearly differentiate between them.

1. Ceylon cinnamon. The National Formulary, Eighth Edition, describes as Ceylon cinnamon the dried inner bark of the shoots of coppiced trees of *Cinnamomum zeylanicum* Nees (fam. *Lauraceae*). The British Pharmacopoeia of 1948 recognizes the same drug under the collective term cinnamon, and specifies that the essential oil distilled from it contain not less than 50 per cent, and not more than 65 per cent, by weight, of cinnamic aldehyde. The British Pharmacopoeia of 1948 does not list cassia or cassia oil.

The present monograph will deal chiefly with Ceylon and closely related cinnamon oils.

2. Saigon cinnamon. The Saigon cinnamon tree is of medium height, originally native to China. Its bark is collected chiefly in the mountains of Anam (French Indo-China) from semiwild trees. Most of the bark comes from branches or from the trunks of young trees, but chips of thicker bark are occasionally included. The principal shipping port is Saigon, although

much of the spice reaches Europe and America through transshipment via Hong Kong.

The Saigon cinnamon bark is used only as spice, not for the commercial distillation of oil.

The U. S. Pharmacopoeia, Thirteenth Revision, recognizes as cinnamon the Saigon variety, i.e., the dried bark of *Cinnamomum loureirii* Nees (fam. *Lauraceae*).

3. Cassia cinnamon. The cassia tree grows semiwild and cultivated in the provinces of Kwangsi and Kwangtung (southeastern China). The dried bark is used in China as spice, or exported via Canton and Hong Kong. The leaves and terminal branches serve for local distillation of cassia oil, large quantities of which are exported (cf. the monograph on "Oil of Cassia").

The U. S. Pharmacopoeia, Thirteenth Revision, recognizes as cinnamon oil, or cassia oil, the volatile oil distilled with steam from the leaves and twigs of *Cinnamomum cassia* (Nees) Nees ex Blume (fam. *Lauraceae*), rectified by distillation. The oil contains not less than 80 per cent, by volume, of total aldehydes.

Hérail[1] considers both the Saigon and the cassia cinnamon to be varieties of *Cinnamomum obtusifolium* Nees, the Saigon bark originating from the var. *loureirii* Perrot and Eberhardt, the cassia bark from the var. *cassia* P. and E. This close botanical relationship seems to be confirmed by the similarities in the volatile oils of the two varieties. Steam distilling imported Saigon cinnamon bark and cassia bark, the present author obtained in both cases almost identical oils, which exhibited all the characteristics of true cassia oil (90 per cent of aldehydes, chiefly cinnamic aldehyde).

The Federal Security Agency, Food and Drug Administration, Washington, D. C.,[2] defines as oil of cinnamon, oil of cassia, and oil of cassia cinnamon the lead-free volatile oil obtained from the leaves and bark of *Cinnamomum cassia* (L.) Blume. The oil contains no less than 80 per cent, by volume, of cinnamic aldehyde.

The same government office specifies as oil of Ceylon cinnamon the lead-free volatile oil obtained from the bark of the Ceylon cinnamon (*Cinnamomum zeylanicum* Nees). The oil contains not less than 65 per cent, by weight, of cinnamic aldehyde[3] and not more than 10 per cent, by weight, of eugenol.

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[1] "Traité de Matière Médicale" (1912), Paris.

[2] "Flavoring Extracts Under the Federal Food, Drug and Cosmetic Act."

[3] The aldehydes present in Ceylon cinnamon bark oil consist chiefly of cinnamic aldehyde. See section on "Chemical Composition," below.

The following will deal chiefly with the oils derived from Ceylon cinnamon bark and leaves. The oil from the bark differs entirely from that of the leaves in regard to chemical composition. The Ceylon cinnamon bush differs from the Chinese cassia tree in morphological and physiological respects: the leaves of the former contain an essential oil which consists of about 80 per cent of eugenol, whereas the leaves of the cassia contain an essential oil which consists of about 90 per cent of total aldehydes (chiefly cinnamic aldehyde).

Oil of Cinnamon Ceylon

Botanical Description.—Ceylon cinnamon is the dried inner bark of the shoots of coppiced bushes (the external coating of the bark having been removed). It is a fancy grade of cinnamon, of characteristic, aromatic, delicate, and sweet flavor, and of uniform light brown-yellowish color.

Cinnamomum zeylanicum Nees, the true Ceylon cinnamon plant, originally occurred on the island in a wild state. As such, it is a much branched and bushy evergreen tree, which attains a height of 30 to 50 ft. The bark is thick and scabrous and has the characteristic odor and flavor of cinnamon. The numerous strong branches are horizontal and declining. The 4 to 7 in. leaves emanate a spicy odor when crushed between the fingers. They are opposite, oblong-oviate, bluntly pointed at the tips and, when mature, shiny green on the upper surface and lighter colored on the under. The wild-growing trees are propagated through the droppings of birds that are very fond of the fruit. The bulk of bark, however, comes from cultivated plants, wild trees being little used for this purpose.

The cultivated plants are not permitted to grow into trees. By vigorous cutting back, they are trained to remain bushes with slender stems; in other words, coppiced shrubs which never exceed 8 ft. in height. They grow well in light, white sand, at altitudes preferably between 200 and 300 ft., in a humid, warm and sunny climate of 80° F. average temperature.

There exist in Ceylon several varieties of *Cinnamomum zeylanicum,* some growing wild, others being cultivated. Some of them produce bark with a very strong flavor, others yield inferior bark. Expert peelers are able to distinguish between them. Care is taken to eliminate undesirable bushes and to plant only the best varieties.

Producing Regions.—There are in Ceylon two chief centers of planted cinnamon: (1) The Negombo district, along the seashore, about 30 miles north of Colombo. Owing to a good soil of sandy texture, this region produces the highest quality of cinnamon. The quills are thinner and of better appearance than those of the cinnamon produced in the southern regions, but the flavor is similar. The Negombo district used to produce large quantities of cinnamon, the best grades of which were exported largely to Spain. The Spanish civil war (1936–1939) and economic and political developments in general have changed the picture, and many of the cinnamon plantings in the Negombo district are now replaced with coconut. (2) The regions south of Colombo, stretching along the seashore, with many small cinnamon plantings. The main centers here are Ambalangoda, Galle, and Matara in the far south of the island. The bulk of cinnamon originates from here, but the quills, probably because of the harder gravel soil, are somewhat thicker and coarser than those from the Negombo district.

In general, cinnamon plantations are scattered along Ceylon's western seacoast, from Negombo all the way down to Matara. The planters, as well as the local dealers, are for the most part Singhalese, who own estates of from 2 to 300 acres, but mostly small holdings of less than 20 acres. For the last twenty-five years, the total plantings have averaged 25,000 acres. As was said, the cinnamon plantings in the south have expanded, while those in the north have been partly abandoned. This movement from north to south is still going on, Matara with its suitable soil becoming an increasingly important center. The acreage of cinnamon plantings directly reflects the market price of the quills, as compared with prices of other Ceylon produce. Recently, rubber and coconut have made large inroads into the acreage formerly devoted to cinnamon.

Aside from the planted cinnamon, there is also a very small amount of wild cinnamon being produced in Ceylon, and used almost exclusively for local consumption. It is difficult to prepare quills from the thick bark of wild growing cinnamon trees, but the native dealers sometimes mix chips of wild cinnamon with those of planted cinnamon, even though this practice is prohibited, as a fraudulent manipulation. Experts can identify wild cinnamon by its appearance and by its somewhat acid and comparatively weak taste. It originates from the Ratnapura and Badulla districts in the southwestern parts of Ceylon, where it grows spontaneously in the jungles, being propagated by birds.

Planting, Cultivating, and Harvesting.—To obtain seed, the fruit on the bushes is either protected with bags against birds, or collected before ripe, after which it is left to rot in the shade until the clean seed can be removed from the mass of pulp by trampling. The washed and shade-dried seed is planted in a nursery (about 8 seeds in one hole), well watered and shaded. After six or seven months, the young plants are ready for transplanting. If a nursery bed is not available, the seedlings are purchased from a neighboring plantation and then set out 6 or 7 ft. apart on virgin land. After about three years, during which they have to be pruned to grow straight, the young stems are cut down to a few inches aboveground. They are sometimes covered with earth to facilitate the development of stools, on which several shoots will grow. Every such coppicing produces a new crop of shoots, so that each stool always has fully developed shoots 6 to 8 ft. high and ready for cutting. The young ones are left until they reach full size about three years later.

The correct time for cutting is during the heavy rains, when an increased flow of sap between wood and bark permits easier separation of the latter. It is then that the reddish color of the young leaves begins to turn into a dark green. Most planters, therefore, prefer to harvest during the rainy season and the weeks immediately following the monsoon. Cutting continues practically throughout the year on a limited scale, however. The main crop reaches the market during July/August, a smaller one following in December/January. Few deliveries are made between February and April.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 19. Cinnamon production in Ceylon. Removal of the outer bark from a twig.

The first cutting of the young bush yields rather thick and hard quills, of somewhat inferior appearance. The quality improves with subsequent cuttings and especially with the pruning of the leaves. In fact, without pruning the growth of the young shoots would be seriously stunted, as they require ample air and sunshine. Depending upon prevailing prices of leaf oil, the pruned leaves and twiglets are used either for green fertilizing or for the distillation of leaf oil.

The cut stalks are brought to the cottages or sheds for immediate processing. The entire work is done by a special caste of cinnamon peelers, the ancient art being passed from father to son.

As has been pointed out, true Ceylon cinnamon is the inner bark of the

Ceylon cinnamon bush, of which the outer coating has been removed. This inner bark, which turns yellow-brown upon drying, contains the essential oil and the flavoring principles. The external coating has a weak and slightly acid flavor, the absence of which seems to account for the fine flavor for which true Ceylon cinnamon is so much appreciated. The same applies to the essential oil distilled from Ceylon cinnamon bark. The quills, under which form Ceylon cinnamon is marketed, consist of two or more dried tubes of inner bark which are tightly rolled together, after the hollow interior has been filled with small pieces of broken bark. Superior grades, however, should not contain any fillings of broken pieces. They are prepared as follows:

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 20. Cinnamon production in Ceylon. Preparation of cinnamon quills.

After the freshly cut branches of the cinnamon bush arrive at the working place, the leaf material is removed with bush knives, and the woody, inert external bark is scraped off with curved knives, great skill being required not to scrape or cut into the valuable inner bark. The removed outer bark may be used for green fertilizing. The longest straight stalks are selected to make the best quills. After the outer bark has been removed, a longitudinal incision, 6 to 8 in. long, is made with a sharp knife into the soft, white, inner bark, which is then very carefully and deftly peeled off the hard core. Thus, hollow tubes 6 or 8 in. long are obtained, into which smaller or broken pieces are packed. Finally, several of the 6 or 8 in. quills are telescoped together to form tubes about 36 in. long. These are rolled by hand while fresh and soft, and very slightly pressed. Obviously, native producers are tempted to fill the hollow tubes with inert foreign material, such as wood, sand, and earth, instead of true cinnamon. However, careful exporters, aware of the possibility of such a fraud, examine the quills when buying from the natives, before they make shipments abroad. It is, therefore, advisable for the consumer abroad to buy cinnamon quills only from reliable shippers who will give full guarantee for purity.

The rolled quills are laid on mats and dried for three days in the sun and for three days in the shade. The quills must be rolled by hand and slightly pressed every day during the drying process, because otherwise they will swell up and split. In the course of the drying operation, the originally white color of the quills slowly turns darker and assumes a yellow-brown tint. Drying also gives the quills the appearance of fairly strong sticks.

Yield per Acre.—One acre planted with cinnamon yields about 1.5 or 2 bales (a bale contains 100 lb.) of cinnamon quills, and, in addition, ½ cwt. of cinnamon chips and 15 to 20 cwt. of fresh, undried cinnamon leaves.

Commerce.—As a rule, the growers do not sell their cinnamon directly to exporters, but transport it to the nearest buying centers (Colombo, Ambalangoda, or Matara), where native dealers collect the bundles, bleach the quills if necessary, assort them into different qualities, and finally make them up into bales of approximately 100 lb. net. These dealers then enter contracts with the exporters in Colombo for 100 or more bales at a time.

Quality of the Cinnamon.—The quality and appearance of assorted cinnamon naturally depend a great deal upon the region of production and the care exercised in its preparation.

(A) Quills:

The quills, which actually consist of compound quills, usually have a length of about 1 m. and a thickness up to 1 cm. or more. They are pale brownish-yellow in color, and thin, brittle, and smooth in texture. They should contain no cork, except for a little around the scars, where the lateral branches have been removed. Every exporter has his own standards (which, however, vary but little). If deliveries are up to standard, no further work in respect to quality is required in the exporters' stores. One of the best known Colombo shippers, for instance, markets the quills under the following designations:

(1) "Fines" 00000 0000 000 00 0	00000 is the finest grade, 0 the coarsest. Best cinnamon is produced largely to the north of Colombo, near Negombo.
(2) "Barcelona" or "Spanish" I II III	A medium quality. B-I is slightly thicker than 0. B-II is about equal to "Hamburg" I. B-III consists of thin but "foxy" (i.e., reddish) quills, which have to be sorted out of

IV	fine cinnamon. B-IV is the same, but slightly thicker. (It should be mentioned here, however, that Barcelona grades are no longer sorted out for lack of demand from Spain.)
(3) "Hamburg" I II III IV	This cinnamon grows chiefly in the Ambalangoda and Matara districts. H-II is the standard grade, and consists of fairly even quills of about the thickness of a thumb. H-I is somewhat thinner, while H-III is very coarse cinnamon. H-IV is the same, but more "foxy" and barky.

(B) Quillings and Featherings:

While the quills arrive from the native dealers in rather uniform quality, the quillings, featherings, and chips require considerably more work in the stores of the exporters before they can be shipped. Quillings are relatively large pieces of quills broken off the regular quills through transport, bleaching, sorting, or baling. The so-called featherings are much smaller than the quillings; they are obtained by peeling off (not scraping) the inner bark of small twigs and twisted stalks. In other words, featherings consist of the inner bark from those parts of stalks and twigs which do not give straight quills of regular length. Featherings very often contain a small amount of chips also.

Although quillings and featherings are usually sold as "fair average quality of the season," it is nevertheless advisable to adhere to uniform quality which varies considerably with every shipper. A low price usually reflects a correspondingly low quality, because it is very easy to mix all sorts of refuse, stones, dust, etc., into featherings and quillings. Frequently newcomers in the trade spoil the market and, as a consequence, the name of the entire Ceylon cinnamon industry suffers. Reliable exporters who sell quillings and featherings as "fair average quality of the season" insist that deliveries from the native dealers be up to a certain standard, and contain only a minimum of dust, wood refuse, etc. If deliveries are not good enough, the merchandise must be cleaned out in the shippers' stores before it can be exported.

(C) Chips:

While quills, quillings, and featherings are still pure cinnamon, i.e., the inner bark of the cinnamon bush, the chips may not be so classified. They consist of shavings of outer (external) bark, together with particles of inner bark, which originate from spots where the outer and inner bark merge and can no longer be separated. Qualities delivered by the native dealers vary considerably, and the chips must always be cleaned in the stores of the exporters before export is possible. Some planters and native dealers distinguish the following two grades of chips:

First Grade "Ekala"—These chips are actually smaller featherings obtained by *scraping* of the very small twigs. For this reason part of the outer bark is also present.

Second Grade "Ekala"—These chips are obtained by scraping and beating of very small twigs with wooden sticks or hammers. They contain many scrapings of outer bark and particles of inert wood. The essential oil content of this grade is very low.

After receiving the chips in their stores, the shippers clean them and finally assort them into various qualities. For example:

Type 1—Free of sand, dust and refuse.
Type 3—Containing little dust.

Type 0—The same as Type 1, but washed and therefore cleaner.
Type 00—The same as Type 0, but bleached.

It has been stated in literature that chips are the most suitable raw material for the production of cinnamon bark oil. This is not always true because the chips often contain much inert wood material (originating mostly from the outer bark), and on distillation, therefore, give a low yield of essential oil.

Packing.—Quills, quillings, and featherings are exported in cylindrical bales of 100 lb. net; chips are exported in pressed bales of 2 or 3 cwt. net.

Exports.—Exports of cinnamon quills, quillings, and featherings from Ceylon averaged from 40,000 to 50,000 bales a year prior to World War II, distributed about as follows:

Europe (with the United Kingdom and Germany as principal buyers)	About 20,000 bales
North and Central America (with Mexico as principal buyer)	About 22,000 bales
South America	About 7,000 bales

The total quantity of exported *chips* ranged from 7,000 to 8,000 cwt. per year, of which more than 5,000 cwt. went to Europe (with England the chief buyer), and more than 2,000 cwt. to Australia.

After the end of World War II exports of cinnamon quills and cinnamon chips were as follows:

	Cinnamon Quills (Long Tons)	*Cinnamon Chips (Long Tons)*
1946	3,563	...
1947	1,835	155
1948	1,859	198

A. Oil of Cinnamon Bark Ceylon

Very small quantities of bark oil are produced on the island of Ceylon by a few native distillers, who produce the oil only occasionally, and, as a rule, only when receiving firm orders from exporters. The latter seem to experience some difficulties in procuring genuine bark oil from native distillers, who are greatly tempted, as are the intermediaries, to adulterate the bark oil with the much cheaper leaf oil. Moreover, many buyers abroad are unwilling to pay the relatively high price of pure bark oil, with the result that dickering about the price often leads to the exportation of substandard oils. It would seem logical that the oil could be distilled more economically in Ceylon than abroad, since distillation on the spot would eliminate the long transport of the bulky raw material to the United States or Europe, but, as was mentioned above, the difficulty lies in finding absolutely reliable native distillers.

The local industry is also in need of improved apparatus, the stills used now being of rather antiquated construction. They are small, made of copper and built into a stone hearth, with direct fire beneath. Five Florentine flasks separate the oil, which distills over in two fractions, one part lighter than water, the other heavier. The distillation water is collected and used again for the next batch; in other words, the principle of cohobation is applied. Most of the Ceylon distillers whom the author visited charged about 60 lb. of chips into the stills, filled them three-quarters with water, and distilled for 5 hr., obtaining about 2 oz. (= 0.2 per cent) of oil. One distiller obtained only about 25 oz. of bark oil from 13 cwt. of chip material, i.e., a yield of only about 0.10 per cent. This very low yield is a result of the use of extremely poor chip material. Grinding of the chips would probably increase the yield. The method of distillation, the condition of the chips, their age, and the presence or absence of outer bark, are of fundamental importance, not only to the yield of oil but also to the quality. The locally distilled oils usually contain about 55 per cent of cinnamic aldehyde, and up to 18 per cent (or even more) of eugenol. This relatively high percentage of eugenol in the local bark oils results chiefly from the quality of the chip material; it may be caused by:

(a) Outright adulteration of the bark oil with leaf oil
(b) The addition of leaves to the chips in the still
(c) The nature of the chip material. Native distillers often use chips from the tops of small branches and branchlets which are close to the leaves, and which therefore contain more eugenol than the regular cinnamon quills or quillings.

These difficulties prove the advisability of distilling exclusively cinnamon quills or quillings in an American or European essential oil factory, if an absolutely genuine bark oil of highest quality is desired. Production of a high-grade cinnamon bark oil, even in modern stills, requires much experience in the selection of the proper bark material, its grinding and the proper methods of distillation. For example, the oils may be oxidized in the course of distillation, with resulting formation of cinnamic acid, and a simultaneous lowering of the cinnamic aldehyde content. Oils properly distilled in modern apparatus from selected quills represent, to a remarkable degree, the delicate and characteristic aroma and flavor of true Ceylon cinnamon.

Physicochemical Properties.—Gildemeister and Hoffmann[4] reported the following properties of Ceylon cinnamon bark oils:

Specific Gravity at 15°	1.023 to 1.040
Optical Rotation	Slightly laevorotatory up to −1°, seldom higher
Refractive Index at 20°	1.581 to 1.591

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[4] "Die Ätherischen Öle," 3d Ed., Vol. II, 612.

Aldehyde Content	65 to 76%
Eugenol Content (Determined with 3% Aqueous Sodium Hydroxide Solution)	4 to 10%
Solubility	Soluble in 2 to 3 vol. of 70% alcohol

While in Ceylon, the author made it a special point to study the local distillation of bark oil. Native producers use chips, almost exclusively, as distillation material. Samples of oils taken from native operated stills had properties indicated in the table below:

	Ambalangoda	*Matara*	*Negombo*
Specific Gravity at 15°	1.021	1.029	1.040
Optical Rotation	−1° 0′	−1° 0′	−0° 24′
Refractive Index at 20°	1.5728	1.5760	1.5674
Aldehyde Content, Calculated as Cinnamic Aldehyde	60.4% (by the hydroxylamine hydrochloride method); 62% (by the sodium bisulfite method)	60.4% (by the hydroxylamine hydrochloride method)	44.5% (by the hydroxylamine hydrochloride method)
Phenol (Eugenol) Content	12%	12%	34%
Solubility at 20°	Soluble in 2 to 2.5 vol. of 70% alcohol; opalescent with more	Soluble in 2 vol. and more of 70% alcohol	Soluble in 1.5 to 2 vol. and more of 70% alcohol

The abnormally high eugenol content of the Negombo oil was surprising and probably related to the quality of the chip material. It was especially puzzling because the three oils possessed a full, rich, and fine odor and flavor. Arrangements were made, therefore, to distill in the same native still, and according to the same process, not only chips but different types of bark material. The resulting oils had these properties:

	Quillings	*Featherings*	*Chips*
Specific Gravity at 15°	1.039	1.039	1.042
Optical Rotation	−0° 20′	−0° 24′	−0° 16′
Refractive Index at 20°	1.5851	1.5836	1.5682
Aldehyde Content, Calculated as Cinnamic Aldehyde (Hydroxylamine Hydrochloride Method)	64.7%	62.7%	44.2%
Phenol (Eugenol) Content	16%	18%	38%
Solubility at 20°	Soluble in 2 vol. and more of 70% alcohol	Soluble in 2 vol. and more of 70% alcohol	Soluble in 2 vol. and more of 70% alcohol

These properties differ somewhat from those of European or American distilled *bark* (quills) oils, the properties of the oil distilled from chips showing the greatest deviation. Because of its very high eugenol content, the latter is almost in a class by itself, standing between bark oil and leaf oil. Yet this oil, too, had a very good odor and flavor; in fact, the eugenol seemed to bring out a characteristic note esteemed by many connoisseurs.

A critical examination of the properties in general reveals that the eugenol content and specific gravity increase, while the cinnamic aldehyde content, refractive index, and the laevorotation decrease, as the raw material is changed from quillings to featherings and finally to chips.

Native-distilled cinnamon oils imported and examined by Fritzsche Brothers, Inc., New York, had properties varying within the following limits:

Specific Gravity at 15°/15°	1.020 to 1.030
Optical Rotation	−1° 0′ to −2° 10′
Refractive Index at 20°	1.5680 to 1.5700
Aldehyde Content, Calculated as Cinnamic Aldehyde (Hydroxylamine Hydrochloride Method)	51.8 to 56%
Phenol (Eugenol) Content	14 to 18%
Solubility at 20°	Soluble in 1.5 to 2.5 vol. of 70% alcohol, occasionally opalescent to hazy with more

The properties of cinnamon oils distilled by Fritzsche Brothers, Inc., New York, from high-grade Ceylon cinnamon quills ("Fines" 0000) have varied within these limits:

Specific Gravity at 15°/15°	1.011 to 1.1030
Optical Rotation	−0° 6′ to −0° 52′
Refractive Index at 20°	1.5748 to 1.5870
Aldehyde Content, Calculated as Cinnamic Aldehyde (Hydroxylamine Hydrochloride Method)	62.2 to 75%
Phenol (Eugenol) Content	6 to 13.2%
Solubility	Soluble in 2 to 3 and more volumes of 70% alcohol; occasionally with opalescence

These oils were of light yellow color; they possessed the delicate odor of true Ceylon cinnamon and a characteristic spicy, sweet, and warm flavor.

In a few cases Fritzsche Brothers, Inc., obtained oils of lower cinnamic aldehyde content, which had a correspondingly lower specific gravity and refractive index.

	Cinnamon Ceylon IV	*Unassorted Cinnamon Ceylon*
Specific Gravity at 15°/15°	0.981	0.978
Optical Rotation	−1° 5′	−0° 56′
Refractive Index at 20°	1.5507	1.5454
Aldehyde Content, Calculated as Cinnamic Aldehyde (Hydroxylamine Hydrochloride Method)	47.1%	42.6%
Phenol (Eugenol) Content	5.4%	5.8%
Solubility at 20°	Soluble in 1 to 1.5 vol. of 80% alcohol; opalescent with more. Insoluble in 70% alcohol	Soluble in 0.5 vol. of 90% alcohol and more; insoluble in 70% alcohol

In other instances Fritzsche Brothers, Inc., obtained oils of high specific gravity, high refractive index, and high cinnamic aldehyde content; they, too, had a good odor. The variations in the properties of these pure oils illustrate the difficulty of establishing exact limits for Ceylon cinnamon bark oil, the properties depending greatly upon the condition of the raw material, its age, and the method of distillation.

The best criterion for cinnamon oils, therefore, is a careful odor and flavor test, without too much emphasis upon physicochemical properties.

Adulteration.—Because of its high price, Ceylon cinnamon bark oil is frequently adulterated.

Some of the oils produced locally in Ceylon are sophisticated with cinnamon leaf oil, or they are distilled from a mixture of bark and leaves. In both cases the result is a marked increase in the specific gravity and in the eugenol content which, in European or American distilled *quill* oils, usually does not exceed 14 per cent.[5]

The addition of cassia oil represents another form of adulteration. It increases the specific gravity, as well as the cinnamic aldehyde content; the latter, in cinnamon bark oils, should not exceed 75 per cent, or fall much below 60 per cent. A questionable oil should be analyzed by determination of the eugenol content (shaking of the oil with aqueous 3 per cent sodium hydroxide solution and separation of the eugenol), and by examination of the nonaldehydic constituents. The latter are chiefly responsible for the delicate odor and flavor which make the Ceylon oil far superior to the much lower priced cassia oil.

The aldehyde content of the Ceylon oil, although an important constituent, is thus not the sole criterion for the evaluation of quality.

In addition to chemical analysis, odor and flavor tests should be carried out. It must be borne in mind that it is possible to compose more or less

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[5] Native distilled oils often have a considerably higher eugenol content (see above).

synthetic cinnamon oils having constants within the limits of pure oils. All this proves that Ceylon cinnamon oil is strictly an article of confidence.

Regarding the determination of eugenol and cinnamic aldehyde the reader is referred to Vol. I of this work, pp. 293 and 285, respectively.

The analytical figure for the percentage of aldehydes (by volume) obtained by the bisulfite method shows no significant difference from the analytical figure for the percentage (by weight) obtained by the hydroxylamine hydrochloride method. This fact was confirmed by the laboratories of Fritzsche Brothers, Inc., New York, from the analyses of pure (own) distillates of Ceylon cinnamon oils of highest quality. Since the bisulfite method usually gives rise to an intermediate layer of sludge which makes the reading of the meniscus somewhat uncertain, the hydroxylamine hydrochloride method is to be preferred for routine analytical control. Because of the presence of phenols in the oil, the neutral sulfite method should not be used.

Chemical Composition.—The first investigations of the chemical composition of Ceylon cinnamon bark oil were carried out by Blanchet,[6] more than a century ago. Somewhat later, Dumas and Péligot [7] reported that the chief constituent of Ceylon cinnamon bark oil, as in the case of cassia oil, is cinnamic aldehyde. The other components now known to occur in Ceylon cinnamon oil were identified by the chemists of Schimmel & Co.,[8] among them particularly Walbaum and Hüthig. According to these investigators, the content of eugenol in the oil derived from the bark of Ceylon cinnamon amounts to only 4 to 10 per cent, whereas it is much higher (up to 95 per cent) in the oil distilled from the leaves of the Ceylon cinnamon bush.

The following constituents have been identified in the volatile oil derived from Ceylon cinnamon bark:

Methyl-*n*-amyl Ketone. Treating the first runs (b. up to 163°) of the oil, with bisulfite solution, the Schimmel chemists [9] obtained a crystalline addition compound from which they were able to regenerate methyl-*n*-amyl ketone. This substance was identified by the preparation of its semicarbazone m. 122°–123°.

Furfural. Characterized by color reactions with aniline hydrochloride.

l-α-Pinene. Identified by means of its nitrosochloride m. 102°–103°, and its nitrolbenzylamine m. 122°–123°.

l-Phellandrene. The fraction b. 170°–174°, α_D $-5° 4'$ yielded a nitrite m. 102°, but despite repeated recrystallization the melting point could not be raised above 103°–104°; $[\alpha]_D$ $+11° 39'$. This fact led the Schimmel chemists [10] to the con-

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[6] *Liebigs Ann.* **7** (1833), 163.

[7] *Ann. chim. phys.* [2], **57** (1834), 305. *Liebigs Ann.* **14** (1835), 50.

[8] *Ber. Schimmel & Co.*, October (1892), 47; April (1902), 65. Cf. *J. prakt. Chem.* [2], **66** (1902), 47.

[9] *Ber. Schimmel & Co.*, April (1902), 65.

[10] *Ibid.*, October (1892), 47.

clusion that the phellandrene present in Ceylon cinnamon oil consists of a mixture of *l*-α- and β-phellandrene, the latter predominating.

p-Cymene. Identified by oxidation to *p*-hydroxyisopropyl benzoic acid m. 154°–156°.

Benzaldehyde. Identified by the preparation of its semicarbazone m. 213°–214°, and of the phenylhydrazone m. 156°.

Nonyl Aldehyde. Oxidation yielded pelargonic acid which was identified by means of its silver salt.

Hydrocinnamic Aldehyde (Phenylpropyl Aldehyde). This aldehyde, hitherto not known to occur in nature, was characterized by the preparation of its semicarbazone m. 126° (semicarbazone of the synthetic product m. 130°–131°) from which the original aldehyde could be regenerated.

Cuminaldehyde. Identified by means of its semicarbazone m. 201°–202° and by oxidation to cuminic acid m. 114°–116°.

Cinnamic Aldehyde (Cinnamaldehyde). According to Gildemeister and Hoffmann,[11] the oil derived from Ceylon cinnamon bark oil contains from 65 to 76 per cent (determined probably volumetrically by the bisulfite method) of aldehydes, cinnamic aldehyde being the chief constituent of this oil.

In the experience of the author,[12] the (cinnamic) aldehyde content of the oil depends greatly upon the method of distillation, upon the kind of bark material used (quills, quillings, featherings, chips) and upon the region from which it originates (cf. "Physicochemical Properties," above). Thus the content of aldehyde may vary from about 42 to 75 per cent of the oil (calculated as cinnamic aldehyde and determined by the hydroxylamine hydrochloride method).

l-Linaloöl. Identified by the chemists of Schimmel & Co.[13] Oxidation yielded citral which could be identified by the preparation of the citryl-β-naphthocinchoninic acid m. 197°.

Linalyl Isobutyrate(?). The same investigations led to the assumption that linalyl isobutyrate is a probable component of the oil.

Eugenol. Schimmel & Co. also expressed the opinion that the oil distilled from the bark of the Ceylon cinnamon bush contains from 4 to 10 per cent of eugenol which was identified by means of its benzoate m. 69°–70°.

In the experience of the author [14] the content of eugenol, like that of cinnamic aldehyde, in Ceylon cinnamon bark oil depends upon several factors, and may range from about 5 to as high as 38 per cent in oil distilled from chips (cf. "Physicochemical Properties," above). Cosgrove and Islip [15] have pointed out that the eugenol content of cinnamon oil from the bark of the cultivated bushes of Ceylon may be much greater than that obtained from the bark of the wild trees growing in the Seychelles.

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[11] "Die Ätherischen Öle," 3d Ed., Vol. II, 612.

[12] Guenther, *Spice Mill* **64** (March 1941), 38.

[13] *Ber. Schimmel & Co.*, October (1892), 47; April (1902), 65. Walbaum and Hüthig, *J. prakt. Chem.* [2], **66** (1902), 47.

[14] Guenther, *Spice Mill* **64** (March 1941), 38.

[15] *Bull. Imp. Inst.* **44** (1946), 188.

Caryophyllene. According to the findings of Schimmel & Co.,[16] this sesquiterpene occurs in the highest boiling fractions of Ceylon cinnamon bark oil. The caryophyllene was characterized by the preparation of its hydrate (caryophyllene alcohol) m. 95°, which yielded a phenylurethane m. 136°–137°.

Use.—Oil of cinnamon bark is one of the most valuable flavoring ingredients, used widely in all kinds of confectioneries, baked goods, candies, soft drinks, table sauces, etc. In many instances the oil has replaced the ground spice, as the oil is more uniform in flavor and can be dosed more exactly.

The oil is also employed, but sparingly, in perfumes of the oriental type.

SUGGESTED ADDITIONAL LITERATURE

Sébastian Sabetay, "A Procedure for the Determination of Essential Oil in Drugs and Spices, by Co-distillation *in vacuo* with Ethylene Glycol," *Ann. chim. anal. chim. appl.* **22** (1940), 217. *Chem. Abstracts* **35** (1941), 4547.

L. Fuchs, "Determination of Cinnamaldehyde in Oil of Cinnamon by Means of Hydrazine Sulfate," *Scientia Pharm.* **16** (1948), 50. *Chem. Abstracts* **42** (1948), 8417.

B. Oil of Cinnamon Leaves Ceylon

Producing Regions.—There are two main areas in Ceylon producing two types of leaf oil:

1. The section near Negombo, north of Colombo. These oils are usually lighter in color and, as a rule, contain less eugenol than the oils distilled in the south. The eugenol content of the Negombo leaf oils varies from 60 to 65 per cent, and is sometimes even lower.
2. The section south of Colombo, near Ambalangoda and Matara in the far south. These oils are usually of darker color and their eugenol content is higher, ranging from 75 to 80 per cent, and even higher.

Years ago, most cinnamon leaf oil was distilled around Negombo, but today the bulk of the oil comes from the south. During the last fifteen years there has been a continuous trend of the entire cinnamon industry toward the south of Ceylon, coconut plantings replacing cinnamon in the Negombo region. While Negombo undoubtedly produces the best and thinnest quills, the leaf oil from that section is considered inferior because of its lower eugenol content. This may be a result of soil conditions or, more likely, of the fact that the native oil producers of Negombo distill a charge

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[16] *Ber. Schimmel & Co.*, October (1892), 47; April (1902), 65. Walbaum and Hüthig, *J. prakt. Chem.* [2], **66** (1902), 47.

of cinnamon leaves for only 7 hr., whereas the producers in the south distill up to 19 hr., or even longer, depending upon the quantity of leaves charged.

The Negombo oils are exported largely to the Straits Settlements and to China, for use in Chinese curries, while the southern oils are shipped to Europe and America for extraction of eugenol. Frequently, exporters bulk the two types of oil and make up standard qualities, guaranteeing a minimum eugenol content of 75 to 80 per cent.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 21. Production of cinnamon leaf oil in Ceylon. A native distillation post.

Distillation.—The production of cinnamon leaf oil is entirely in the hands of natives. It is a very primitive industry; in fact, the oil must be considered only a by-product in the growing of cinnamon and the preparation of the quills.

The leaves of the cut cinnamon stalks are removed prior to the preparation of the quills and are used either for green fertilizing or, if the price of leaf oil is sufficiently attractive, for distillation.

The producing season lasts practically all year; but the best yield of oil is said to be obtained from July to September. During the heavy monsoon rains of May, the leaves are too wet to be distilled. Before being distilled, the leaves are dried for about three days, distillation of the fresh, green material requiring too much time and fuel.

The stills found on the larger native-owned cinnamon estates are quite crude. They consist of large wooden vats, to which a gooseneck is attached with mud paste. The condensers are equally primitive. Cold water is poured into the tank housing the condenser whenever the cooling water becomes too warm. Steam is generated in a simple, separate direct fire still, the gooseneck of which serves as steam connecting pipe, and leads into the bottom of the larger wooden still. Wood collected from the forests, or the hard center core of the cinnamon stalks, after removal of the bark, serves as fuel. Roughly estimated, there are about 150 such cinnamon stills scattered over the producing regions.

The usual charge per still is four large bundles of leaves, each weighing about 1 cwt. Distillation lasts from 7 to 24 hr., depending upon the region and quantity of leaves charged. A charge of 4 cwt. of leaves yields on the average 1½ to 2 bottles, or 37 to 50 oz. of leaf oil. Approximately 30 to 35 lb. of leaf oil are annually obtained from one acre of cinnamon plantings.

Since not all growers of cinnamon possess their own stills, the owners of larger estates frequently rent out their equipment to the smaller growers on a share basis, the owner receiving one-sixth of the oil produced, and the distiller five-sixths, from which he must pay all the operating expenses such as labor, fuel, etc.

The native producers sell their oil mostly to native dealers, who, in turn, supply the exporters in the shipping ports of Ceylon. The oil, usually exported in 5 or 10 cwt. tin lined, sometimes in galvanized, iron drums, Colombo shipped weight, may darken if kept too long in contact with metal.

Physicochemical Properties.—Cinnamon leaf oils imported from Ceylon by Fritzsche Brothers, Inc., New York, had properties which varied within these limits:

Specific Gravity at 15°/15°	1.037 to 1.055
Optical Rotation	−1° 36′ to +0° 40′
Refractive Index at 20°	1.5288 to 1.5350
Phenol (Eugenol) Content	77.3 to 90.5%
Solubility at 20°	Soluble in 1.5 vol. and more of 70% alcohol, sometimes with opalescence or paraffin separation

Gildemeister and Hoffmann [17] reported the following figures:

Specific Gravity at 15°	1.044 to 1.065
Optical Rotation	−0° 15′ to +2° 20′ (mostly dextrorotatory)
Refractive Index at 20°	1.531 to 1.540
Eugenol Content	65 to 95%
Aldehyde Content	Up to 4%
Solubility	Soluble in 1 to 3 vol. of 70% alcohol, sometimes cloudy with more alcohol

Two samples of pure oils secured by the author in the producing regions of Ceylon had these properties:

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[17] "Die Ätherischen Öle," 3d Ed., Vol. II, 620.

	Negombo	*Ambalangoda*
Specific Gravity at 15°	1.050	1.048
Optical Rotation	+0° 20′	+0° 16′
Refractive Index at 20°	1.5344	1.5332
Aldehyde Content, Calculated as Cinnamic Aldehyde (Hydroxylamine Hydrochloride Method)	2.8%	2.8%
Phenol (Eugenol) Content	82.5%	83%
Solubility at 20°	Soluble in 1.5 vol. of 70% alcohol; opalescent with more	Soluble in 1 vol. and more of 70% alcohol

The high eugenol content of the Negombo oil is remarkable, as oils distilled in that region usually contain less eugenol.

Exports.—Prior to World War II export figures of cinnamon leaf oil from Ceylon varied from 170,000 to 190,000 lb., two-thirds of which usually went to the United States, while the balance was divided about equally between Europe and the Far East. Since the end of the war, Ceylon has been exporting about 100,000 lbs. of cinnamon leaf oil per year.

Adulteration.—Oils of high phenol (eugenol) content are occasionally cut with kerosene or with denatured alcohol, sometimes with both. As protection against such adulteration, buyers abroad should insist upon a eugenol content of 78 to 80 per cent, which leaves very little room for adulteration with kerosene. Shippers in Ceylon guarantee a minimum eugenol content of 75 per cent. A separate test should be made for added alcohol, because it would appear as eugenol in the assay of eugenol by means of the potassium hydroxide method. Each drum of cinnamon leaf oil should be tested separately, both for alcohol and kerosene. For details, see Vol. I of this work, pp. 291, 332, 338.

Chemical Composition.—That the chief constituent of cinnamon leaf oil is eugenol (up to 95 per cent of the oil), was recognized by Stenhouse[18] almost a century ago. Later investigations by Schaer,[19] Weber[20] and by the chemists of Schimmel & Co.[21] revealed the presence of the following substances:

Eugenol. Identified by means of its benzoyl compound m. 69°–70° (Weber).

Cinnamic Aldehyde. The oil investigated by Schimmel & Co. contained about 0.1 per cent of cinnamic aldehyde. Weber characterized the aldehyde by the preparation of its phenylhydrazone m. 167°.

Terpenes(?). Not definitely identified (Weber).

Safrole. Oxidation gave piperonylic acid m. 226°–227° (Weber).

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[18] *Liebigs Ann.* **95** (1855), 103.

[19] *Arch. Pharm.* **220** (1882), 492.

[20] *Ibid.* **230** (1892), 232.

[21] *Ber. Schimmel & Co.,* April (1892), 45; October (1892), 47; October (1902), 86.

Benzaldehyde. Identified by means of its phenylhydrazone m. 151°–152° (Weber).

l-Linaloöl. Oxidation yielded citral which could be characterized by preparation of the β-naphthocinchoninic acid compound m. 198° (Schimmel & Co.).

These early findings, however, were not quite reliable as there existed some doubt regarding the origin of the oils investigated by the above-named workers.

More recently Glichitch[22] examined a cinnamon leaf oil produced in Madagascar which contained about 50 per cent of free eugenol. After removing the free eugenol by means of a 3 per cent sodium hydroxide solution at room temperature, Glichitch fractionated the nonphenolic portion of the oil at 11 mm. pressure and obtained six fractions. A closer investigation of these fractions revealed the presence of the following constituents:

Benzaldehyde. Traces were observed in the forerun. Identified by means of the semicarbazone m. 214°–215° and by oxidation to benzoic acid.

l-α-Pinene. Nitrosochloride m. 103°–104°; nitrosopinene m. 131°–132°. Oxidation to pinonic acid, semicarbazone m. 203°.

l-β-Phellandrene. Glichitch[23] proved the presence of *l*-β-phellandrene in Madagascar cinnamon leaf oil by the preparation of nitrites m. 95°–96° and m. 100°–101°.

d-α-Phellandrene. More recently, West,[24] by the formation of characteristic derivatives with nitrosyl chloride and maleic anhydride, has shown that Ceylon cinnamon leaf oil contains *d*-α-phellandrene.

Dipentene. In the Madagascar oil which he investigated, Glichitch[25] also identified dipentene. Tetrabromide m. 124°–125°.

l-Linaloöl. In addition, the oil contained *l*-linaloöl in free form.

Geraniol. Silver salt of the geranyl phthalate m. 133°.

l-Borneol. M. 202°; phenylurethane m. 138°.

l-α-Terpineol. Phenylurethane m. 112°.

Safrole. About 0.5 per cent.

α- and β-Caryophyllene. The sesquiterpene fraction of the Madagascar oil consisted chiefly of α- and β-caryophyllene (nitrosate m. 148°, decomp.), and of a dextrorotatory sesquiterpene, perhaps *d*-caryophyllene.

Eugenol. In combined form, probably as acetyl eugenol.

Cinnamyl Alcohol. In free and in combined form. Oxidation yielded cinnamic aldehyde.

Alcohols(?) (Probably Phenylpropyl Alcohol). These alcohols were not definitely identified.

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[22] *Parfums France* No. 14 (1924), 66.

[23] *Ibid.*

[24] *J. Soc. Chem. Ind.* **58** (1939), 122T.

[25] *Parfums France* **3** (1925), 125.

Cinnamic Aldehyde. About 0.2 per cent.

Benzoyl Benzoate. B_{11} 170°–172°; hydrolysis gave benzoic acid and benzyl alcohol.

1-Menthen-3-one(?) (Piperitone). Presence possible. Semicarbazone m. 224°–226°. In the opinion of Glichitch this ketone probably originated from terpinen-1-ol.

Three Sesquiterpene Alcohols, viz.: By treatment with phthalic anhydride Glichitch finally isolated three bicyclic sesquiterpene alcohols $C_{15}H_{26}O$ containing one double bond which he named:

Cinnamonol. A primary alcohol $b_{2.5}$ 130°–135°, a viscous oil of tenacious, agreeable odor.

Foliol. A secondary alcohol $b_{2.5}$ 133°–135°, a more viscous oil of similar but fainter odor.

Combanol. A tertiary alcohol $b_{1.5}$ 115°–116°, a very viscous oil with an odor reminiscent of certain waxes.

Further details regarding these three sesquiterpene alcohols will be found in Vol. II of this work, p. 756.

His investigation led Glichitch[26] to the conclusion that Madagascar cinnamon leaf oil is composed quantitatively of the following:

50.0% of eugenol in free form
Traces of benzaldehyde (in the forerun)
1.5% of terpenes (*l*-α-pinene, *l*-β-phellandrene, and dipentene)
1.0% of terpene alcohols in free form (*l*-linaloöl, geraniol, *l*-borneol, and *l*-α-terpineol)
0.5% of safrole
6.0% of α- and β-caryophyllene
1.0% of eugenol in combined form (probably acetyl eugenol)
7.0% of cinnamyl alcohol in free and combined form
2.0% of alcohols (probably phenylpropyl alcohol?)
0.2% of cinnamic aldehyde
Small quantities of 1-menthen-3-one (piperitone) (?)
Small quantities of sesquiterpene alcohols (cinnamonol, foliol, and combanol)
27.0% of benzyl benzoate

The fact that the benzyl benzoate content of the above described Madagascar oil was unusually high led Glichitch to investigate cinnamon leaf oils of other origin, among them one oil distilled by Chiris[27] in Combani on the Comoro Islands. Glichitch found that these oils also contained benzyl benzoate, although in smaller quantities. Glichitch finally arrived at the conclusion that, in general, cinnamon leaf oils of low eugenol content contain relatively large quantities of benzyl benzoate and of cinnamyl esters. Perhaps there exist two varieties of *Cinnamomum zeylanicum* which differ in the content of benzyl benzoate in their essential oils derived from the leaves.

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[26] *Ibid.* No. 14 (1924), 66. Cf. *Ber. Schimmel & Co.* (1925), 97.
[27] *Parfums France* No. 16 (1924), 152.

A very unusual oil of cinnamon leaves was distilled in Bangalore (India) from fresh leaves of the cinnamon bush *Cinnamomum zeylanicum* Breyne (yield 0.25 per cent) and analyzed by Shintre and Rao.[28] It had these properties:

Specific Gravity at 15°	0.9223
Optical Rotation at 20°	−2° 54′
Refractive Index at 20°	1.5070
Phenol Content	15%

The oil contained:

4.0% of terpenes (*l*-α-pinene and *l*-β-phellandrene)
3.0% of γ-terpineol and other terpene alcohols
15.0% of eugenol
62.0% of sesquiterpenes (chiefly α-caryophyllene)
7.0% of sesquiterpene alcohols

Use.—Owing to its high eugenol content, oil of cinnamon leaves is a convenient starting material for the extraction of eugenol and its conversion into vanillin. In this respect, cinnamon leaf oil competes with clove stem oil and with clove leaf oil.

OIL OF CINNAMON SEYCHELLES

Development.—In the latter half of the eighteenth century, the Ceylon cinnamon plant was introduced to the Seychelles Islands. The idea was to create a source of supply independent of the Hollanders, who had imposed a production and price monopoly upon the Ceylon cinnamon industry. The plants were first cultivated in the Royal Gardens of Mahé, and later on private plantations, following the methods practiced in Ceylon. For a time the industry flourished, but with the introduction of vanilla, it fell into neglect, and declined further when interest shifted to the growing of coconuts. However, during all this time, the cinnamon plant had continued to be propagated spontaneously by a species of bird (*Acridotheres tristis* or "Mynah," as it is locally called), which is very fond of the fruit and drops the seed over wide areas. These wild-growing trees attained considerable height with age and had to be felled to obtain the bark (which naturally was thick and coarse and included also the cork-like outer coatings). The small quantities of oil distilled before World War I from such old, scabrous bark possessed a poor odor and flavor. The aldehyde content seldom exceeded 36 per cent, and the specific gravity of the oils was correspondingly low. By 1927, production of bark oil in the Seychelles had come to a complete standstill.

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[28] *J. Indian Inst. Sci.* **15A** (1932), 84. *Ber. Schimmel & Co.* (1934), 75.

A. Bark Oil

Physicochemical Properties.—According to Gildemeister and Hoffmann,[29] five locally distilled cinnamon bark oils had the following properties:

Specific Gravity at 15°	0.943 to 0.967
Optical Rotation	−2° 30′ to −5° 10′
Refractive Index at 20°	1.52843 to 1.53271
Aldehyde Content	21.7 to 35%
Eugenol Content	6 to 15%
Solubility	Not clearly soluble in 10 vol. of 70% alcohol; soluble in 0.6 to 5 vol. of 80% alcohol, opalescent with more alcohol

The low specific gravity and low aldehyde content of these oils were probably caused by improper distillation or by the use of too primitive stills.

The same authors recorded for oils distilled in Germany from imported Seychelles cinnamon these properties:

Specific Gravity at 15°	1.0058 to 1.0382
Optical Rotation	−0° 57′ to −3° 5′
Refractive Index at 20°	1.57157 to 1.59347
Aldehyde Content	63 to 84%
Eugenol Content	8 to 12%
Solubility	Soluble in 2.5 to 3 vol. of 70% alcohol; opalescent to turbid with more alcohol. Some oils are insoluble in 70% alcohol

The properties of these oils resembled those of oils distilled in Europe from imported Ceylon cinnamon.

In 1930, Holdsworth-Haines[30] made the first effort to revive local production by distilling the bark of branches and trunks of young cinnamon trees. Such bark, which closely resembled that of Ceylon, yielded about 0.8 per cent of oil; the oil had a specific gravity of 1.016, and an aldehyde content of 65 to 72 per cent.

Two locally distilled bark oils exhibited the following properties:[31]

	A	*B*
Specific Gravity at 15.5°/15.5°	1.0142	1.0160
Optical Rotation	−2° 1′	−1° 44′
Refractive Index at 20°	1.5845	1.5812
Aldehyde Content (Hydroxylamine Method)	71.1%	67.3%

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[29] "Die Ätherischen Öle," 3d Ed., Vol. II, 612.

[30] *Perfumery Essential Oil Record* **27** (1936), 6.

[31] *Bull. Imp. Inst.* **35** (1937), 298.

	A	*B*
Solubility....................	Insoluble in 10 vol. of 70% alcohol; soluble in 0.7 and 0.8 vol. of 80% alcohol	Insoluble in 10 vol. of 70% alcohol; soluble in 0.7 and 0.8 vol. of 80% alcohol

The aldehyde content of both oils and the refractive index of oil A were too high to conform with the specifications of the British Pharmacopoeia; neither were the oils sufficiently soluble. None of the oils had the delicate odor and flavor characteristic of true Ceylon cinnamon bark oils.

Chemical Composition.—According to Schimmel & Co.,[32] the chemical composition of the Seychelles cinnamon bark oil closely resembles that of the Ceylon cinnamon bark oil, but differs from the latter in that the Seychelles oil also contains camphor.

Years later, during which period the cinnamon industry in the Seychelles Islands had undergone considerable changes and made much progress, Cosgrove and Islip [33] investigated four samples of genuine Seychelles cinnamon bark oil but were unable to detect the presence of camphor. These researchers expressed the belief that the poor solubility of the Seychelles oil in alcohol of 70 per cent strength is caused by the presence of an unduly large amount of terpenes. In the opinion of Cosgrove and Islip there must be some other substance in the Ceylon oil which is responsible for its better solubility in alcohol. They also concluded that the eugenol content of cinnamon oil derived from the bark of the cultivated bushes of Ceylon may be much greater than that obtained from the bark of the wild trees growing in the Seychelles. Cosgrove and Islip attribute the deficiency of eugenol in the Seychelles oil, compared with that of the Ceylon oil, to climatic and soil conditions, or to variations in the age of the barks from the two sources prior to distillation.

Years before the investigation of Cosgrove and Islip, the chemists of Schimmel & Co.[34] had identified the following constituents of Seychelles cinnamon oil:

A Hydrocarbon(?). Small quantities; b. below 155°. Its nitrosochloride decomposed spontaneously at 86°–87°.

Camphene. Hydration yielded isoborneol m. 209°–210°.

β-Pinene. Oxidation to nopinic acid m. 125°–126°.

l-Limonene. Traces of *l*-limonene occur in the foreruns of the oil. Identified by preparation of the nitrosochloride m. 103°–104°, and of the nitrolpiperidine m. 93°.

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[32] *Ber. Schimmel & Co.*, October (1908), 142; April (1913), 106.

[33] *Bull. Imp. Inst.* **44** (1946), 188. Cf. Greene, *Drug Cosmetic Ind.* **60** (1947), 480.

[34] *Ber. Schimmel & Co.*, October (1908), 142; April (1913), 106.

p-Cymene. Oxidation gave *p*-hydroxy isopropyl benzoic acid m. 156°–157°.

l-*β*-Phellandrene. Nitrite m. 103°.

Benzaldehyde. Identified by means of its semicarbazone m. 212°–214°.

Linaloöl. Phenylurethane m. 59°–62°.

An Aldehyde(?) (Probably Nonyl Aldehyde). Very small quantities.

Cinnamic Aldehyde. The chief constituent; identified by means of its semicarbazone m. 211°.

Eugenol. Benzoate m. 69°–70°.

Camphor. Oxime m. 116°–118°.

B. Leaf Oil

Prior to World War II, approximately 60,000 liters of cinnamon leaf oil used to be exported yearly from the Seychelles Islands, about 90 per cent of which went to the United States. The balance went to England. These oils were very similar to the previously described Ceylon cinnamon leaf oils.

Gildemeister and Hoffmann[35] reported the following limits:

Specific Gravity at 15°	1.0206 to 1.0604
Optical Rotation	−2° 32′ to +1° 27′
Refractive Index at 20°	1.533 to 1.537
Phenol Content	78 to 94%
Aldehyde Content	Up to 5%
Solubility	Soluble in 1 to 1.5 vol. of 70% alcohol, sometimes slightly opalescent with more alcohol

OIL OF CINNAMON MADAGASCAR

The Ceylon cinnamon plant was introduced to Madagascar and the Comoro Islands about a century ago.

According to the author's[36] own observations, the cinnamon producing regions are along Madagascar's east coast, near Fénérive, Maroantsetra, and Tamatave, the latter being also the shipping port. The plant thrives in the hot and humid climate of the lower coastal regions up to 200 m. altitude; it prefers alluvial soil but grows also in red laterite. Originally cultivated on plantations, the cinnamon plant has since, through propagation by birds, become a wild growing, much branched and bushy tree. Due to shortage of labor, the shoots are not cut every year. In fact, only sufficiently attractive bark prices induce growers to cut the plants, with the result that in Mada-

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[35] "Die Ätherischen Öle," 3d Ed., Vol. II, 620.

[36] *Spice Mill* **61** (1938), 464.

gascar the cinnamon tree is usually allowed to grow two to three years. Thus, the trees attain a height of 4 to 6 m. Their branches are much thicker than those of the Ceylon bush which is regularly coppiced. Harvesting takes place from August to October. The fresh, soft bark is immediately removed from the branches and cut into simple, hollow tubes of rather coarse appearance, about 30 cm. long. Because of labor shortage the Madagascar product is not prepared as carefully as that of Ceylon. The entire industry is in the hands of natives who sell the bark through Chinese and Indian intermediaries to the exporters in Tamatave. Before World War II almost 30 metric tons of dried cinnamon bark were exported yearly from Madagascar, chiefly to France. No cinnamon bark oil is distilled in Madagascar.

Judging from the plant physiological point of view, it would seem that the Madagascar cinnamon plant is related to a variety of *Cinnamomum zeylanicum,* as the essential oils of both are very similar in composition. However, according to Jaeger and Duquénois,[37] it is dubious whether the Madagascar cinnamon actually comes from *Cinnamomum zeylanicum.* The Madagascar product is inferior to the product from Ceylon; it has a less fine flavor, a lower essential oil content, and a high development of sclerified tissue and ballast substances.

Distilling (in France) cinnamon bark imported from Madagascar, the author obtained 0.61 per cent of an oil with these properties:

Specific Gravity at 15°	1.016
Optical Rotation	−2° 34′
Refractive Index at 20°	1.5746
Acid Number	5.6
Phenol (Eugenol) Content	10%
Aldehyde Content:	
By the Bisulfite Method	63%
By the Hydroxylamine Hydrochloride Method[38]	61.4%
Solubility in 70% Alcohol, at 20°	Opalescent in 2.5 vol.; cloudy with more

The odor of the oil was not quite as fine as that of oils derived from true Ceylon cinnamon quills. Nevertheless it was far superior to the odor of oils distilled from cinnamon types resembling cassia.

So far as cinnamon *leaf* oil is concerned, Madagascar proper and the Comoro Islands have been producing several tons per year, most of which, prior to World War II, was exported to the United States. The quantities of oil produced annually, however, depend greatly upon the market price and the availability of labor. The principal center of production is near Combani on the island of Mayotte, where the cinnamon plant was intro-

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[37] *Ann. pharm. franç.* **7 (1949), 51, 61.**

[38] **Calculated as cinnamic aldehyde.**

duced about a century ago. Since then the plant has escaped cultivation and now grows semiwild. Cinnamon does not occur on the other islands of the Comoro group. To harvest the leaf material, the natives climb into the trees and cut the smaller branches and adhering leaves with machetes. Trees should be topped every other year only.

The Madagascar cinnamon industry is native and primitive, following no definite plan. Only as much leaf material is collected as the market price of the oil warrants.

Distillation is carried out in crude stills of about 3,000 liters capacity, one charge of leaf material yielding about 3.5 kg. of oil.

The oil contains from 70 to 90 per cent of phenols (chiefly eugenol). An oil collected by the author near Tamatave (Madagascar) had these properties:

Specific Gravity at 15°.........	1.054
Optical Rotation..............	−1° 4′
Refractive Index at 20°........	1.5352
Phenol (Eugenol) Content......	78%
Solubility at 20°...............	Soluble in 1 and more vol. of 70% alcohol

In regard to production, the cinnamon industry of Madagascar and the Comoro Islands cannot be compared with those of Ceylon and the Seychelles Islands.

The chemical composition of the Madagascar and Comoro cinnamon leaf oils is described in the section "Oil of Cinnamon Leaves Ceylon" (see above).

OIL OF CINNAMON LEAVES INDIAN

Krishna and collaborators[39] investigated oils distilled in Mangalore (India) from the dried leaves of *Cinnamomum zeylanicum* (yield 2 per cent) and found that the physicochemical properties varied within these limits:

Specific Gravity at 30°......	1.0443 to 1.0620
Refractive Index at 30°....	1.5223 to 1.5305
Eugenol Content...........	70 to 87.2%
Solubility..................	Soluble in 1.5 vol. of 70% alcohol

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[39] *J. Sci. Ind. Research India* **4** (1946), 464. *Chem. Abstracts* **42** (1948), 6059.

OIL OF CASSIA

Essence de Canelle de Chine *Aceite Esencial Cassia (Canela de China)*
Cassiaöl *Oleum Cinnamomi Cassiae*

The Chinese cinnamon and the Ceylon cinnamon constitute two distinct species of *Cinnamomum, C. cassia* (Nees) Nees ex Blume, and *C. zeylanicum* Nees, respectively, differing morphologically as well as physiologically. The leaves of *C. zeylanicum* contain an oil in which eugenol is the chief constituent (about 70 to 95 per cent), whereas the leaves of the Chinese cinnamon (or cassia, by which name we shall refer to this species in the following pages) contain an oil in which cinnamic aldehyde is the main constituent (about 70 to 95 per cent). Cassia leaf oil and cassia bark oil are of identical chemical composition, whereas Ceylon cinnamon leaf and bark oil differ greatly in composition. (Cf. the monograph on "Oil of Cinnamon Ceylon.")

The leaves of the Chinese cassia tree resemble those of other species of the genus *Cinnamomum* in being three-nerved; they differ in being oval-oblong, and narrowed at each end. The flowers are pale yellow in color, are borne in panicles, and are smaller than those of other species. The bark of the tree is pale and smooth, with corky patches; on old trees it becomes quite thick. The dried bark, from which the outer layer (epidermis) may or may not have been removed, is bundled and exported as cassia bark, or *Cassia lignea,* which, in ground or powdered form, is a widely used spice. The dried unripe fruit is exported under the somewhat misleading designation of "cassia buds." These cinnamon flavored, brown colored *Flores cassiae* consist of the calyx surrounding the young ovary and have some resemblance to cloves. The separated stalks, which are about 1 mm. thick and 10 mm. long, are a valuable article of commerce in China, where they find use in medicinal preparations.

The low priced leaves, leaf stalks, and young twigs, together with various refuse products worthless for other purposes, are employed by the native growers for the distillation of cassia oil.

Producing Regions.—Oil of cassia is produced in the provinces of Kwangsi and Kwangtung, Southeastern China.

Kwangsi: In the districts surrounding the market centers of Tai On, Luk Chan and Yung Yuen.

Kwangtung: In the districts surrounding the market centers of Lo Ting and Luk Po.

Habitat and Range.—The cassia tree grows best on the slopes of hills. It seems to be rather selective, and efforts to raise it outside of the present producing regions of China have not been too successful. The fruit is eagerly eaten by birds, and there exist many wild trees grown from dropped seed. When left alone, the wild growing trees attain great height; ten to thirty year old trees may reach 30 to 60 ft. Their highly valued bark is not exported. It is used in expensive Chinese medicinal specialties.

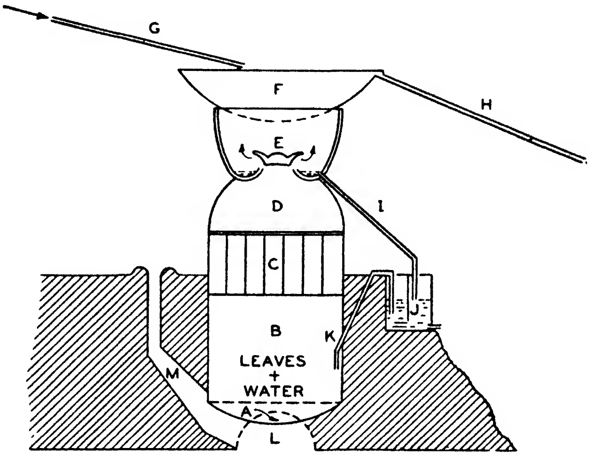
Planting.—Most of the cassia trees that are exploited for bark and oil grow on plantations cared for in the manner typical of Chinese patch or garden farming, whereby families and groups cultivate certain hillsides or small sections. (Similar conditions exist in regard to rice and star anise oil.) In some cases the trees are raised from seed sown in nursery beds. When one to two years old, the seedlings are set out, on the hillsides, 50 cm. apart. More frequently the trees are propagated from cuttings planted during the first three months after the Chinese New Year.

Harvesting.—On plantations cassia is grown as a coppiced bush. At five to seven years of age, the trees are from 5 to 9 ft. high, and ready for cutting. The trunks are cut close to the ground, and new shoots spring up from the remaining stumps and roots. A plantation, once started, may thus last almost indefinitely. The principal harvest takes place in June–July, a smaller one in January–February.

The twigs which have attained a thickness of about 4 cm. are cut into pieces. The bark is loosened by longitudinal slits and deftly stripped from the wood. The bitter tasting outer part (epidermis) is then scraped off and discarded. The inner bark is dried in the sun until it turns brown and curls into a hollow tube. The quills or rolls are finally bundled, sold through a number of middlemen to dealers in Hong Kong, and exported.

The small twigs and leaves obtained as by-products are dried and submitted to distillation, when time permits. Some of the more prosperous peasants have their own stills; but usually the leaf material is sold through intermediaries to a still owner. The whole system is in accordance with the principles of ancient Chinese economy, which allows the greatest number of people in an overpopulated, poverty-ridden country to participate in the minute profits of small transactions.

Distillation.—The stills are generally located on the slopes of glens or ravines, or in places to which water can be brought through a system of bamboo pipes. The stills are of local construction, very similar to those used for the distillation of star anise oil. The distillation material, which is usually semidry, consists of about 70 per cent leaves and 30 per cent small branches and twigs. One picul (133⅓ lb.) of this material is charged into a still and 2½ piculs of water are added. The stills are heated by slow fire to prevent the escape of oil vapors through the rather loose-fitting joints of still and condenser. The steam and oil vapors, passing through three holes in the still head, are reliquefied on the bottom of a cooling vessel (a flat vase through which cold water flows) above the still head. The condensed water and oil drip from the bottom of this vase into the lower part of the still head, from where the oil-and-water mixture flows through a pipe into a sort of Florentine flask. Oil and water separate in this flask. The water is refluxed into the still and cohobated. Instead of cohobating, some distillers use several Florentine flasks; the oil which is heavier than water separates at the bottom of these containers, while the supernatant water is milky because of suspended oil. In the last Florentine flask the distillation water should be clear to indicate that it contains no more oil. If the water is not clear, it is returned into the still for the next operation.



A Chinese cassia still.

A. Still bottom made of cast iron.
B. Part of still made of special Chinese cement.
C. Wooden or tin-plated vessel.
D. Cast-iron head.
E. Condenser.
F. Cooling vessel.
G. Water inlet to the cooler.
H. Water outlet from the cooler.
I. Outlet for the water and oil.
J. Metal oil separator (many stills have several oil separators, arranged in cascade form).
K. Cohobation pipe.
L. Fire grate.
M. Chimney.

Beneath the still is the fire kindled with the wood of cassia twigs from which the bark has been removed. Distillation of one charge usually lasts about 3 hr., but the period may be longer if the fire is kept very low. Distillation of cassia leaves, like that of star anise oil, is a primitive home industry, which goes on aside from regular daily tasks.

Yield of Oil.—The yield of oil is said to be fairly constant throughout the year. One picul ($133\frac{1}{3}$ lb.) of leaves and small twigs yields about fivetwelfths of a pound of oil, which is a little more than 0.31 per cent. This represents less than one-half the yield (0.77 per cent) obtained by Schimmel & Co.[1] who experimentally distilled imported leaves, leaf stems, and young twigs. The probable explanation is that the imported leaf material was much drier than that used locally by the natives; furthermore, the Chinese stills are much less efficient. Von Rechenberg[2] concludes that these stills are particularly deficient in regard to condensation, necessitating very slow distillation. As a result, hydrodiffusion in the tightly packed leaf material is inhibited, and the oil is not fully recovered from the leaves. (For details see Vol. I of this work, p. 176.)

Experimenting with different parts of the cassia tree, Schimmel & Co. also demonstrated that the leaves yield more oil than the twigs (0.54 per cent against 0.2 per cent). According to the statements of Chinese producers, the highest yield of oil is obtained from vigorous, five to seven year old trees. Fully grown leaves are supposed to give better results than small young leaves.

Quality of Oil.—Quality depends upon the leaf material used for distillation; it varies also according to season. In winter and in early spring, the leaves and twigs contain oil said to be inferior to that from leaves harvested in midsummer and fall. The aldehyde (chiefly cinnamic aldehyde) content of Chinese cassia oil ranges from 70 to 95 per cent. In pure oils it is usually about 90 per cent. Only very young leaves, which are seldom used for distillation, yield oils with an aldehyde content as low as 70 per cent. Since such oils do not meet the required standards, the Chinese distillers have no interest in producing them.

Marketing of the Oil.—Like cassia bark, the oil passes through many hands before it reaches the exporters in Hong Kong. There exists a network of field brokers, intermediaries, village merchants, and agents of Hong Kong dealers and exporters, all of whom have their share in the handling of cassia oil. It has been suggested that cassia oil be purchased directly from the producers through reliable white purchasing agents, but such a procedure is absolutely impossible because of the peculiar conditions prevailing in the interior of China. The whole economic system would have to be changed before trading could be done so directly, and this applies not only to cassia oil but to all Chinese products (tung oil, for example).

The native dealers and intermediaries in the interior usually judge the quality of an oil lot by mere appearance and physical behavior. By tasting a drop of oil, by shaking a bottle to watch formation and disappearance of bubbles and foam, and by pouring the oil from a certain height into a filled container, these Chinese experts are able to evaluate, with amazing accuracy,

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[1] *Ber. Schimmel & Co.*, October (1892), 12.

[2] "Theorie der Gewinnung und Trennung der ätherischen Öle," Leipzig (1910), 448.

the quality of an oil, the amount of kerosene and rosin present, and even the content of cinnamic aldehyde.

The chief trading center in the interior is Wuchow, the seaport of Kwangsi Province, from where the oil is shipped down the West River, on junks, to Canton and Hong Kong. Since the province of Kwangsi levies an export duty on cassia oil, a large amount of oil does not go via the river (the most direct and natural route), but is smuggled out, carried across the frontier by coolies to Macao, the Portuguese port near Hong Kong, and from there is imported to Hong Kong.

At the time of the author's visit (1939), there were operating in that seaport two Chinese dealers in whose hands practically the entire cassia oil trade was concentrated. For years they exercised virtual control over this commodity, buying the oil from the distillers and small traders in the interior, and selling it to the European exporters in Hong Kong. In fact, every exporter had to purchase his required lots of oil from these two long-established Chinese dealers who enjoyed a very good reputation as honest and reliable merchants. One of them also owned a separate export firm through which he supplied his own customers abroad. No European firm ever succeeded in setting up its own purchasing organization in the remote and primitive producing regions.

The two Chinese dealers in Hong Kong analyzed every incoming lot, especially for its content of cinnamic aldehyde[3] by the sodium bisulfite method in the well-known cassia oil flask. They sold to the European exporters large lots of oil bulked according to specifications demanded by buyers abroad. In other words, almost every lot of cassia oil reaching the United States or Europe had passed through the hands of one of the two Chinese dealers in Hong Kong. The oil used to be handled like any other Chinese product, and the exporting houses in Hong Kong had neither the technical knowledge nor the facilities to give cassia oil the expert care required by such delicate items as essential oils.

In the course of years certain norms for Chinese cassia oil exported from Hong Kong have been developed. Genuine oil (that is, oil free of any additions whatsoever) was seldom, if ever, shipped, however.

1. Cassia oil containing 80 to 85 per cent of cinnamic aldehyde.

This type of oil is prepared by cutting natural cassia oil of high cinnamic aldehyde content with a mixture of kerosene and rosin, by a process described below. It was exported mainly to England, Germany, and France. A lesser quantity was shipped to the United States. This quality originated

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[3] The aldehydes contained in cassia oil consist chiefly of cinnamic aldehyde. For the sake of brevity we shall refer to these aldehydes simply as cinnamic aldehyde, the usual trade practice.

a number of years ago, when some European buyer had the "bright idea" of insisting upon a lower grade and cheaper cassia oil. The Chinese dealers and intermediaries soon learned to oblige such buyers by resorting to adulteration, natural cassia oils with a low cinnamic aldehyde content being quite rare. Actually, the cost of distilling natural oils of high and low cinnamic aldehyde content is almost identical. To give an idea of the price differential between the various types of oil, we might mention that, during the author's stay in Hong Kong in 1939, this grade was quoted on the spot at $285 (Hong Kong) per picul, f.o.b. Hong Kong.

2. Cassia oil containing 85 to 90 per cent of cinnamic aldehyde.

This type was exported to the United States and Europe. Like type 1, it is prepared by adding kerosene and rosin to oils of high cinnamic aldehyde content.

3. Cassia oil containing 90 to 95 per cent of natural cinnamic aldehyde.

This type is closest to a pure oil, and usually contains only very small amounts of kerosene and rosin. It was exported mainly to the United States. The price per picul in 1939 was $330 (Hong Kong).

4. Cassia oil containing 90 to 95 per cent of cinnamic aldehyde, part of which consists of synthetic cinnamic aldehyde.

This type of oil is prepared by adding synthetic cinnamic aldehyde to oils containing 80 to 85 per cent of natural aldehyde. When analyzed, such oils show a rather high percentage of kerosene and rosin, despite their high cinnamic aldehyde content. In 1939 the oil was quoted at $300 (Hong Kong) per picul. It might be interesting to mention that at the same time synthetic cinnamic aldehyde was offered in Hong Kong at $240 (Hong Kong).

Adulteration.—Cassia oil is adulterated in three ways:

1. Addition of kerosene and rosin, by the native dealers and intermediaries, to the small lots which they handle.

Such adulterated lots are often bulked with pure oils, so that the addition of kerosene and rosin in the final larger lots is not very evident. The small lots pass through so many hands that it is impossible to determine by whom the additions have been made. One small dealer usually blames it on another. Since cassia oil is often stored and transported in the interior in former kerosene cans, there also exists the possibility of contamination.

2. Regular addition of kerosene and rosin to lots of oil with a high cinnamic aldehyde content, lowering the quality to the 85 to 90 per cent type.

This is done either by the larger dealers in Wuchow or by the two previously mentioned Chinese merchants in Hong Kong. They informed the author that they prepare low-priced cassia oils upon request for such quality on part of the Hong Kong exporters. The pure oils are cut with a mixture of

1 part natural cassia oil
1 part rosin
1 part kerosene
—
3 parts

This mixture is heated for about 6 hr. until the rosin is dissolved. The cinnamic aldehyde content of the mixture is determined by the bisulfite method. The compound serves for the cutting of natural oils (of 90 to 95 per cent cinnamic aldehyde content) to any grade specified by exporters or by buyers abroad. The compound also has been exported as low-grade "cassia oil" to Japan and India, which countries do not insist upon a high percentage of cinnamic aldehyde in a cassia oil.

3. Sophistication with synthetic cinnamic aldehyde.

This used to be done chiefly in Macao, the Portuguese free port on the South China coast, into which much cassia oil is smuggled overland from the interior of China in order to avoid export duty in the province of Kwangsi. Because frequently adulterated with synthetic aldehyde, the Macao oils for a long time stood in ill repute. Since a great deal of cassia oil is shipped from Macao to Hong Kong, and re-exported from there, the Hong Kong Chamber of Commerce became quite alarmed over the danger that buyers abroad, discouraged with adulterated oils, might finally decide to replace cassia oil altogether with synthetic cinnamic aldehyde. Obviously, this would have meant a serious loss to Hong Kong. Statistics show that during 1937 substantial quantities of "cassia oil" were imported from France to Macao and Hong Kong. Since France does not produce cassia oil, it can be assumed with some certainty that this so-called "cassia oil" consisted of synthetic cinnamic aldehyde.

The synthetic cinnamic aldehyde imported to Macao and Hong Kong usually came from Europe, and when the European war broke out in 1939, these ports were cut off from their former sources of supply. At the end of 1939, Fritzsche Brothers, Inc., New York received from Hong Kong an inquiry for 15,600 lb. of cinnamic aldehyde and 2,240 lb. of benzyl acetate, which aroused their suspicion. The laboratories of this firm then prepared mixtures of these two compounds in the ratio given above, viz., 87 per cent of cinnamic aldehyde and 13 per cent of benzyl acetate. Analysis of the mixture showed that it had almost normal properties for cassia oil which would pass the U.S.P. test, assaying about 87 per cent of cinnamic aldehyde. Using this synthetic mixture as a base, the dealers in Macao or Hong Kong could easily mix 20 or 30 parts of it with 70 or 80 parts of natural cassia oil. The finished product would then contain 2.6 to 3.9 per cent of benzyl acetate. Only by careful fractionation of the nonaldehydic portion of the oil could the presence of benzyl acetate (which is not a natural constituent of cassia oil) be identified. In fact, up to 60 or 65 per cent of the cinnamic aldehyde-benzyl acetate mixture could be added to a natural oil. Obviously this would result in a substantial percentage of benzyl acetate in the oil and permit easier detection, but even then it is quite possible that the benzyl acetate would elude observation in the course of a routine analysis.

Examples:

"Base"

87%	Cinnamic aldehyde (free from chlorine)
13%	Benzyl acetate (free from chlorine)
100%	

(a)

20%	"Base"
80%	Natural cassia oil
100%	

This mixture would contain 2.6 per cent of benzyl acetate. Detection: doubtful.

(b)

60%	"Base"
40%	Natural cassia oil
100%	

This mixture would contain 7.8 per cent of benzyl acetate. Detection: probable, but only if the analyst were looking for it.

As a safeguard against purchasing cassia oils adulterated with synthetic cinnamic aldehyde, it has been recommended that the purchaser demand from the exporter in Hong Kong a guarantee that the oil was shipped to Hong Kong via West River cargo, which means directly from the producing regions to Hong Kong, avoiding Macao.

Total Production and Exports.—The total production of cassia oil in Kwangsi and Kwangtung amounts to about 200 tons a year. In 1938, 285,795 lb. were exported from Hong Kong. Of this, 138,498 lb. went to the United States, which has always been the most important buyer of Chinese cassia oil, consuming one-third to one-half of the total production.

Physicochemical Properties.—Because of government regulations no crude cassia oil (which usually contains rosin, kerosene, and traces of lead) is used in the United States. After arrival in the United States and before being placed on the market, the crude oil is, therefore, first rectified to remove any rosin, kerosene, and lead. The U. S. Pharmacopoeia requires specifically that cassia oil be rectified.

Gildemeister and Hoffmann[4] report the following properties for crude cassia oil:

Specific Gravity at 15°	1.055 to 1.070
Optical Rotation	−1° 0′ to +6° 0′
Refractive Index at 20°	1.600 to 1.606
Acid Number	6 to 15, in exceptional cases up to 20
Cinnamic Aldehyde Content	75 to 90%
Solubility	Readily soluble in 1 to 2 vol. of 80% alcohol. Most oils are soluble in 2 to 3 vol. of 70% alcohol. Some, otherwise good, oils are soluble in 70% alcohol with opalescence or turbidity, a feature that may perhaps be explained by the presence of lead cinnamate in these oils

The oils boil between 240° and 260° with part decomposition and cleavage of acetic acid. From 6 to 10 per cent of a thick, pasty mass will remain as residue in the distillation flask. For details see Vol. I of this work, p. 335.

So far as the rectified cassia oils are concerned, Gildemeister and Hoffmann[5] reported:

Specific Gravity at 15°	1.053 to 1.065
Solubility	Clearly soluble in 2 vol. of 70% alcohol

The properties of cassia oils rectified by Fritzsche Brothers, Inc., New York, have varied within these limits:

Specific Gravity at 25°/25°	1.046 to 1.059
Optical Rotation at 25°	−0° 40′ to +0° 30′
Refractive Index at 20°	1.6045 to 1.6135, in exceptional cases as high as 1.6188
Aldehyde Content (Bisulfite Method)	88 to 99%
Solubility	Soluble in 2 vol. of 70% alcohol

The properties of the rectified oils depend upon those of the crude oils used for rectification. Thus crude cassia oils containing 85–90 per cent of aldehydes yield rectified oils with a lower aldehyde content than crude oils containing 90–95 per cent of aldehydes would yield.

Rectified cassia oil is a mobile, yellow to slightly brownish, highly refractive oil possessing a characteristic sweet and burning flavor. Odor and flavor are powerful, typical of cassia bark.

Analysis.—Since practically all lots of cassia oil exported from China are adulterated (see above), it is necessary to submit them to careful analytic control, to assure a shipment's being of acceptable quality. Since the oil is

[4] "Die Ätherischen Öle," 3d Ed., Vol. II, 626.

[5] *Ibid.*, 627.

important in the flavoring of food products, attempts were made years ago to develop rapid and reliable testing methods. In 1889, Schimmel & Co.[6] developed a simple distillation test for the presence of rosin, and in 1890, introduced the bisulfite assay for the determination of the cinnamic aldehyde content. These two tests, in addition to that for kerosene, are still the most important assays to which every lot of cassia oil should be submitted. They are enumerated below; a fuller account will be found in Vol. I of this work.

Determination of the Aldehyde Content.—

A. The Bisulfite Method: A simple volumetric assay (cf. Vol. I of this work, p. 279).
B. The Neutral Sulfite Method: This assay, also volumetric, is now (1949) official in the United States Pharmacopoeia (cf. Vol. I of this work, p. 283).

Both methods permit the separation of the nonaldehydic portions of the oil for further analytical or organoleptic tests, which in some cases may be of great help for the identification of certain adulterants (benzyl acetate, for example).

C. The Hydroxylamine Method: This rapid method assays the aldehyde content of the oil as weight percentage by titration and is very exact (cf. Vol. I of this work, p. 285).

Investigating the accuracy of the bisulfite method and of the hydroxylamine hydrochloride method for the determination of the cinnamic aldehyde content in an artificial mixture and in crude cassia oil, the British Aromatic Compound Manufacturers' Association [7] arrived at these results:

1. An artificial mixture was prepared in which the cinnamic aldehyde used contained 97.6 per cent of pure cinnamic aldehyde, and 2 per cent of free acid, calculated as cinnamic acid. The cinnamic aldehyde was completely soluble in sodium bisulfite solution. The mixture was made by diluting 60 parts by weight of the aldehyde with 40 parts by weight of copaiba oil; thus it contained 58.6 per cent by weight of cinnamic aldehyde.

Seventeen determinations of the aldehyde content of the mixture by the hydroxylamine hydrochloride method showed 57.1 to 58.8 per cent (by weight), or an average of 57.9 per cent of cinnamic aldehyde. Eleven determinations by the bisulfite method showed 56.6 to 60 per cent (by volume),

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[6] *Ber. Schimmel & Co.*, October (1889), 15; October (1890), 12.

[7] *Perfumery Essential Oil Record* **39** (1948), 255.

or an average of 57.9 per cent of cinnamic aldehyde. When calculating the results of the bisulfite method on a percentage by weight basis, the results were 60.5 to 64.1 per cent, or an average of 61.8 per cent of cinnamic aldehyde.

2. Crude oil of cassia examined by the hydroxylamine hydrochloride method in 21 determinations showed 74.8 to 76.3 per cent (by weight), or an average of 75.5 per cent of cinnamic aldehyde, whereas 15 determinations by the bisulfite method showed 79.5 to 82 per cent (by volume), or an average of 81 per cent of cinnamic aldehyde.

Undoubtedly, the hydroxylamine hydrochloride method is the more exact assay, particularly in the hands of a skilled analyst. But in the shipping ports of China (Canton and Hong Kong) the necessary laboratory equipment and skill may not be readily available.

Darlington and Christensen[8] suggested a combined sulfite-bisulfite method for the assaying of cinnamic aldehyde in cassia and cinnamon oil. These authors found their method to give more exact results than the neutral sulfite method, official in the United States Pharmacopoeia (1949).

Detection of Rosin.—Reliable tests for this purpose have been described in Vol. I of this work, p. 335.

Detection of Kerosene.—As was pointed out above, practically every lot of cassia oil exported from China is adulterated with mineral oil fractions, particularly kerosene. The addition of substantial amounts of kerosene will lower the specific gravity and the refractive index of the oil, and render it less soluble. However, a combination of kerosene and rosin may affect the specific gravity and the refractive index only slightly.

Place 100 cc. of the oil in a 250 cc. Ladenburg flask, and distill slowly, at atmospheric pressure, over an open flame. Collect the first 10 per cent of the distillate. Test the solubility of this fraction in 70 per cent alcohol. If a clear solution is not obtained in 10 vol. of 70 per cent alcohol, subject 5 cc. of the distillate to fuming sulfuric acid by following the so-called Oleum Test described in Vol. I of this work, p. 332.

If the amount of kerosene present in the oil is relatively large, the distillate may appear in two layers, the upper being kerosene saturated with cassia oil, the lower, cassia oil saturated with kerosene.

If only small quantities of kerosene are present, it is advisable to test the nonaldehydic portions of the oil (separated after treatment of the oil with saturated bisulfite or sulfite solution) with fuming sulfuric acid. As little as 2 per cent of kerosene may be detected in this manner.

Detection of Alcohol.—Tests for the detection of alcohol will be found in Vol. I of this work, p. 338. Since cassia oil may contain small amounts of

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[8] *J. Am. Pharm. Assocn.* **32** (1943), 118; **33** (1944), 298.

water in solution, it is necessary to dry a sample of the oil over anhydrous sodium sulfate before the refractive index is determined.

According to Gildemeister and Hoffmann,[9] small amounts of alcohol may be detected by determination of the flash point of the oil. The flash point, determined in a Pensky-Martin closed tester, of a cassia oil containing no alcohol lies, in most cases, above 100° C. However, flash points slightly below 100° have occasionally been observed in rectified cassia oils which contain no alcohol whatsoever. For practical purposes, Gildemeister and Hoffmann suggested a flash point of not lower than 75° C.

Detection of Chlorine-Containing Synthetics.—Sometimes a synthetic adulterant of the oil, if not carefully prepared, may contain impurities which can readily be recognized. Thus, synthetic cinnamic aldehyde, benzaldehyde, benzyl alcohol, and benzyl acetate may contain traces of organic chlorides whose presence can be utilized as the basis for testing. For details see Vol. I of this work, p. 307.

Detection of Benzyl Acetate.—As has been mentioned in the section "Adulteration," cassia oil is occasionally adulterated with benzyl acetate. For isolation of this synthetic, the oil is first treated with a concentrated sodium bisulfite or neutral sulfite solution, and the nonaldehydic portion is fractionated.

Detection of Benzaldehyde.—According to Dodge,[10] cassia oils adulterated with benzaldehyde are occasionally encountered. The detection of the latter presents no difficulties. If benzaldehyde is present in large amounts, the solution obtained in the sulfite assay may crystallize on cooling. To separate the benzaldehyde, the solution should be neutralized, a little carbonate added, and the reaction mass then distilled with steam. The benzaldehyde can be identified in the distillate (cf. Vol. I of this work, p. 282, footnote 78).

Detection of Synthetic Cinnamic Aldehyde.—The detection of chemically pure, synthetic cinnamic aldehyde added to cassia oil is not easy, as only indirect methods are available.

Dodge[11] observed disagreements in the apparent aldehyde content of cassia oils, depending upon whether this had been determined by the volumetric neutral sulfite method or the cold hydroxylamine titration method. Results obtained with the latter were 4 to 8 per cent lower than those obtained with the former, whereas when applied to pure cinnamic aldehyde the two methods agreed fairly well in result. The differences in the apparent aldehyde content of cassia oil are due to two facts: (1) In the sulfite method the acids and coumarin present in the oil are included and determined as apparent aldehydes. (2) In the calculation of the aldehyde content by

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[9] "Die Ätherischen Öle," 3d Ed., Vol. II, 634.

[10] *Am. Perfumer* **38**, No. 3 (1939), 31.

[11] *Ibid.*

hydroxylamine titration the mol equivalent of cinnamic aldehyde is used, although cassia oil also contains *o*-methoxy cinnamaldehyde. (In fact, the latter aldehyde is a more important constituent of the oil than used to be believed.)

From an examination of about 30 cassia oils Dodge arrived at the conclusion that in commerce two types of oil may be distinguished: oils containing from 12 to 13.7 per cent of *o*-methoxy cinnamaldehyde, and free from kerosene; and oils with a low *o*-methoxy cinnamaldehyde content, and containing kerosene. In the opinion of Dodge, the inference seems justified that the first represent authentic oils, and the second, oils which have been blended with synthetic cinnamic aldehyde, and whose properties have been roughly adjusted by the addition of small amounts of kerosene. Oils with a low *o*-methoxy cinnamaldehyde content generally yield rectified oils with a high aldehyde content and high refractive index, occasionally above the U.S.P. limits.

For the determination of the *o*-methoxy cinnamaldehyde content, Dodge suggested Zeisel's methoxy method (more exactly, the method of Benedikt and Grüssner,[12] modified by Gregor,[13] and Weishut[14]).

Methoxy determination, in the opinion of Dodge, thus becomes a measure of purity, as the higher the methoxy value of a cassia oil, the greater the probability that the oil is genuine and not adulterated with synthetic cinnamic aldehyde.

In conclusion, it should be mentioned, however, that, valuable as it may be, methoxy determination of a cassia oil offers no definite criterion of its purity. Dodge examined only commercial oils: in absolutely pure oils, the methoxy content may be even higher. As Dodge himself has pointed out, owing to the practical impossibility of procuring absolutely authentic samples, one cannot state the actual *o*-methoxy cinnamaldehyde content for a normal oil.

Subsequent to the work of Dodge, the *o*-methoxy cinnamaldehyde content of cassia oil was investigated by Darlington and Christensen.[15] These authors examined four commercial cassia oils and found that they contained from 10.43 to 12.61 per cent of *o*-methoxy cinnamaldehyde, confirming the findings of Dodge. For their methoxy assay, Darlington and Christensen used the method of Vieböck and Schwappach as modified by Clark,[16] and with certain precautions.

Since the purity of their commercial cassia oils was not absolutely guar-

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[12] *Chem. Ztg.* **13** (1889), 872.

[13] *Monatsh.* **19** (1898), 116.

[14] *Ibid.* **33** (1912), 1165.

[15] *J. Am. Pharm. Assocn.* **32** (1943), 118; **33** (1944), 298.

[16] *J. Assocn. Official Agr. Chem.* **15** (1932), 136.

anteed, Darlington and Christensen [17] experimentally distilled small quantities of cassia oil from imported cassia bark. The oils thus obtained assayed only 3.21 to 4.40 per cent of *o*-methoxy cinnamaldehyde. The discrepancy with the figures quoted above may be explained by the fact that commercial cassia oil is distilled in China from the leaves and twigs of the cassia tree, but not from the bark. Moreover, the bark examined by Darlington and Christensen may have been derived from a different species of *Cinnamomum.*

Chemical Composition.—Oil of cassia resembles oil of cinnamon bark Ceylon in that the chief constituent of both oils is cinnamic aldehyde which in crude (natural) cassia oil ranges from 80 to 95 per cent (determined by the volumetric neutral sulfite method), whereas in Ceylon cinnamon bark oil it is substantially lower. (Cf. "Oil of Cinnamon Ceylon.") The difference in odor and flavor between cassia oil and the much higher priced Ceylon cinnamon oil is the result of the presence of additional substances, which differ in the two oils, or which occur in cassia oil and Ceylon cinnamon oil in different proportions. These facts were known even to the early workers who investigated the chemical composition of cassia oil during the first part of the nineteenth century, among them Blanchet,[18] Dumas and Péligot,[19] Mulder,[20] and later Bertagnini [21] and Heusler.[22]

In the course of years the following constituents have been identified in oil of cassia:

Cinnamic Aldehyde (Cinnamaldehyde). The chief constituent, the natural (nonrectified) oil containing from 80 to 95 per cent of this important aromatic aldehyde (see above).

Cinnamyl Acetate. This ester b_{11} 135°–145°, was identified by the Schimmel chemists,[23] and was found to possess a somewhat harsh flavor.

Phenylpropyl Acetate(?). The above-named ester is accompanied by small quantities of another ester, probably phenylpropyl acetate.

Trace Substances. Other substances, although present in small quantities only (trace substances, amounting to 0.5 per cent of the oil), nevertheless exert a considerable influence upon the odor and flavor of the oil. According to Dodge and Sherndal,[24] most of these compounds can be separated from the oil by treatment of the latter with a 2 per cent aqueous solution of sodium hydroxide:

Salicylaldehyde. Identified by means of its semicarbazone m. 228° (with decomposition).

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[17] *J. Am. Pharm. Assocn.* **33** (1944), 298.

[18] *Liebigs Ann.* **7** (1833), 164.

[19] *Ann. chim. phys.* **57** (1834), 305. *Liebigs Ann.* **12** (1834), 24; **13** (1835), 76; **14** (1835), 50.

[20] *Liebigs Ann.* **34** (1840), 147. *J. prakt. Chem.* **15** (1838), 307; **17** (1839), 303; **18** (1839), 385.

[21] *Liebigs Ann.* **85** (1853), 271.

[22] *Ber.* **24** (1891), 1805.

[23] *Ber. Schimmel & Co.,* October (1889), 19.

[24] *J. Ind. Eng. Chem.* **7** (1915), 1055.

Cinnamic Acid. M. 123°–128° (see also below).

Salicylic Acid and Benzoic Acid. Salicylic and benzoic acids were also identified among the trace substances present in cassia oil.

Higher Fatty Acids(?). Isolated not in crystalline, but in oily form. Esterification of the mixture yielded substances which had the typical odor of esters of higher fatty acids.

Coumarin. M. 67°.

Benzaldehyde. Dodge [25] identified very small quantities of benzaldehyde by oxidation to benzoic acid m. 91°–93°.

o-Methoxy Benzaldehyde (Methyl Salicylaldehyde). Characterized by oxidation to *o*-methoxy benzoic acid m. 89°.

Methyl-*o*-coumaraldehyde (*o*-Methoxy Cinnamaldehyde). (Cf. Vol. II of this work, p. 360.) This substance, which possesses a most tenacious but rather disagreeable odor, on rare occasions is observed as a crystalline separation product in old cassia oils. It was first noted by Rochleder et al.[26] and named "Cassia-stearoptene." Much later, Bertram and Kürsten [27] proved that "Cassia-stearoptene" is actually methyl-*o*-coumaraldehyde m. 45°–46°, which can be prepared synthetically by condensation of methyl salicylaldehyde and acetaldehyde.

Examining the list of constituents present in cassia oil it seems rather surprising that the oil contains only small quantities (about 1 per cent) of free cinnamic acid. Considering the ease with which cinnamic aldehyde, the chief constituent of cassia oil, undergoes autoxidation, one should expect much larger quantities of free cinnamic acid in the oil, particularly in old oils.

The chemists of Schimmel & Co.[28] explain the low content of this acid by the theory that the autoxidation of cinnamic aldehyde is inhibited by the presence of cinnamyl acetate in the natural oil, this ester acting as a very efficient preservative. These researchers exposed a very old sample of cassia oil (aldehyde content 77.7 per cent) to heat, air, and light for one year, and found that under these adverse conditions the content of free cinnamic acid (originally 0.7 per cent) increased to only 8.5 per cent. Pure cinnamic aldehyde, under the same conditions, would soon have been converted into a mass of free cinnamic acid.

The presence of free cinnamic acid, even in very small quantities, in oil of cassia leads to crystalline precipitations of lead cinnamate, if the oil is shipped from China in lead containers, the usual trade practice in former years.

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[25] *Ibid.* **10** (1918), 1005.

[26] *Ber. Acad. Wissensch. zu Wien, mathem. phys. Klasse,* June (1850), 1; *ibid.* **12,** 190. *Pharm. Zentr.* (1851), 46; (1854), 701. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 628.

[27] *J. prakt. Chem.* [2], **51** (1895), 316.

[28] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 630.

Tests for the presence of heavy metals in cassia oil will be found in Vol. I of this work, p. 309.

Use.—Oil of cassia is one of the most important flavoring ingredients, used widely in all kinds of food products and beverages, such as meats, table sauces, cakes, baked goods, confectionery, desserts, soft drinks, pickles, candies, chewing gums, etc.

The oil is employed also in perfumes, cosmetics, and for the scenting of soaps, but in the latter case care has to be exercised as cassia oil is liable to cause discoloration in white soaps.

SUGGESTED ADDITIONAL LITERATURE

J. F. Clevenger, "Volatile Oil in Cassia Bark," *J. Assocn. Official Agr. Chem.* **24** (1941), 461.

OIL OF CAMPHOR

Essence de Camphre *Aceite Esencial Alcanfor* *Campheröl*
Oleum Camphorae

by
TEIKICHI HIRAIZUMI, PH.D.*

Foreword.—In respect to total production per year, oil of camphor is undoubtedly the most important of essential oils, outranking even oils of eucalyptus and citronella. In 1936, for example, the island of Formosa and Japan proper produced about 9,000 metric tons of camphor oil (including the natural camphor extracted from the oil). With the production of synthetic camphor on a very large scale, the natural product has lost some of its former importance. Nevertheless, prior to World War II, the natural product still supplied half of the demand for camphor on the world markets.

Although it is true that the natural camphor could be replaced completely by the synthetic product, if necessary, the oil of camphor has managed to retain its important position because it contains, aside from camphor, a number of other components which are used in different industries, or which can be converted into valuable aromatic isolates and synthetic aromatics. In this respect oil of camphor, like oil of citronella, is a real "gold mine." It should be pointed out here that the oil of camphor originally obtained by

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distillation of the wood of the camphor tree will yield, on further treatment, something less than 50 per cent of natural camphor (cryst.), and slightly more than 50 per cent of (residual) camphor oil. The latter is then processed for the isolation of various fractions and aromatics. By exploiting such important by-products, the Japanese, Formosan, and Chinese camphor and camphor oil industries have survived competition on the part of the synthetic camphor industry.

Prior to World War II, the island of Formosa, the world's most important producer of camphor oil and camphor, formed part of the Japanese empire, and Formosa's camphor industry was completely controlled by, and intimately connected with, the chemical industry of Japan proper. The original oil obtained by distillation of the wood was separated in the producing regions of Formosa into crude camphor and residual crude camphor oil, which two main products were then refined in modern, well-equipped factories located in Formosa and Japan. The government of Japan contributed a great deal to the development of camphor oil production in Formosa's primitive interior.

In 1939 the author[1] had occasion to make a personal study of Japan's camphor industry and was deeply impressed by the efficiency of its organization. Since the end of the war, however, fundamental changes have taken place, the consequences of which cannot yet be foreseen. At the time of this writing (1949), it is very difficult for an outsider to give an exact report on the present state of the camphor oil industry in Formosa, Japan, and China. The island of Formosa has been returned to China, and conditions are changing constantly. Japan is now trying to enlarge her own camphor oil industry in the southern part of the island group. By planting trees on a large scale the government is endeavoring to salvage an industry which for many years has been the source of large exports and revenues.

In view of these complicating factors, the author considers himself fortunate in having secured the collaboration of his friend, Dr. Teikichi Hiraizumi, President of Takasago Chemical Industry Co., Ltd., of Tokyo, one of the largest manufacturers of camphor oil by-products in Japan, who wrote the following monograph. No one is better qualified to deal with the subject.

ERNEST GUENTHER.

JAPANESE CAMPHOR OIL

(The Camphor Oil Industry of Japan)

Introduction.—Formosa and the southern part of Japan are located in the temperate and subtropical zones of Asia, eminently suited to the growth of

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[1] Guenther, "Japan's Vast Camphor Industry," *Am. Perfumer,* March (1942), 27; April (1942), 23; May (1942), 39.

the camphor tree. Aware of the favorable conditions, the government of Japan has for many years made great efforts toward reforestation and has embarked on a far-reaching program to develop the production of camphor oil and camphor into a national industry.

As a result of World War II, Japan had to restore the island of Formosa, the largest producer of camphor oil, to China. Nevertheless, about 3,000 metric tons of camphor oil (and camphor) were produced after the war in Japan proper. In 1948 a strictly enforced, large-scale reforestation program in the south of Japan was begun.

For quite a number of years the production of synthetic camphor, particularly in the United States and in Europe, has offered a serious threat to the natural camphor industry. So far, however, the natural product has always been able to withstand competition with the synthetic product on the world market, for the simple reason that camphor *oil,* a most important by-product, is obtained in the extraction of camphor from its natural source. Several valuable compounds contained in natural camphor oil cannot readily be synthesized, and in this respect the synthetic camphor industry is at a disadvantage. Not only have the Japanese been able to isolate and utilize the constituents of camphor oil to the utmost for the production of aromatics and aromatic isolates, ore flotation oils, solvents, insecticides, etc., but they also managed, before the war, to export ever-increasing quantities of aromatics. Japan thus developed a domestic industry of aromatic isolates that is based chiefly on camphor oil. Moreover, the development of the camphor industry lent impetus to the growth of the Japanese chemical industry in general.

In recent years the so-called Brazilian sassafras oil has made its appearance and become a serious menace to the "Brown Camphor Oil," one of the fractions of natural camphor oil. Similarly, Brazilian oil of bois de rose is threatening the position of Formosa's "Ho Oil," a sort of camphor oil. In the face of this competition the leaders of Japan's camphor oil industry have come to realize that the days of their monopoly are over. The position of the natural camphor and camphor oil can be maintained only by a program of extensive reforestation, by the scientific utilization of all constituents of camphor oil, and by a general lowering of the cost of production. Fortunately, the Japanese government and the leaders in Japan's camphor oil industry are now well aware of these factors and are taking the necessary steps.

Historical Development.—It is very difficult to trace the date at which camphor made its first appearance, because in early literature camphor seems to have been confused with borneol. The "Kafur" mentioned in Arabian writings of the sixth century was probably borneol, produced in Sumatra or other parts of Malaya. Through Marco Polo's journal, which appeared in the thirteenth century, camphor became widely known as a curious and valuable product of the Orient. From that time on, camphor, which resembles "Kafur" (or borneol), has occupied an important position in commerce, and as a result of increasing demand, camphor production was started in China, where the tree had been growing in great abundance since time immemorial.

The reliable scientific Chinese work "Honzo-Komoku" published in 1596 states: "Camphor wood is boiled in water for three days; on evaporation of the aqueous extract, snow-white and borneol-like camphor is then obtained." This record proves that in China camphor was already being extracted from the wood in the sixteenth century; but it seems quite likely that natural camphor had been produced since a much earlier date, probably since the end of the thirteenth century. Undoubtedly, the clever Chinese naturalists, keen observers of nature, had noted the white camphor crystals which, as the result of natural sublimation, form deposits in the clefts of the wood of the camphor tree. Surely the Chinese must have known how to scratch these crystals from the wood and collect them (as was the practice with borneol).

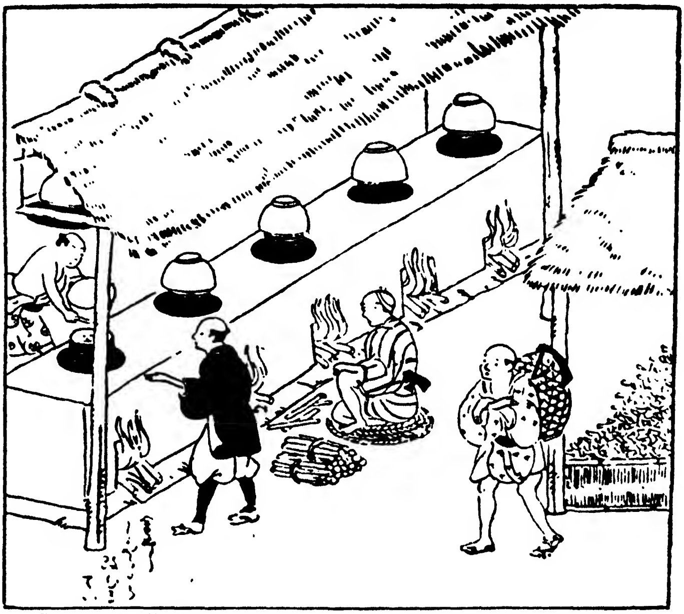
The first reference to camphor in Japanese literature concerns a product imported from China. The Japanese had known the camphor tree since ancient times, as the tree grows profusely in the Kyu-Shu regions, and for a long time had been used as timber for shipbuilding. With the establishment of regular trade between China and Japan the process of isolating camphor from the tree was introduced into Japan (probably in the early part of the seventeenth century or, according to other sources, in the Genroku period between 1688 and 1703). This took place in Kagoshima, the southern part of Kyu-Shu, the process having come from China via the Loochoo (Ryu-Kyu) islands. From Kagoshima the new industry then spread to other districts of Kyu-Shu Island and Shikoku Island.

According to some historians the Chinese method of camphor preparation from the tree may have started during the sixteenth century, being introduced to Japan about a century later.

It should be kept in mind, however, that the early camphor industry aimed solely at the recovery of camphor, no attention being paid to the production of camphor oil. Therefore no condensers were used in the wood distillation, which was thus actually a process of sublimation. The vapors were conducted into porcelain bowls, and the camphor was condensed by air cooling. This procedure, the so-called "bowl method," was practiced for nearly 300 years.

In the Tempo period (1830–1843), water-cooled condensers were devised in the province of Tosa (Shikoku Island), and from then on the camphor industry made remarkable progress. From Tosa the new method of distillation, called "Tosa method," spread to the other camphor producing regions of Japan proper, and finally to Formosa and China, replacing the old "bowl method." The new process of distillation yielded not only camphor, but also an approximately equal amount of (residual) camphor oil which, as has been pointed out, has lately reached almost greater importance than the camphor itself. However, when the new distillation process was first introduced, little attention was paid to the liquid phase of the distillate (the camphor oil) which was either thrown away or used as lamp oil.

In 1879, new progress was made in Japan's camphor industry with the discovery that the residual camphor oil (after removal of the crystallized camphor) still contains substantial quantities of camphor which can be recovered by fractionation. The industry entered a new era, and in 1903 the government proclaimed the camphor industry of Japan proper and that of newly conquered Formosa a state monopoly.



Copy of an illustration published in "Nippon-Sankai-Meibutsu-Zue," Japan (1754).

Preparation of camphor by the old-fashioned "bowl method."

Botany.—In Formosa several species of the camphor tree are known (and exploited for their oil), but in Japan there exists only one variety, viz., Hon-Sho, the *true* camphor tree, *Cinnamomum camphora* Sieb.[2] However, this tree occurs in two forms, which can be distinguished by the color of the young sprouts at the time when the tree develops new leaves. The sprouts

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[2] Of late seed and young plants of the Ho-Sho tree have been brought from Formosa to Japan for propagation on a large scale. The wood of this tree yields the so-called Ho oil, an essential oil containing a high percentage of linaloöl. (Cf. the monograph on "Formosan Camphor Oil.") In years to come Japan will be able to produce Ho oil in competition with the island of Formosa.

of about 80 per cent of the trees (the true camphor tree) exhibit a red color, whereas the sprouts of about 20 per cent of the trees have a green color. The trees of the latter group grow more rapidly and contain more essential oil than those of the former group. As the leaves of both groups develop, their color changes into green and the difference disappears. For this reason, the two groups of trees are not considered to be distinct botanical varieties. Nothing is known about the cause of the color change in the sprouts of the two types of trees.

Geographical Occurrence and Distribution of the Tree.—In Japan, the camphor tree grows in localities with a temperature above 13° C. and at altitudes below 800 m.; it flourishes best in sections with a temperature above 15° C. and at altitudes below 300 m. The islands of Kyu-Shu and Shikoku, and the southern part of Hon-Shu (the main island of the Japanese group) offer suitable conditions for the growth of the camphor tree.

On December 20, 1947, the Government Monopoly Bureau of Japan published the following figures on the number of camphor trees growing in Japan proper, the volume of wood represented by these trees, and the acreage covered by the trees:

STATISTICS OF CAMPHOR TREES OF JAPAN

December 1947

Investigated by the Government Monopoly Bureau of Japan

	Kyu-Shu Island					
Districts	*Kagoshima and Miyazaki*	*Kumamoto*	*Fukuoka*	*Shikoku Island*	*Other Districts*	*Total*
(A) Total number of trees	8,726,084 (70.6%)	786,366 (6.3%)	593,849 (4.8%)	1,772,212 (14.3%)	485,597 (4.0%)	12,364,108
(B) Number of trees, except small ones with a diameter less than 15 cm.	7,001,574 (75.4%)	629,164 (6.8%)	505,748 (5.5%)	768,656 (8.3%)	375,650 (4.0%)	9,280,792
Calculated wood volume of (B) in koku * units	5,161,757 (68.5%)	457,972 (6.1%)	956,331 (12.7%)	585,283 (7.8%)	365,390 (4.8%)	7,526,733 (koku) 2,090,760 (cu. m.)
Areas of camphor forests above 1 hectare	12,652 (69.8%)	1,256 (6.9%)	1,610 (8.3%)	1,920 (10.5%)	804 (4.4%)	18,244 (ha.)

* 1 koku = 0.278 cu. m., 3.6 koku = 1 cu. m. = 1 metric ton.

The government owns 57 per cent of all trees; public corporations such as prefectures, cities, towns, villages, schools, temples, shrines, etc., own 8 per cent of all trees; the balance (35 per cent) is privately owned.

As can be seen from these figures, about 80 per cent of all camphor trees in Japan grow on the island of Kyu-Shu. There the meteorological observations shown in Table 2.1 have been made:

TABLE 2.1. METEOROLOGICAL OBSERVATIONS

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Through Year
Average temperature (°C.)													
Kagoshima...	7.1	7.5	10.8	15.5	18.8	22.3	26.1	26.8	24.2	18.9	13.7	8.9	16.7
Fukuoka.....	5.0	5.1	8.1	13.1	17.1	21.3	25.6	26.4	22.2	16.3	11.5	7.0	14.9
Kochi........	5.5	6.1	9.5	14.7	18.2	21.6	25.2	26.2	23.2	17.7	12.4	7.4	15.6
Average amount of rainfall (mm.)													
Kagoshima...	83	101	156	217	214	400	297	187	222	125	94	86	2,182
Fukuoka.....	69	81	110	132	121	240	254	132	191	95	76	82	1,582
Kochi........	67	101	182	275	275	340	321	303	417	215	116	79	2,690
Average humidity (%)													
Kagoshima...	73	72	73	76	77	83	82	80	79	74	75	74	77
Fukuoka.....	74	74	74	77	78	81	81	82	83	80	77	74	78
Kochi........	67	66	69	74	77	84	85	83	82	76	77	70	76

Planting and Cultivating.—The camphor tree is usually planted by seed. Propagation can be effected also by root cuttings or by branch cuttings, but in Japan and in Formosa the method of planting by seed is preferred for reforestation.

The camphor tree is not classified into male and female trees. Those growing gregariously seldom develop blossoms, and therefore do not bear fruit. On the other hand, those occurring isolated in sunny spacious places will bloom when about fifteen years old and then bear fruit. Isolated trees about fifty years old are ideally suited for the collection of seed. These trees flower and sprout simultaneously in May and then bear fruit. The fruit ripens in the fall and is gathered in December and January. The pulp should be removed immediately after collection of the fruit, and nothing but the seeds picked out, lest the pulp undergo fermentation. Since the seed loses its germination power after six months, only freshly collected seed should be used for planting. One peck (16 pt.) contains about 35,000 grains of seed, germination being about 60 per cent. The seed is sown into nursery beds toward the middle or end of March.

After three or four weeks in the nursery bed the seeds start to sprout. One year later, fresh and vigorous plants are selected and transplanted to another, more spacious, nursery bed, where they remain for one year and attain a height of about 80 cm. For fertilization, ammonium sulfate, soyabean cake, wood ash, and potassium phosphate are used.

The two-year-old plants are set out in the field between the end of March and the beginning of April, after their stalks have been cut back to 3 cm. length. If only camphor trees are planted, one hectare will hold from 2,000 to 3,000 plants. There are two methods of planting: either camphor trees are planted exclusively, or camphor trees are planted together with pine, oak (*Quercus serrata*), or other trees, in the proportion of one to one. In some cases the plantations must be weeded for seven years following planting.

When the trees have attained an age of about twenty years, they should be thinned out to facilitate growth. By the time they are forty or fifty years old, so many trees have been cut out that one hectare holds only about 400 trees. In Japan, trees over forty years are considered well suited for distillation and extraction of camphor. However, any tree felled in the process of thinning the forest is also used for distillation, no matter how young it may be.

The camphor tree is attacked by a variety of insects, the most harmful being "Kusunoha-Shirami" (*Trioza camphora* Sasaki) and "Kusu-Mukuge-Mushi" (*Liothrips setinodis*).

Trioza camphora Sasaki: Although young as well as old camphor trees are liable to be infested by this insect, the younger trees (one to ten years old) suffer more from it than the older ones. When young leaves are infested, a great many oval or roundish galls may form on the surface, and the growth of the leaves will be retarded.

Liothrips setinodis: This insect may damage the stalks and twigs of young trees in the nursery.

A common preventive is to apply 1 to 2 per cent whale oil soap solutions to the infested leaves and wood; or the injured trees may be cut out and burnt.

Reforestation.—Years ago there were many wild-growing camphor trees in Japan; these were used chiefly for the extraction of camphor. As a result of reckless exploitation, most of the naturally growing trees have disappeared, and the number of camphor trees has decreased to such an extent that at present only relatively few are left, in public parks, in the compounds of shrines and temples, or on private property. Japan's biggest and most venerable camphor tree grows in the precinct of Hachiman Shrine, Gamo, in the prefecture of Kagoshima. At its root this tree has a circumference of 38 m., and at a man's height a circumference of 23 m.; its trunk is 31 m. tall. The age of the tree is estimated at 1,200 years.

Between 1906 and 1913 the government of Japan enacted a program of reforestation, and a great many camphor trees were planted in Kyu-Shu, Shikoku, and other districts. The wood material used at present for the extraction of camphor oil and camphor comes chiefly from trees planted at that time.

As was mentioned above (cf. the table), the Government Monopoly Bureau computed the number of camphor trees in Japan in December, 1947, at 12 million, covering about 18,000 hectares, and representing 2 million metric tons of wood. On the basis of a yield of 2 per cent this means about 40,000 metric tons of camphor and camphor oil. If 2,500 to 3,000 tons of camphor and camphor oil should be produced per year, the present total quantity of wood would be used up in the course of the next fifteen years, provided, of course, that no reforestation were carried out in these years.

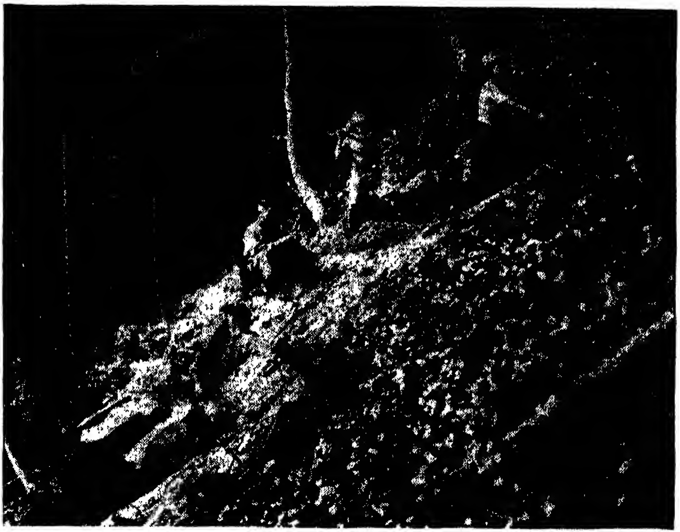
To prevent exhaustion of the present camphor tree forests and to tide the camphor industry over any shortage of wood, the Japanese Government embarked on a five-year plan of reforestation, according to which every year 2,750 hectares of land will be planted with camphor trees. This means that after five years there will be 13,750 hectares planted with camphor trees, managed by the government. This undertaking is being widely publicized among the rural population, and planting of camphor trees by private growers is being encouraged. Depending upon the results obtained, a second and third five-year plan of reforestation may be carried through. Since the loss of Formosa after World War II, the government of Japan has been making the greatest effort to create a new supply of camphor wood in Japan, so that in future the world can rely upon regular supplies of camphor and camphor oil from Japan.

Cutting of Trees and Chipping of the Wood.—Before a camphor tree is felled, the soil is removed from the root system, and the small roots and runners are hacked off one by one; then the tree is felled close to the ground. The roots, the stump, the trunk, and the branches are then reduced to a convenient size, bundled, and carried on carts, sleighs, via horseback (or manback) to the nearest road. From this point the material is hauled by wagon or truck to the nearest distillery which may be as far as 10 km. away.

At the distillery every piece of wood is first sawed by hand into large pieces, and then reduced to small chips. For the latter purpose motor-driven sawing machines (3 to 5 h.p.), provided with a flywheel, are used. In the camphor sawmills of Japan any one of the following three types of flywheels are employed:

(a) The "Hiramokuhen" type. The wheel has a diameter of 4 ft.; a single cutting blade is attached. The chips produced with this type of wheel are flat and rather large, a feature not conducive to effective distillation of the chips. However, 1,000 kg. of chips can be produced per hour.

(b) The "Tamazato" type. The wheel has a diameter of 3 ft.; 7 blades are attached. This yields a very desirable size and shape of chip. About 600 kg. of chips can be produced per hour.



Courtesy of Nippon Camphor Manufacturing Co., Ltd., Tokyo, Japan.

FIG. 22. Production of camphor and camphor oil in Japan. Felling of a camphor tree.

Courtesy of Nippon Camphor Manufacturing Co., Ltd., Tokyo, Japan.

FIG. 23. Production of camphor and camphor oil in Japan. Haulage of pieces of a felled camphor tree to the nearest distillery.

(c) The "Fukuoka" type. The wheel has a diameter of 5 ft., and 7 to 9 blades are attached. The shape of the chips is very suitable to their distillation, but only 500 kg. of chips can be obtained per hour. Nevertheless, the "Fukuoka" type of flywheel is increasing in popularity because of its low price and the small power required for its operation.

Distillation Apparatus.—Whereas in Formosa camphor wood distillation posts are usually erected in isolated places in the forests, jungles, and mountains, in Japan the distilleries are located chiefly in villages, or in convenient spots nearby. This feature alone, aside from others, constitutes a striking difference between the distilleries of Formosa and those of Japan.

The camphor wood hauled to a distillery may be stored there for quite some time, but once the wood is reduced to chips, it has to be charged into the stills immediately.

A typical distillation post consists of three parts: (a) a water kettle (boiler); (b) a retort (vat or still), called "Koshiki"; and (c) several condensers.

(a) The water kettle or boiler is simply an iron pan in which water is brought to boiling. Depending upon the size of the retort ("Koshiki"), the diameter of the boiler ranges from 1.2 to 1.5 m. The fire-box beneath the water kettle is constructed of stone or fire-brick; it has a diameter of 1.3 to 1.6 m. Some hearths are provided with a simple wooden chute (stoker) through which exhausted chips are fed into the fire.

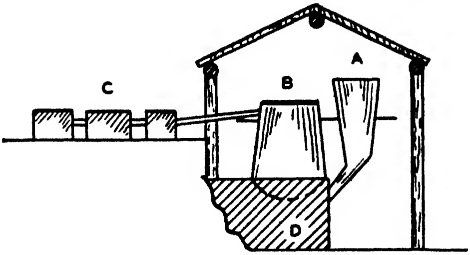
(b) The retort (vat, still) or "Koshiki" consists of a wooden tank, without a bottom, made of cider boards 3 to 5 cm. thick; this rests upon the water kettle. Retort and water kettle are separated from one another by a grid, which consists of pine timbers about 8 x 8 cm. The grid must be provided with numerous narrow gaps or holes to permit easy passage of the steam. A heavy lid is placed on top of the still, to cover the opening through which the chips are charged. Distillation completed, the exhausted chips are discharged through a man-hole on the side of the retort, just above the grid.

The capacity of the stills varies according to the size of the distillery. The most common stills hold from 600 to 800 kg. of chips. A "Koshiki" of this capacity has a diameter of 1.4 to 1.5 m. at the bottom, 0.8 to 0.9 m. at the top, and a height of 1.7 m. The largest "Koshiki" in Japan holds 1,800 kg. of chips.

A bamboo pipe, 10 cm. in diameter, runs from the upper part of the still to the condenser. All connections are tightly sealed with loam, to prevent leakage of steam and oil vapors. In some distilleries the side walls of the

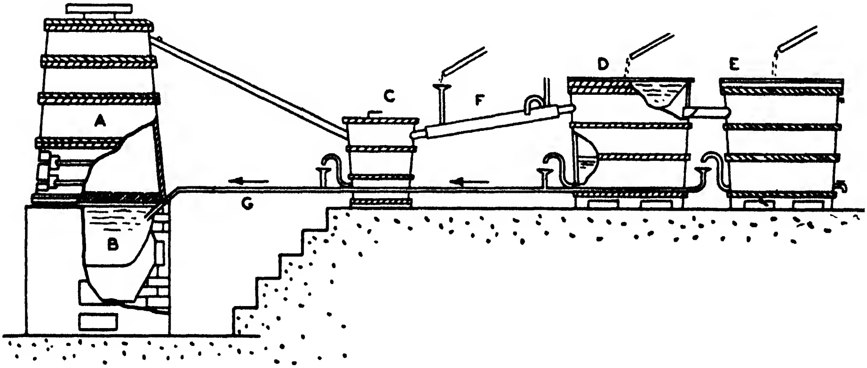
"Koshiki" are insulated by a thick layer of loam or concrete, to prevent loss of heat.

(c) The condenser is the most bulky and troublesome unit of the distillation apparatus. Camphor oil crystallizes in part at ordinary temperature; therefore specially constructed condensers have to be used. Spiral condensers, such as are employed for the distillation of most essential oils, will not do for camphor oil. Several attempts have been made, in the course of years, to improve the antique type of condenser, and the type now used was finally evolved. Undoubtedly, it is still rather crude by comparison with modern equipment in large chemical factories; but, considering the generally primitive conditions prevailing in the field and the low price of camphor



Schematic view of a camphor wood distillery.

A. Wooden feeding stoker of exhausted chips.
B. Retort ("Koshiki").
C. Condensers.
D. Hearth.

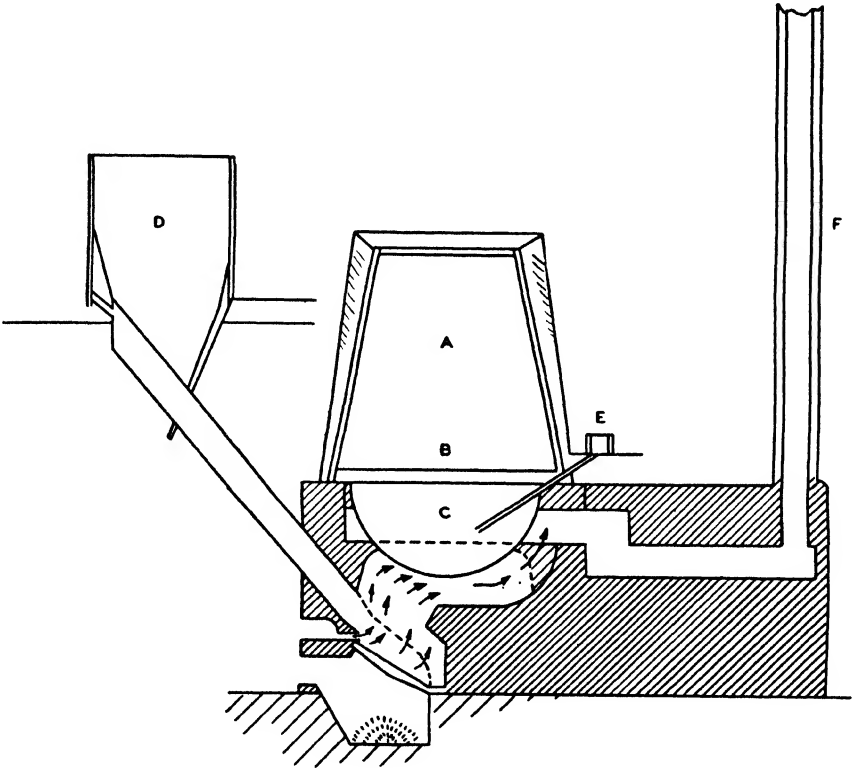


Drawing of a camphor wood distillation post.

A. Retort ("Koshiki").
B. Kettle.
C. 1st condenser.
D. 2nd condenser.
E. 3rd condenser.
F. Liebig condenser.
G. Pipe for return of distillation water (cohobation water pipe).

oil, the condensers now employed in the field distilleries of Japan are relatively efficient. The chief difficulty consists in the fact that the camphor vapors turn into crystals as soon as they enter the condenser system.

In the equipment now in use the vapors driven from the wood in the "Koshiki" are conducted through a large pipe into two to four (usually three) wooden barrels or boxes. Box condensers are called "Tosa type." Both barrel and box condensers, fulfill the same function.



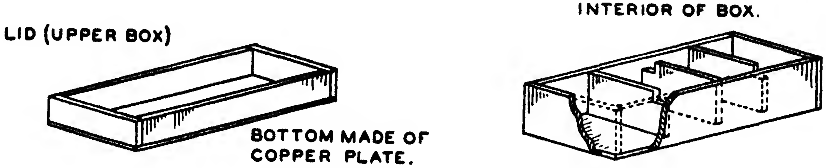
Section of hearth with stoker and still.

A. Retort ("Koshiki").
B. Wooden grid.
C. Kettle.
D. Feeding stoker.
E. Box receiver of distillation (cohobation) water.
F. Chimney.

The first condenser serves for preliminary and part cooling only; in it the distillate should not be cooled too much, and only the heavier, high boiling fractions of the oil should be condensed. Therefore, the first condenser is smaller than the second and third ones.

The second condenser is the main part of the condenser system. In the case of barrel condensers it has a diameter of 0.9 m. and a height of 0.9 m. It is covered with a shallow V-shaped basin made of copper, which is fed with running water throughout the operation. Prior to distillation the barrel is half-filled with water.

The "Tosa type" of condenser consists of a big box, constructed of heavy wooden planks, 1.8 m. long, 1.2 m. wide, and 0.85 m. deep. Partitions divide the interior into several compartments; each compartment is connected with the adjacent compartment by a hole in the upper corner of each partition. Prior to distillation the box is half-filled with water. The lid of the box consists of a shallow tray of the same length and width, but only 10 cm. deep, its bottom made of copper. By conducting water over this shallow tray throughout the distillation, the lower box is kept cool.



Section of "Tosa type" box condenser.

The third condenser is of the same construction as the second barrel or box, but smaller. It serves to condense those parts of the distillate which have not been caught in the second condenser.

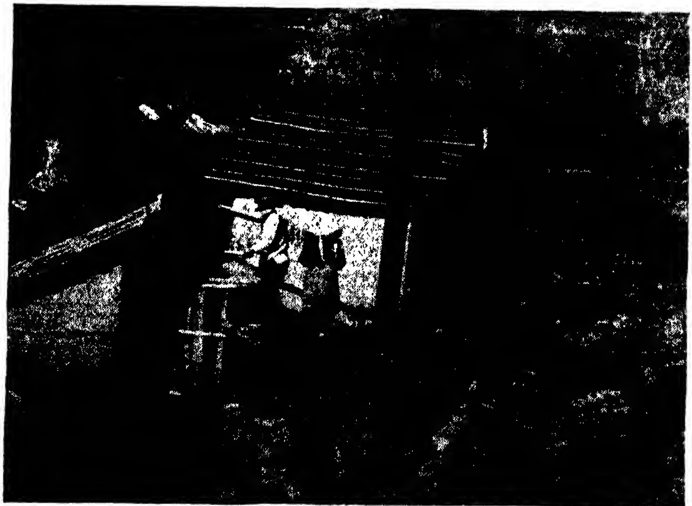
Distillation.—The chipped wood material is charged tightly into the wooden retort ("Koshiki"), through the opening in the wooden top, and the water in the kettle is brought to a boil. Steam, camphor vapors, and camphor oil vapors condense in the barrel or box condensers, the camphor separating in the form of white crystals along the walls of the condensers, particularly on the cooled ceiling. The distillation water may be returned into the retort and redistilled (cohobated) during distillation.

The length of distillation depends upon the quantity of chips charged and upon the parts of the tree from which the wood originated. Eight hundred kilograms of chips from roots require about 15 hr., whereas the same quantity of chips from the trunk need only 8 to 10 hr. of distillation. It should be mentioned here that, although 17 hr. are required theoretically for complete exhaustion of a batch, practically 90 per cent (or more) of the camphor and camphor oil will distill over within 7 to 8 hr. The ratio between length of distillation and yield of distillate has been thoroughly studied and most interesting results have been obtained, as can be seen from Table 2.2 and graphs.

The optimum rate of distillation is attained when, with a charge of 500 kg. of wood material, 700 to 800 cc. of distillate come over per minute. The

Courtesy of Takasago Chemical Industry Co., Ltd., Tokyo, Japan.

FIG. 24. Production of camphor and camphor oil in Japan. View of a Koshiki (wooden still) condenser.



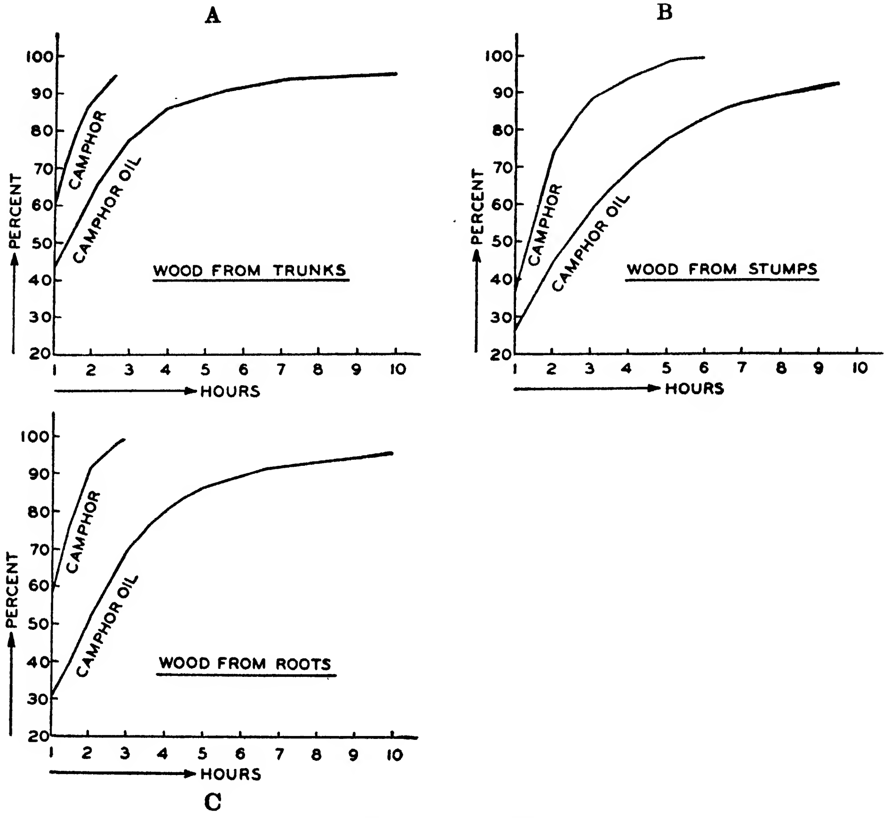
Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 25. Production of camphor and camphor oil in Japan. Charging of a still with chipped camphor wood.

TABLE 2.2

Hrs.	Wood from Trunks (2,500 kg.)				Wood from Stumps (3,000 kg.)				Wood from Roots (3,000 kg.)			
	Camphor	Camphor Oil			Camphor	Camphor Oil			Camphor	Camphor Oil		
	Amount (g.)	Amount (g.)	Density	Camphor Cont. (%)	Amount (g.)	Amount (g.)	Density	Camphor Cont. (%)	Amount (g.)	Amount (g.)	Density	Camphor Cont. (%)
1	11,535	14.585	0.935	53.6	11,460	19,370	0.940	51.8	9,340	21,330	0.967	48.9
2	5,075	6,800	0.947	53.6	10,850	14,090	0.970	51.3	5,340	15,410	0.992	48.9
3	2,055	5,405	0.947	53.6	4,305	10,525	0.973	51.3	1,495	12,245	0.991	48.9
4	350	2,511	0.940	52.4	1,920	7,750	0.972	50.7	70	7,080	0.991	47.1
5	55	1,312	0.929	44.9	890	6,565	0.968	50.2	...	3,865	0.989	42.8
6	...	669	0.920	35.8	420	3,935	0.966	50.0	...	1.932	0.988	37.4
7	...	461	0.915	31.8	30	2,945	0.964	49.4	...	1,502	0.987	35.2
8	...	253	0.906	23.0	...	2,025	0.954	39.5	...	1,140	0.986	30.5
9	...	184	0.905	21.6	...	1,460	0.954	39.0	...	888	0.982	26.6
10	...	127	0.905	19.5	...	1,108	0.954	37.1	...	679	0.977	25.5
11	...	83	0.907	24.9	...	641	0.948	32.9	...	460	0.976	23.0
12	...	79	0.907	22.2	...	643	0.945	29.3	...	427	0.975	16.7
13	...	50	0.907	22.2	...	517	0.942	25.1	...	361	0.974	15.9
14	...	45	0.905	17.7	...	452	0.942	23.2	...	308	0.974	15.3
15	...	...	...	...	...	342	0.942	22.0	...	233	0.974	15.3
16	...	...	...	...	...	274	0.940	18.7	...	192	0.971	13.1
17	...	...	...	...	...	178	0.940	17.4	...	137	0.967	13.1
*	...	1,189	0.905	27.1	...	2,802	0.914	18.2	..	2,024	0.941	14.0
Total	19,070	33,753			29,875	75,622			16.245	70.213		

* Distillation completed by distilling charge an additional 3 hr. with pressure.

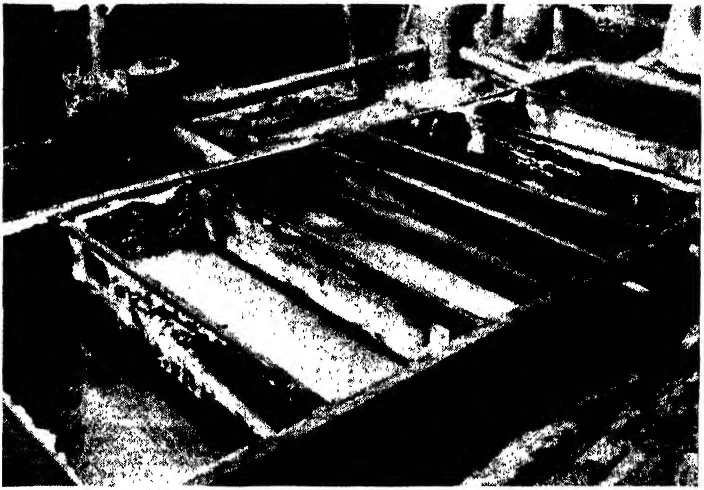


A. Wood from trunks.
B. Wood from stumps.
C. Wood from roots.

ratio of oil and water in the distillate is about 1 to 25. To maintain this rate, the flow and temperature of the cooling water have to be adjusted.

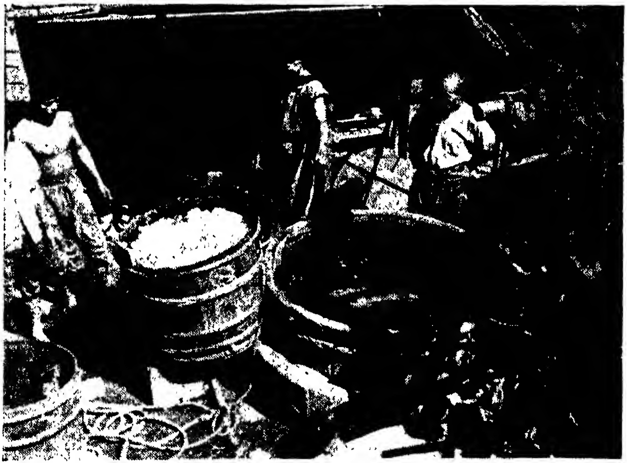
On completion of the distillation, the exhausted chips are discharged through the man-hole in the side of the retort, just above the grid, and after drying are used as fuel for one of the next charges. The amount of exhausted chips retrieved from one charge amply suffices for the heating of a new charge, and no other fuel needs to be added. However, if the quantity of chips to be burned as fuel is measured exactly in a feeding stoker it will be found that 80 per cent of the exhausted chips from a charge are sufficient to heat a new charge.

The total quantity of camphor and camphor oil accumulating in the condensers is usually removed once a month, after about 40 distillations. Nothing delights a distiller more than to lift the cover of his barrel or box con-



Courtesy of Nippon Camphor Manufacturing Co., Ltd., Tokyo, Japan.

FIG. 26. Production of camphor and camphor oil in Japan. View of a "Tosa type" box condenser.



Courtesy of Takasago Chemical Industry Co., Ltd., Tokyo, Japan.

FIG. 27. Production of camphor and camphor oil in Japan. Transferring of the crude camphor from a barrel condenser to a wooden settling tank.

denser and see before his eyes a snow-white mass of camphor, the fruit of his month's labor.

The semicrystalline camphor is first separated from the camphor oil by crude filtering; but since the camphor thus obtained retains some adhering oil, the mass is left, for about a week, in a wooden settling tank provided with a small hole in the lower part. The oil flows out drop by drop, and the camphor remains in the box. The ratio of crude camphor thus obtained to the crude camphor oil (which still contains about 50 per cent of camphor in solution) is approximately two to three.

The oil is poured into cans, the camphor packed into barrels, and the two products are carried to the collecting stations of the Nippon Camphor Manufacturing Company, scattered throughout the regions where camphor trees grow.

	Number of Camphor Distilleries in Japan
1926	2,237
1935	1,468
1942	990
1945	785
1948	790

As can be seen from these figures, the number of camphor distilleries has been decreasing in the past twenty years, the result both of a reduced demand for natural camphor on the world market and of increased capacity in individual distilleries. In October 1948 the number of distilleries belonging to the Nippon Camphor Manufacturing Company was 790; they contained 868 stills. The number of people occupied in the camphor distilleries was 5,189.

After inspection of the crude camphor and the crude camphor oil at the collecting stations, the products are delivered to the Government Monopoly Bureau, and then shipped to the Saisei Camphor Manufacturing Co. in Kobe, the concern entrusted by the Monopoly Bureau with the final purification of the camphor and rectification (fractionation) of the camphor oil.

Yield of Oil.—The yield of camphor and camphor oil from the trees depends upon many factors. Summarizing, it may be said that:

1. Naturally growing (spontaneously propagated) trees contain more camphor and camphor oil than planted (reforested) trees.
2. Isolated trees contain more camphor and camphor oil than trees growing in dense stands.
3. Healthy and strong trees contain more camphor and camphor oil than weak trees.

As regards the content of camphor:

4. Old trees contain more camphor than young trees.
5. Trees growing on sandy soil contain much more camphor than trees growing on argillaceous soil.
6. Trees growing on well-drained soil contain more camphor than trees growing on damp ground.

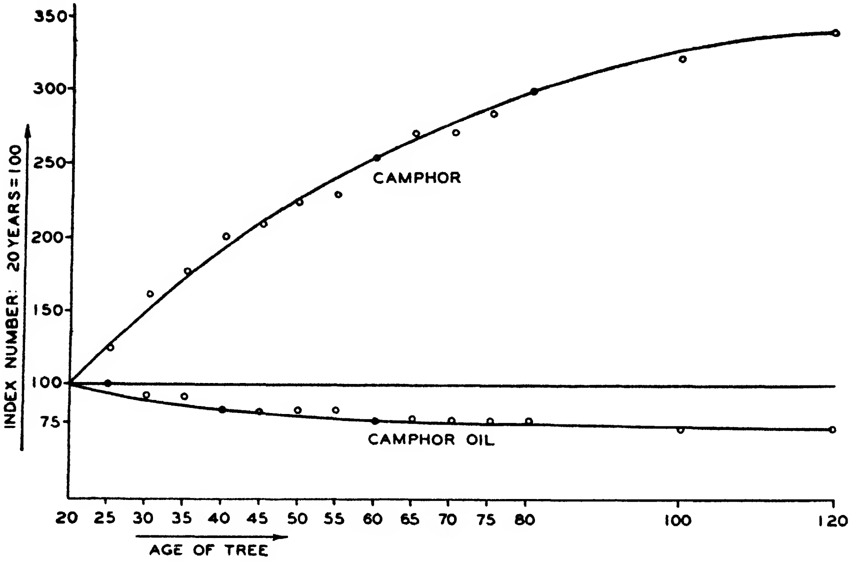
The relation between the yield of camphor and camphor oil, and the age of the trees can be seen from Table 2.3:

Table 2.3

Age of Trees in Years	Growth of Tree			Camphor and Camphor Oil		
	Height (m.)	Diameters at Breast Height cm.	Volume (cu. m.)	Camphor (%)	Camphor Oil (%)	Total (%)
5	1.75	1.19	0.0006		1.00	1.00
10	1.68	5.92	0.0095	0.13	1.08	1.21
15	6.95	10.65	0.0503	0.27	1.15	1.42
20	8.78	15.37	0.1170	0.50	1.50	2.00
25	10.27	20.10	0.2160	0.63	1.50	2.13
30	11.52	24.82	0.3473	0.82	1.40	2.22
35	12.57	29.55	0.5164	0.88	1.40	2.28
40	13.48	34.22	0.7255	1.00	1.30	2.30
45	14.26	39.00	0.9770	1.05	1.30	2.35
50	14.94	43.72	1.2760	1.10	1.30	2.40
55	15.55	48.45	1.6210	1.14	1.30	2.44
60	. .	50.90	...	1.28	1.20	2.48
65	...	56.20	...	1.35	1.20	2.55
70	...	60.00	...	1.35	1.20	2.55
75	...	62.80	...	1.42	1.20	2.62
80	...	65.70	...	1.52	1.10	2.62
100	...	78.10	...	1.60	1.10	2.70
120	...	85.70	...	1.70	1.10	2.80

From the above table it appears that young trees contain much oil and little camphor; in sixty-year-old trees the quantity of oil almost equals that of camphor. In trees older than sixty years, the content of camphor increases, and that of oil decreases.

If the content of camphor and camphor oil in a 20-year-old tree is assigned an index value of 100, the ratio of camphor to camphor oil in older trees may be seen from the following graph:



Ratio of quantity of camphor and camphor oil contained in camphor trees based upon age of the tree.

From this diagram it appears that a 120-year-old tree yields about 3.4 times as much camphor as a twenty-year-old tree; on the other hand, the yield of oil is 25 per cent less.

When a thirty to forty-year-old camphor tree is felled and cut up, it yields the following weight percentages of trunk, roots, stump, branches, and leaves:

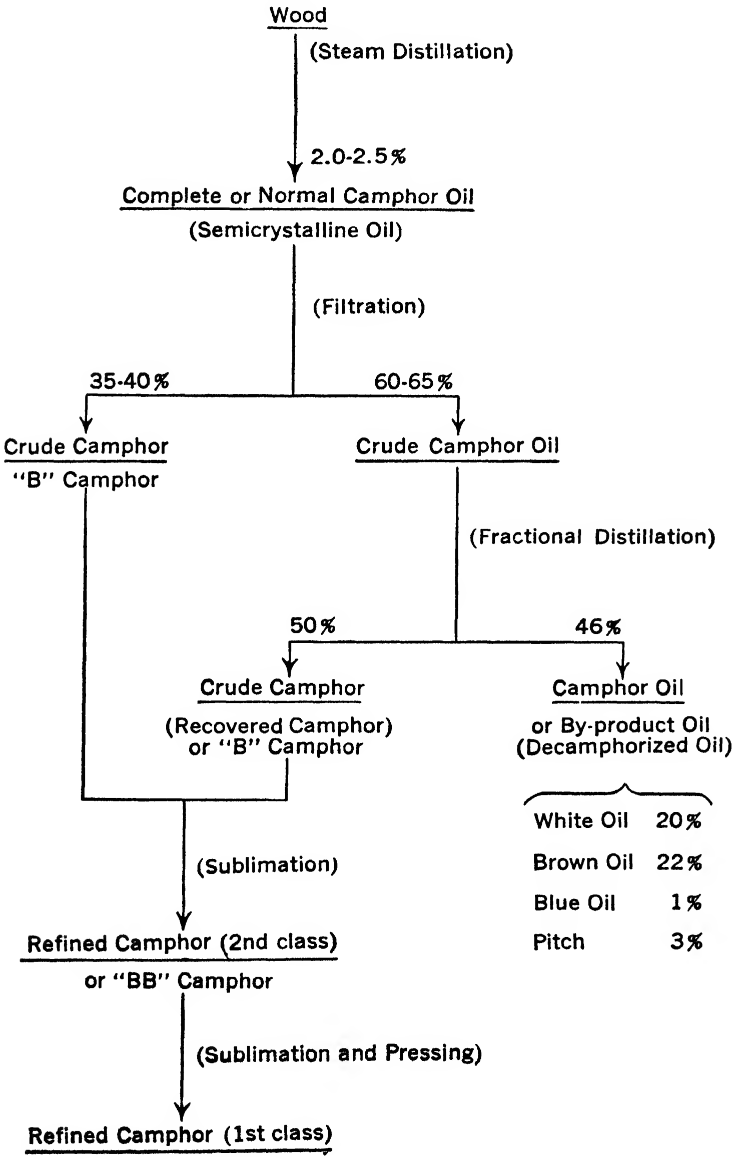
	Trunk	*Roots*	*Stump*	*Branches*	*Leaves*
Weight Percentage........	48	20	14	13	5

Of course, the ratios vary with the age of the tree. As a camphor tree grows older, it develops fewer leaves, and the root system enlarges. Trees growing naturally contain fewer leaves than planted trees. The various parts of a camphor tree yield the following average weight percentages of camphor and camphor oil:

	Leaves	*Branches*	*Trunk*	*Stump*	*Roots*
Camphor (%)..........	1.0	0.3	0.8	1.3	0.8
Camphor Oil (%)......	0.3	0.6	1.4	1.8	2.5
Total Yield (%)........	1.3	0.9	2.2	3.1	3.3

In the above table the branches, trunk, stump, and roots are listed according to ascending total yield of camphor and camphor oil. The leaves contain a good deal of camphor, whereas the roots contain a good deal of camphor oil. On the average the whole tree yields 0.8 per cent of camphor and 1.5 of camphor oil. However, since the oil contains about 50 per cent of camphor in solution, the absolute yield of camphor from the whole tree amounts to 1.5 per cent, whereas the yield of decamphorized oil amounts to only 0.7 per cent. The ratio of camphor to decamphorized oil is, therefore, 7 to 3.

The following flow sheet indicates the various products (camphor and the several types of camphor oil) obtained in the industrial distillation of camphor wood, and fractionation of the distillate:



Government Control of Japan's Camphor Industry.—Since 1903 the government of Japan has enforced a strict monopoly over the camphor industry of the country. On June 1, 1950, this monopoly became a public corporation, the Japan Monopoly Corporation, with authority to fix production schedules for camphor and camphor oil. On the basis of these schedules, a second organization, Nippon Camphor Manufacturing Co., Ltd., collects the products of its affiliated distilleries (which are operated on allotment) and delivers them to the Japan Monopoly Corporation. The latter then distributes the supply of camphor and camphor oil, but only to dealers who have facilities for exporting or selling domestically, after processing the crude material. For example, crude camphor is sold to the Nippon Camphor Co., Ltd.—not to be confused with the Nippon Camphor Manufacturing Co., Ltd.—and crude camphor oil to the Saisei Camphor Manufacturing Co., Ltd., among others. There the crude camphor oil is submitted to fractional distillation and separated into crude camphor (recovered camphor), "White Camphor Oil," "Brown Camphor Oil," and "Blue Camphor Oil."

The recovered camphor and the crude camphor obtained on steam distillation by the producers in the field are called "B" camphor. On purification by means of sublimation the "B" camphor becomes "BB" camphor. The latter may then be employed in celluloid and other industrial materials. The refining of the "BB" camphor into the refined camphor takes place in the Kobe factory of the Nippon Camphor Co., Ltd. The refined camphor serves to supply both domestic and foreign demand.

Any camphor oil fractions containing less than 5 per cent of camphor fall outside of the monopoly control and are sold to the following two companies:

1. Takasago Perfumery Co., Ltd. (established in 1920), which owns factories in Tokyo, Hiratsuka near Yokohama, Wakayama, and Sapporo.
2. Nippon Koryo Yakuhin Co., Ltd. (established in 1927), which owns factories in Kobe.

These two firms are the sole refiners of camphor oil. They not only rectify the white, brown, and blue camphor oils into many fractions and isolates, but also manufacture derivatives, such as synthetic aromatics, ore-flotation oils, solvents, insecticides, etc. They supply the local demand and sell abroad through their own agents overseas.

The Japan Monopoly Corporation has no factory itself, but nevertheless keeps strict control over all camphor enterprises; it owns the Central Research Institute in Tokyo, the Camphor Laboratory in Kagoshima, and it studies and guides the camphor industry in every respect.

In 1933 the engineers—private individuals and government officials—engaged in the camphor and camphor oil industry of Japan and Formosa (which was then under Japanese rule) founded a national research organization under the title "The Association of Camphor Industry Engineers." The association has been fostering and carrying out research work on camphor, camphor oil, and related technical problems. Through its reports, which are read before the annual meetings, the association has rendered a most valuable service not only to the camphor industry, but to the chemistry of terpenes in general.

FORMOSAN CAMPHOR OIL

(The Camphor Oil Industry of Formosa)

Introduction.—When the Japanese discuss Formosan agricultural and related industries, they frequently employ the abbreviations "A.B.C." and "R.S.T." These stand, respectively, for Ananas (pineapple), Banana and Camphor, and Rice, Sugar and Tea, respectively. The presence of camphor in this list testifies to its importance among Formosa's staple products.

For half a century Japan bent every effort toward the improvement of the camphor and sugar industries of Formosa. As a result, the Formosan industry secured the leading position in the camphor industries of the world.

We have previously discussed the camphor industry of Japan itself, with frequent reference to the closely related Formosan industry. We will now turn to the Formosan industry, in particular, and discuss the differences between the camphor industries of Japan and Formosa.

Historical Development.—According to tradition, the process of camphor recovery was introduced into Formosa from Japan between 1664 and 1683 by Chang Chang-Kong (Koxinga). However, it seems more probable that the process came to Formosa from the Loochoo Islands, or from Fukien (located on the coast of China, opposite Formosa) at about the same time the camphor extraction process was introduced into Japan.

When China, under the Ching dynasty, conquered the island of Formosa in 1683, she began a policy of protecting the camphor trees, to safeguard the camphor supply. In the nineteenth century the camphor industry began to prosper, and the camphor produced on the island became world famous. Formosa opened trade with certain foreign firms—a policy that resulted occasionally in trouble. In 1869 the Chinese Government made certain agreements with British, American, and German firms in regard to the export of camphor. However, soon after Japan seized Formosa, in 1895, she established a monopoly over the industry, for the purpose of protecting and developing the industry.

Varieties of the Camphor Tree in Formosa.—There are four morphologically distinct species and varieties of the camphor tree in Formosa. One of these (Kusunoki) is subdivided into 3 physiological forms, according to the components of the essential oils present:

1. Kusunoki (*Cinnamomum camphora* Sieb.)
    - (a) Hon-Sho
    - (b) Ho-Sho
    - (c) Yu-Sho
2. Rau-Kusu (*Cinnamomum camphora* Sieb. var. *nominale* Hayata)
3. Sho-Gyu (*Cinnamomum kanahirai* Hayata)
4. Ohba-Kusu or Pha-Chium (*Cinnamomum micranthum* Hayata).

1(a). Hon-Sho (Hon = true, Sho = camphor tree).

The Hon-Sho is the most important of the camphor varieties for the extraction of camphor. It grows all over the island. In the northern part it occurs up to 1,200 m. altitude, in the southern part up to 1,800 m. Morphologically the Formosan Hon-Sho is identical with the Japanese, yet trees grown from seed of the Japanese Hon-Sho develop less vigorously than those grown from seed of the Formosan Hon-Sho (a result, possibly, of climatic differences). Since 1922 all Hon-Sho trees have therefore been planted exclusively from Formosan seed. It should be mentioned here that some botanists classify the Japanese Hon-Sho as *Cinnamomum camphora* Sieb., and that of Formosa as *Cinnamomum camphora* Sieb. var. *formosana*.

1(b). Ho-Sho (Ho = fragrant). Formerly the tree was called Shiu-Sho (Shiu = bad smelling), and the oil obtained from it was known as Shiu Oil.

The characteristic feature of the Ho-Sho is that, while its essential oil contains compounds also found in Hon-Sho oil, its chief component is linaloöl. At one time oil of Ho-Sho was not produced at all, since it contains less camphor than Hon-Sho oil, but when it was realized that linaloöl could be used and exported as a valuable perfume ingredient, the exploitation and distillation of Ho-Sho trees were started (1920). The rectified oil, obtained from crude Ho-Sho oil by fractional distillation, gained a world-wide reputation as an excellent source for the isolation of linaloöl. In this respect it competes now with oil of bois de rose and oil of linaloe. The Ho-Sho trees always grow in stands with Hon-Sho trees. In the northern and central parts of Formosa they occur more abundantly than in the southern parts.

Some botanists have classified the Ho-Sho as *Cinnamomum camphora* Sieb. var. *glaucescens* Alex. Braun, but Y. Fujita,[3] objecting to this classi-

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[3] *Koryo,* No. 10 (Jan. 1950), 11. (Published by the Japan Perfumery and Flavouring Association.)

fication, declares the Ho-Sho to be *Cinnamomum camphora* Sieb. var. *linaloölifera* Fujita.

1(c). *Yu-Sho* (Yu = oil, Sho = camphor tree).

In China the majority of camphor trees belong to this physiological variety, but in Formosa it occurs only in the southern part of the island and in certain sections of the western part. On distillation, the wood of the Yu-Sho yields an oil which contains only little camphor, hence the name "Camphor *Oil* Tree" (Yu = oil). On the other hand, the oil contains a high percentage of cineole. At present Yu-Sho oil, being unimportant, is not produced.

To summarize: the three above-described varieties of Kusunoki (*Cinnamomum camphora* Sieb.) are identical morphologically, but they differ in regard to the chemical composition of their oils. For this reason they may be considered physiological varieties.

2. *Rau-Kusu*, also called Kusunoki-Damashi (*Cinnamomum camphora* Sieb. var. *nominale* Hayata).

This morphologically distinct variety occurs along the eastern coast of Formosa, where the weather is usually dry, sunny, and windy. The tree is small—about 3 m. tall and 5 to 10 cm. in diameter. After a tree has been felled, new sprouts develop from the stump. Rau-Kusu is a camphor tree variety characteristic of Formosa; it seems to be a deformed variety of Kusunoki. The oil of Rau-Kusu may resemble the oils of the Hon-Sho and Ho-Sho varieties of Kusunoki in composition and is therefore classified either as Ho-Sho or as Hon-Sho type, depending upon whether it contains linaloöl or not. The fact that the stumps of the variety Rau-Kusu grow new sprouts vigorously is important; it means that there is an abundance of leaf material available for distillation. In this respect the variety Rau-Kusu resembles certain *Eucalyptus* species. A study of the distillation of Rau-Kusu leaves, begun in 1937 by N. Hirota,[4] chemical engineer of the Formosan Monopoly Bureau, revealed some interesting facts. Hirota found that there are five distinct types of Rau-Kusu leaf oil, containing, respectively, 78 per cent of camphor, 59 per cent of cineole, 87 per cent of safrole, 85 per cent of linaloöl, and sesquiterpenes only. Here again, we have undoubtedly a typical case of physiological varieties such as exist and have been discovered by Penfold et al., among the eucalypts. (Cf. the monograph on "Australian Eucalyptus Oils.")

Some day extensive bush cultivation of the above-named five Rau-Kusu

[4] *Sho-No*, No. 2 (July 1948), 32. (Published by the Nippon Camphor Association.)

varieties will permit leaf distillation on an organized large scale, and this will have a most far-reaching effect upon the natural camphor industry.

3. Sho-Gyu (*Cinnamomum kanahirai* Hayata).

This is a variety of camphor tree characteristic of Formosa, being found in the prefecture of Hsin-Chu, and in the massif surrounding Mt. A-li. It grows at altitudes ranging from 1,000 to 1,700 m. in the northern part of the island, and between 1,600 and 1,800 m. in the southern part. The Sho-Gyu tree resembles the Kusunoki in appearance, except that its leaves are blackish and its bark lustrous. The essential oil derived from the Sho-Gyu tree contains no camphor; its chief constituent is terpinen-4-ol.

4. Ohba-Kusu, also known locally as Pha-Chium (*Cinnamomum micranthum* Hayata).

Ohba-Kusu is a camphor tree characteristic of Formosa, growing wild in the northern part of the island at altitudes lower than 1,000 m. The timber is fragile and soft, the bark dark. The leaves are thick and large (whence the Japanese name Ohba = large leaf, Kusu = camphor tree). The essential oil derived from the Ohba-Kusu contains 95 per cent of safrole.

To summarize: although there exist altogether six types of camphor trees in Formosa, only two (Hon-Sho and Ho-Sho) are commercially exploited for the extraction of camphor and camphor oil. For the same reason only Hon-Sho and Ho-Sho are planted for reforestation purposes. The other four types of camphor tree are found only in the natural state. Compared with Hon-Sho and Ho-Sho their number is very small, and distillation of them has been carried out on an experimental basis only.

Total Number of Camphor Trees in Formosa.—The Government Monopoly Bureau has counted the total number of camphor trees in Formosa—a most difficult undertaking which required seven years to accomplish. The first count was completed in 1924, the second in 1939–1940. The following figures were obtained:

Variety of Tree	*Number*	*Volume of Wood in Cubic Meters*
Hon-Sho Ho-Sho	17,653,331 *	. . .
Ohba-Kusu	87,000	290,000
Sho-Gyu	46,000	370,000

* 71.5 per cent of which were natural growing, and 28.5 per cent planted trees.

These figures represent the total of all camphor trees in Formosa, including those sufficiently large to be utilized for distillation. The same applies to the census of trees made in Japan in 1947, the count there having been 9,280,792. There are thus almost twice as many camphor trees in Formosa as in Japan.

As regards trees with a diameter above 30 cm.,[5] the following figures were established for Formosa in 1940:

	Hon-Sho	*Ho-Sho*	*Total*
Number of Trees	6,955,472	389,154	7,344,626
Volume of Wood (in cubic meters)	2,067,085	618,496	2,685,581
Area covered (hectares)	...	..	694,719

From the volume of wood represented by these trees the quantities of camphor and camphor oil (Hon-Sho oil and Ho-Sho oil) contained therein were calculated:

	Kilograms
Camphor	7,854,330
Hon-Sho Oil	30,983,507
Ho-Sho Oil	11,922,153
Total	50,759,990

In the course of seven years (from 1941 to 1947), 9,588 metric tons of camphor and camphor oil were produced in Formosa:

	Metric Tons
Camphor	1,340
Hon-Sho Oil	4,706
Ho-Sho Oil	3,542
Total	9,588

The difference between the figures noted immediately above and those listed previously indicates the quantity of camphor and camphor oil stored in the live trees now growing in Formosa (1948):

	Metric Tons
Camphor	6,514
Hon-Sho Oil	26,277
Ho-Sho Oil	8,379
Total	41,170

To remain prosperous, the Formosan camphor and camphor oil industry will have to continue the program of constant reforestation initiated by the

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[5] The Government Monopoly Bureau prohibits the felling of trees of lesser diameter for distillation purposes.

Japanese Government shortly after the Japanese conquest and carried out for almost fifty years. If the present Chinese Government should relax the strict measures of enforcement, the Formosan camphor and camphor oil industry will be faced with a severe crisis within a few decades.

Geographical Distribution.—As was mentioned in the section on "Varieties of Camphor Trees in Formosa," the Hon-Sho and Ho-Sho trees grow all over the island, from about 500 to 1,200 m. altitude in the northern part, and from 500 to 1,800 m. in the southern part. The Sho-Gyu occurs from 1,000 to 1,700 m. in the north, and from 1,600 to 1,800 m. in the south. The Ohba-Kusu grows below 1,000 m. altitude, the Rau-Kusu in the lowlands, particularly along the seashore.

Meteorological Condition.—Meteorological conditions prevailing on Formosa may be judged from Table 2.4:

TABLE 2.4. METEOROLOGICAL OBSERVATIONS

(Formosa)

Prefecture	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Through Year
Average temperature (°C.)													
Tai-peh......	15.1	14.6	16.9	20.8	23.7	26.8	28.0	27.8	26.3	23.1	19.7	16.7	21.6
Tai-chung....	15.6	15.4	18.2	22.0	24.7	26.8	27.6	27.3	26.3	23.7	20.3	17.1	22.1
Tai-nan......	16.8	16.7	19.6	23.4	25.8	27.3	27.7	27.4	26.9	24.8	21.6	18.3	23.0
Hong-chan ..	20.2	20.2	22.2	24.6	26.1	27.5	27.5	27.1	26.6	25.3	23.3	21.3	24.3
Tai-tong.....	18.9	18.7	20.7	23.3	25.0	27.0	27.5	27.2	26.4	24.4	22.1	19.9	23.4
Hoa-lien-chiang.....	16.7	17.4	18.9	21.8	23.7	26.5	27.2	27.0	25.9	23.4	21.1	18.7	22.4
Average amount of rainfall (mm.)													
Tai-peh......	87.6	121.8	181.7	135.5	242.3	269.4	227.5	265.7	245.3	132.8	74.7	88.0	2,072.3
Tai-chung....	35.6	46.8	97.4	115.3	246.5	324.9	296.9	290.5	164.5	32.4	20.1	24.2	1,695.1
Tai-nan......	28.9	26.6	46.5	62.9	181.3	335.1	375.6	432.0	169.0	37.6	18.5	11.8	1,725.8
Hong-chan...	24.9	18.6	22.1	58.4	30.5	287.4	450.9	588.6	291.8	172.2	23.9	17.0	2,166.3
Tai-tong. ...	38.3	33.2	58.5	78.9	181.1	207.7	339.0	339.5	274.4	208.6	53.3	35.3	1,847.8
Hoa-lien-chiang.....	66.7	68.4	93.6	103.6	169.4	172.2	247.8	224.6	241.4	289.8	105.8	74.5	1,857.8
Average humidity (%)													
Tai-peh......	83	84	85	83	82	81	78	78	79	81	82	84	82
Tai-chung....	81	81	83	83	83	82	81	82	81	79	79	81	81
Tai-nan......	78	78	79	78	80	82	82	84	81	78	77	78	80
Hong-chan...	74	74	75	77	79	83	84	85	81	77	74	73	79
Tai-tong.....	74	75	77	80	82	81	81	82	81	79	76	75	79
Hoa-lien-chiang.....	77	80	81	83	85	84	81	81	81	80	79	79	81

Reforestation.—In 1900 the government of Formosa started a large-scale program of reforestation which was carried through systematically until

Japan lost Formosa to China after World War II. For the reforestation of camphor trees, a system of mixed planting was adopted.

In the northern part camphor trees were planted together with an equal number of Formosan pine trees; in the central and southern parts with an equal number of *Acacia confusa* Merrill.

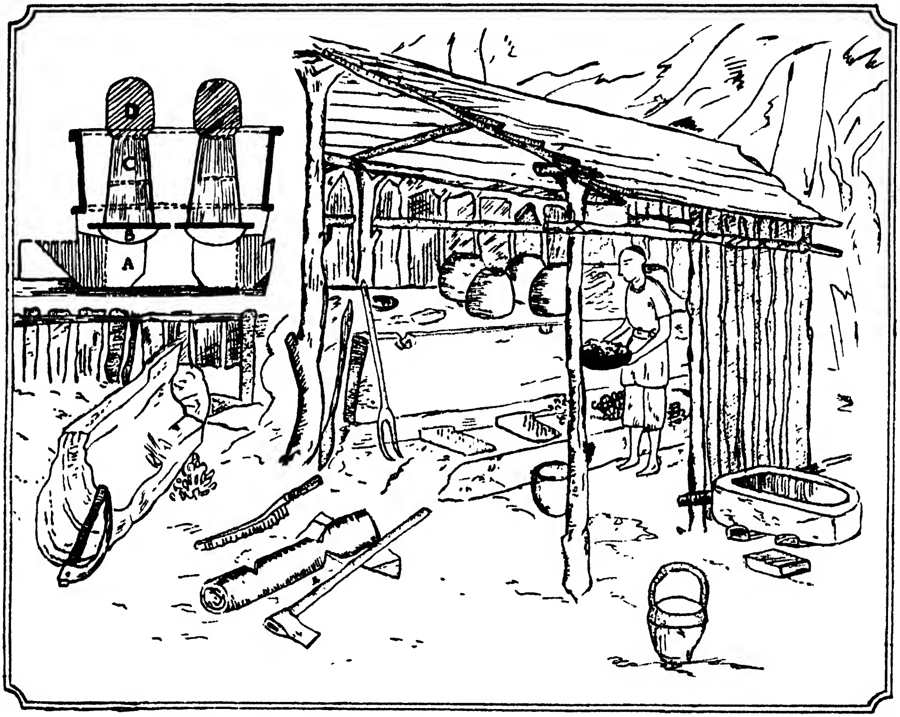
Up to the present time about 44,000 hectares have been reforested. Aside from these planted forests, there is a protected forest of natural camphor trees that comprises about 6,500 hectares. This latter consists exclusively of camphor trees and is very interesting, from a botanical point of view. In 1935, cutting of trees from the reforested area was permitted for the first time. Until then, no camphor trees, except natural growing ones, could be felled in Formosa.

The wood material serving for distillation originates chiefly from trees 150 to 500 years old, or from stumps, or roots of trees cut down long ago. Only a small proportion of replanted trees is employed for distillation. At present, about 80 per cent of naturally growing trees, and 20 per cent of replanted trees are being felled. While Japan controlled Formosa, about 90 per cent of all camphor trees were government property, and only 10 per cent were owned by private interests.

The biggest camphor tree on the island of Formosa was discovered in 1920. It grows at the foot of Mt. A-li, in the prefecture of Tai-chung. This tree belongs to the variety Hon-Sho and at breast height has a circumference of 16.4 m.; its diameter is 5.3 m. In other words, 12 men, arms outstretched, are required to ring the trunk. The trunk is 51 m. tall, and the lowest branch 20 m. above the ground. The volume of the tree has been calculated to amount to 588 cu. m. From the wood 2,743 kg. of camphor and 7,200 kg. of camphor oil could be produced. The age of the tree has been estimated at 1,400 years. As a mark of veneration, the people have erected a shrine at the foot of the tree.

Cutting of Trees and Methods of Wood Chipping.—Because of the above-described government regulations, the camphor and camphor oil industry has to rely, for its raw material, chiefly upon old trees growing feral high in the mountains or in deep ravines. The woodcutters, therefore, have to go through far greater hardships than they do in Japan. The stations of the Monopoly Bureau which collect the crude camphor and camphor oil are connected by roads and railroads with the distilleries, which may be as far as 50 km. distant. Since in the interior of Formosa the distilleries are much farther removed from the camphor forests than they are in Japan, distillers are unable to carry the logs to the distilleries (as is the practice in Japan). In Formosa, the wood has first to be reduced to chips by hand, with special hatchets, or in portable chipping machines driven by gasoline motors. This work must be done on the spot where the camphor trees grow. The workers then pack the chips into bags and carry them over steep and often dangerous paths to the distilleries.

The natives of Formosa hold their camphor trees in great veneration, because they assume every tree to be the home of a god. To their way of thinking, it would be a sacrilege to cut a tree, depriving a god of his abode without his permission. Vengeance would fall upon any mortal who thus provoked the ire of a god. To placate him, offerings are therefore brought by the woodcutters to every single tree before it is felled.



From J. W. Davidson, "The Island of Formosa," London, Macmillan, 1903.

Old Chinese method of preparing camphor.

Distillation.—The first method of camphor recovery in Formosa was the ancient "Bowl Method," also called the "Old Chinese Method." In 1894 the so-called "Tosa Method" was introduced, in time partly replacing the "Bowl Method." Moreover, the old "Bowl Method" was improved, and in this form became quite popular among the native distillers. In this modified apparatus the upper lid of a barrel condenser is replaced with a bowl that stands on top of the condenser like a bell. The bowl is kept cool with water that flows from a bamboo pipe. The method thus represents a combination of the old Chinese and the newer Japanese camphor distillation methods. However, when in 1934 the recovery of camphor became a government monopoly, the method was abandoned in favor of the more efficient Japanese method. The steam stills now used in Formosa are of the same type as those employed in Japan, except for the dimensions which, in the Formosan stills, are as follows:

(a) Kettle: diameter 1 m., depth 0.45 m.
(b) Retort (Koshiki): height 2.3 m., bottom diameter 1.1 m., top diameter 0.45 m.; weight of charge 540 kg. of chips.
(c) Feeding stoker: every still is equipped with a wooden, box-shaped feeding chute, through which exhausted chips are fed into the fire beneath the kettle.
(d) Condenser: either barrel or box condensers are used. In the case of distillation of Ho-Sho, spiral condensers are employed, because no solid camphor separates, as is the case with Hon-Sho.

Needless to say, the woods from Hon-Sho and Ho-Sho must be distilled separately; their ratio is about one to one.

In Formosa the distillation of camphor wood usually requires more time than in Japan, because the Formosan trees are older and harder, and the oil cannot be isolated from the wood as easily. However, even if this were not the case, longer distillation is generally preferable for complete recovery of the camphor oil, provided consumption of fuel does not exceed economical limits.

In Formosa the total area of camphor and camphor oil production (cutting of trees, transport of chips, and distillation) covers about 1,400,000 hectares. One-fourth of this area lies in the prefecture of Tai-chung, with Hsin-chu and Tai-peh following in importance. According to a survey conducted in 1938, the number of camphor and camphor oil distilleries in that particular year was 4,000, and the number of people employed in the industry about 8,500.

The center of production of camphor and camphor oil is in the prefecture of Tai-chung. Listed according to importance of production, the various provinces of Formosa rank as follows:

	Per Cent
Tai-chung	40
Hsin-chu	21
Tai-peh	12
Ta-kou	11
Hoa-lien-chiang	7
Tai-nan	5
Tai-tong	4

Yield of Oil.—The various factors (condition of the plantings, age of the trees, parts of the trees, etc.) influencing the yield of camphor and camphor oil were discussed above, in the section on "Japanese Camphor Oil." These factors operate also in Formosa. The following will deal with the yields obtained from Formosan Hon-Sho and Ho-Sho trees.

1. Average yield of camphor and camphor oil from the various parts of the tree.

	Roots		*Trunk*		*Boughs, Twigs*		*Whole Tree*	
	Camphor (%)	*Camphor Oil* (%)	*Camphor* (%)	*Camphor Oil* (%)	*Camphor* (%)	*Camphor Oil* (%)	*Camphor* (%)	*Camphor Oil* (%)
Hon-Sho	1.02	1.87	0.67	1.53	0.47	1.07	0.80	1.60
Ho-Sho *	...	3.43	...	2.26	...	0.91	...	2.40
Leaves of Hon-Sho							0 7	0.4

* As has been pointed out, the Ho-Sho tree, on steam distillation, does not yield any free crystalline camphor, but the oil contains about 40 per cent of camphor *in solution.*

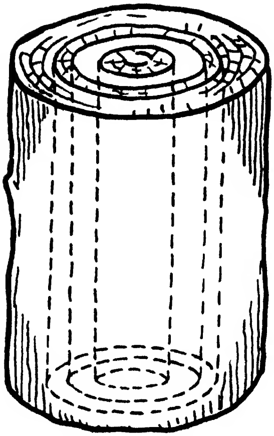
2. Average yield of camphor and camphor oil from trees of different height.

The content of camphor and camphor oil in the trunk decreases from ground level to the top, as the following table illustrates:

	Hon-Sho Tree (120-year-old)			*Ho-Sho Tree (120-year-old)*	
Height above ground (m.)	*Diameter (cm.)*	*Content of Camphor (%)*	*Content of Camphor Oil (%)*	*Diameter (cm.)*	*Content of Ho-Sho Oil (%)*
0.30	107.3	1.73	2.24	109.1	2.68
3.03	80.6	1.11	1.61	74.5	2.19
6.67	71.8	0.82	1.26	67.9	1.72
12.12	54.5	0.48	0.81	60.9	1.55
15.76	40.0	0.17	0.58	51.8	1.47
19.39	24.2	0.06	0.34	42.4	1.26
21.21	23.0	0.02	0.22	39.7	0.98
23.03	21.2	...	...	34.5	0.89
26.66	11.2	...	...	26.1	0.56
30.30	...	...	...	17.3	0.27

3. Relation between the position of the camphor and camphor oil in the tree trunk, and the yield of each of these.

To determine this relationship, a study was made of the percentage of camphor and camphor oil contained in each five-year series of annual tree rings. The trunks of Hon-Sho and Ho-Sho trees, 120 years old, were cut vertically along their annual rings, each segment including five years. It



Vertical cuts along the annual rings (every five years).

was found that the camphor and camphor oil accumulate on the outer side of the trunk (away from the center), as can be seen from the following table:

Series Number of Annual Rings Studied	*Hon-Sho Tree*		*Ho-Sho Tree*
	Camphor (%)	*Camphor Oil (%)*	*Ho-Sho Oil (%)*
1- 5	...	...	...
11- 15	...	0.083	0.028
21- 25	0.007	0.346	0.194
31- 35	0.133	0.616	0.478
41- 45	0.303	0.796	0.847
51- 55	0.473	0.909	1.156
61- 65	0.622	1.000	1.363
71- 75	0.755	1.090	1.602
81- 85	0.855	1.166	1.846
91- 95	0.948	1.240	2.130
101-105	1.043	1.329	2.411
111-115	1.135	1.430	2.723

4. Content of camphor and camphor oil in the root system.

The roots of a camphor tree contain much more camphor and camphor oil than any other part of the tree. The root system consists of a large stump with many roots attached. The yield of camphor and camphor oil in every part of the root system of a 120-year-old tree has been studied, with the following results:

	Hon-Sho Tree		*Ho-Sho Tree*
	Camphor (%)	*Camphor Oil (%)*	*Ho-Sho Oil (%)*
Main Root..................	2.17	2.70	3.47
Root with Diameter of 30 cm...	1.51	1.77	2.68
Root with Diameter of 18 cm...	1.28	1.68	2.02
Root with Diameter of 6 cm....	0.04	0.88	1.63

The yield of camphor and camphor oil from Formosan Hon-Sho trees is sometimes higher than that obtained from the same type of tree in Japan. The reason is simply that in Formosa much older trees (often 150 to 500 years old) are used for distillation, with a consequent higher yield. In Formosa the Hon-Sho trees yield on the average 0.8 per cent of crude camphor, and 1.6 per cent of crude camphor oil.

Formosan Ho-Sho trees yield an average 2.4 per cent of oil.

The oils derived from Hon-Sho and Ho-Sho trees yield the following main fractions, in per cent:

	Camphor (%)	*White Oil* (%)	*Ho Oil* (%)	*Brown Oil* (%)	*Terpineol* (%)	*Blue Oil* (%)	*Pitch* (%)
Hon-Sho Oil.......	50	22	...	20	2	2	2
Ho-Sho Oil........	40	18	20	13	2	2	2

The so-called "White Oil" contains 25 per cent of cineole, the Ho oil 80 to 85 per cent of linaloöl, the "Brown Oil" 50 to 60 per cent of safrole, and the "Terpineol" contains 70 per cent of α-terpineol.

Some years ago the Monopoly Bureau prohibited the export of the crude (nonrectified) Hon-Sho and Ho-Sho oils, and their use on the domestic market. All lots of crude Hon-Sho and Ho-Sho had to be delivered to the government-owned Nan-Mon Factory in Tai-peh, where they were bulked and fractionated into six fractions in a large continuous vacuum distillation plant (see below).

In 1937 the Nan-Mon Factory fractionated 3,800 metric tons of bulked crude Hon-Sho and Ho-Sho oils (in the proportion of 1:1), and produced the following fractions (in metric tons):

	Camphor	*White Oil*	*Ho Oil*	*Brown Oil*	*Terpineol*	*Blue Oil*	*Pitch*	*Water*	*Loss*
Tons (metric)	1,780 *	701	327	665	69	49	85	38	86
Per Cent	46.8	18.5	8.6	17.5	1.8	1.3	2.2	1.0	2.3

* Aside from this quantity, the factory processed 800 metric tons of crude camphor obtained by steam distillation of the wood.

The flow sheet reproduced in the section on "Japanese Camphor Oil," which shows the various products obtained from the wood of Hon-Sho trees, applies also to the Formosan camphor and camphor oil industry.

Yield of Sho-Gyu Oil (*Cinnamomum kanahirai* Hayata).—A 159-year-old Sho-Gyu tree (22 m. tall, with a diameter of 0.79 m. at breast height) was cut up and submitted to steam distillation. The whole tree (except for the leaves) yielded 2.01 per cent of oil. Of the total quantity of oil obtained, 53 per cent was oil from the trunk, 35 per cent oil from the roots, and

12 per cent was oil derived from the branches. The various parts of the tree therefore contained:

	Per Cent of Oil
Branches	1.21
Roots	2.67
Trunk:	
Lower Part (from ground to 11 m.)	2.03
Middle Part (from 11 to 20 m.)	1.99
Upper Part (from 20 to 22 m.)	1.58

Yield of Ohba-Kusu Oil (*Pha-Chium*).—This oil contains from 90 to 95 per cent of safrole and has a specific gravity (at 20°) of 1.089. The oil is thus heavier than water, which fact renders separation of the oil from the distillation water difficult and lowers the yield. The average yield ranges from 1.3 to 1.5 per cent.

A 130-year-old tree was cut apart and, on distillation, the following yields were obtained:

	Per Cent of Oil
Leaves	0.014
Branches	0.367
Roots	2.185
Trunk:	
Lower Part	1.326
Middle Part	1.015
Upper Part	0.643

Yield of Rau-Kusu Oil (*Cinnamomum camphora* Sieb. var. *nominale* Hayata).—This tree yields on the average 1.1 per cent of oil.

Organization of Formosa's Camphor and Camphor Oil Industry.—In 1900, five years after Formosa had come under Japanese rule, the government of Formosa declared the camphor production of the island a monopoly. In 1903 the monopoly system of Japan proper was extended to Formosa, and from that time on the camphor industry has continued under strict control. (However, little is known about the present enforcement of the regulations.) In 1919 the Taiwan Seino Co. (Formosa Camphor Manufacturing Co., Ltd.) was established. This was the only firm permitted to produce camphor. In 1934 the entire camphor and camphor oil industry (reforestation, distillation, fractionation, refinement, etc.) came under the control of the Monopoly Bureau.

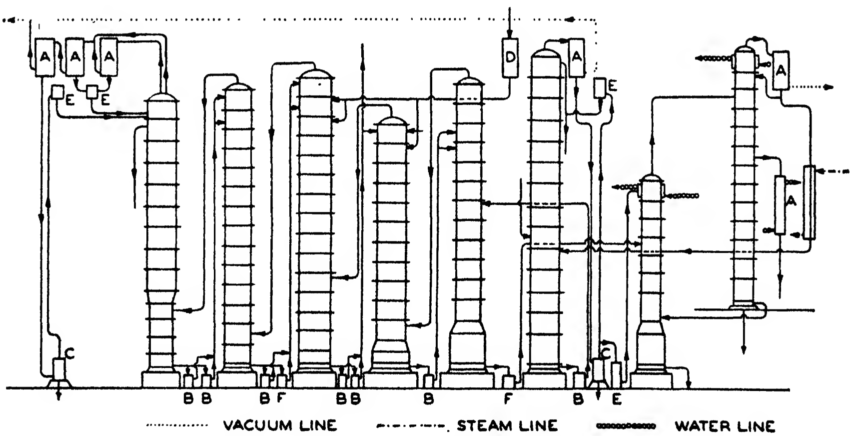
In Tai-peh the Monopoly Bureau owns a government-operated factory, the Nan-Mon Factory, equipped with a continuous vacuum distillation and fractionation unit, one of the largest and most efficient being used anywhere in the essential oil industry. It was designed by Dr. T. Ikeda, the factory manager, and his staff, and began operation in 1933. As may be seen from the drawing on page 293, the plant consists of eight distillation towers, the tallest of which is 50 ft. high. From 500 to 600 kg. of crude camphor oil can be processed per hour, distillation and separation into several fractions taking place as a continuous operation. The unit permits the sharp separation of the camphor and linaloöl-containing fractions, and produces a rectified Ho oil that contains more than 85 per cent of linaloöl.

The government also owns the Central Research Institute in Tai-peh, which has published a number of valuable papers on essential oils.

While the Japanese ruled Formosa, the above-mentioned Nan-Mon Factory was operated on the same lines as the Saisei Camphor Manufacturing Co. in Japan, except that it exported its "BB" camphor directly to America and other countries. The Ho oil produced in the factory was of high quality, with a very fine odor. This oil was either exported to America and Europe or sold to the Takasago Chemical Industry Co., Ltd., which had a factory in Tai-peh. In this factory the Ho oil was acetylated and subjected to fractional distillation to separate the linalyl acetate. Both Ho oil and linalyl acetate were then sold abroad.

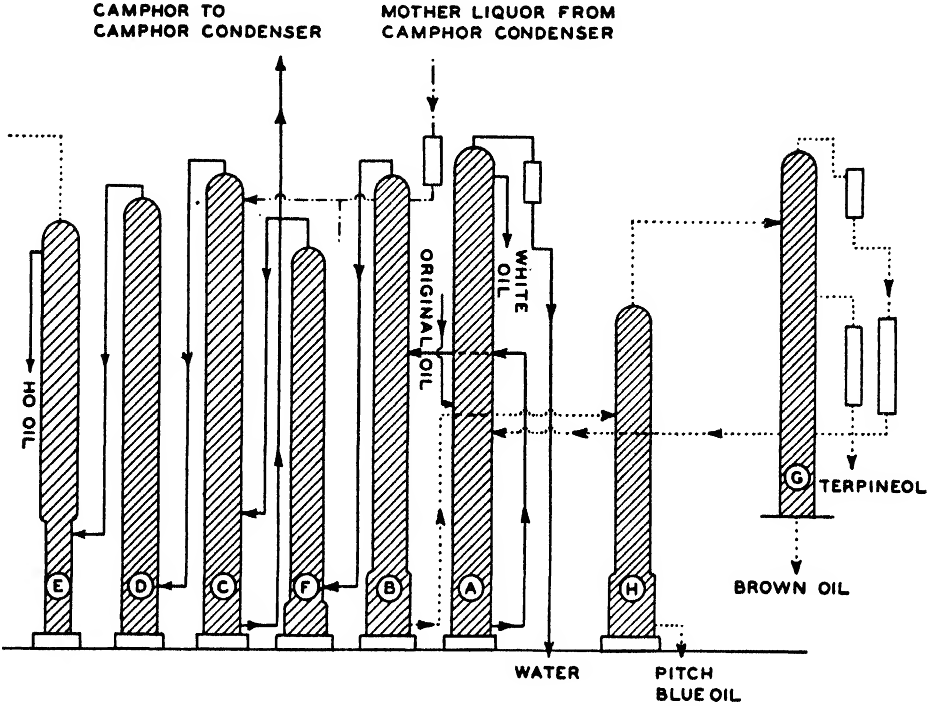
The crude camphor was refined in the factory of the Nippon Camphor Co., also located in Tai-peh.

Research on the synthesis of camphor from pinene was conducted in laboratories in Formosa and Japan for many years. In 1937 a pilot production plant was erected in the Nan-Mon Factory. The synthesis was an improved version of the Schering process: pinene → bornyl chloride → camphene → camphor. The pilot plant produced about 10,000 kg. of camphor



Continuous-vacuum-distillation apparatus in the Nan-Mon Factory.

A. Condensers.
B. Pumps.
C. Water separators.
D. Preheater.
E. Measuring tanks.
F. Tanks.



EXPLANATION OF THE CONTINUOUS VACUUM FRACTIONATION UNIT

Tower A: From 500 to 600 kg. of oil per hour are charged into this tower. Any water contained in the crude oil is removed. "White Oil" is produced in tower A.

Tower B: The residual oil from tower A is pumped to the center plate of tower B.

Tower C: Through tower F the camphor and linaloöl fractions are transferred to tower C. From the bottom of this tower the camphor fractions are delivered to the camphor condenser.

Tower D: The linaloöl fraction is further purified from the camphor fraction. The linaloöl vapors are conducted to the next tower.

Tower E: Rectified Ho oil (containing 85 per cent of linaloöl) is obtained here.

Tower H: The residual oil from tower B is pumped into the middle of tower H. The heavy oil ("Blue Oil" and pitch) is removed from the bottom of this tower.

Tower G: From the top of tower H the vapors flow to tower G. Terpineol distills from the middle plate of tower G, while the "Brown Oil" is removed from the bottom. The vapors from the top of this tower contain some camphor and are returned to tower A.

Heat Source: Superheated steam rises through colanders in every tower.

per year. To prepare camphor from pinene in only three stages represented quite an improvement upon the old Schering process, but operation had to be suspended in 1944, as a result of war conditions.

In 1945 Japan restored Formosa to China. Since then efforts have been made to operate Formosa's camphor industry along the same lines as Japan's camphor industry. Nevertheless, since the end of World War II the camphor and camphor oil industry of Formosa has been declining rapidly.

Problem of Leaf Distillation.—While it is true that some producers in Formosa and Japan distill the leaves of a felled camphor tree together with the chips of the root and the trunk, the practice of leaf distillation is certainly not general, and for a number of reasons. For one thing, it has been observed that cutting of the leaves from live trees inhibits the growth of the tree. The cost of labor, as well as difficulties of transport, have been additional discouraging factors. In Formosa, especially, where steep mountain paths make transportation of the bulky leaf material to the distilleries well-nigh impossible, the use of such material is uneconomical.

The Japanese government has at various times given serious attention to the problem and attempted to encourage distillation of the camphor leaf. In the province of Tosa, for example, experiments were made over a number of years; in addition, the Monopoly Bureau, beginning in 1920, sponsored studies, offering bounties as an inducement to the distillation of the leaves. Results, however, were disappointing, and the fact would appear to be that, under present conditions, distillation of the leaves is not a paying business.

All attempts along these lines have up to the present been confined to the leaf material collected from the Hon-Sho tree, which cannot withstand loss of the foliage. However, it is known to be true of certain other camphor species that leaves and twigs spring abundantly from the cut stumps—as is the case with certain *Eucalyptus* varieties. To render distillation of the leaves commercially successful, the possibility of distilling the leaves of varieties having the characteristics of shrubs ought to be investigated. For example, the subspecies Rau-Kusu discovered in Formosa might be well suited to leaf distillation. In future, emphasis should be laid upon the cultivation, on a large scale, of such species.

Leaves containing about 1 per cent of camphor can be utilized for distillation. For the development and future prosperity of Japan's natural camphor industry, it will be necessary to select and propagate species which produce large quantities of high-yielding leaf material that can be harvested regularly. For Japan this is a most serious and pressing problem.

Oil Occurrence in the Camphor Tree.—About 50 per cent of the camphor tree consists of water; the remainder of the tree (the wood) contains 30.8 per cent of lignin (and other compounds), 18.0 per cent of pulp, 0.8 per cent of camphor, and 0.4 per cent of camphor oil (decamphorized).

The general problem of the formation of essential oils in plants is a most complicated one. A good deal of attention has been devoted to it, but no satisfactory conclusions have been reached.[6] Tschirch [7] has suggested that, in the course of plant growth, the internal membranes of the oil glands or sacs in essential-oil-bearing plants become mucilaginous and are converted gradually into the precursors of the essential oil. As the oil is formed it accumulates as droplets within the oil glands. While this theory accounts, perhaps, for the formation of the oil by changes brought about upon the mucilaginous matter [8] in the cell substance that forms the oil receptacles, it offers no description of the process of conversion itself, nor of what causes it.

According to the theory advanced by Charabot and Gatin,[9] the oil components themselves are first formed in the green organs of the plant, then, dissolving in the sap, circulate through the system. In certain areas of the plant (described as secreting organs) they come in contact with a solution already saturated with oily matter; the oil is then precipitated. This theory—which may be called the oil-precipitation theory—postulates that the oil-charged sap of the plants seeps into the oil glands by osmosis, causing the precipitation of oil described above. Like the theory of Tschirch, the oil-precipitation theory of Charabot and Gatin offers no adequate explanation of why the oil components are formed in the first place. Moreover, the sap of the camphor tree contains practically no camphor or camphor oil; therefore the theory of Charabot and Gatin cannot be applied to the camphor tree.

Accepting the theory of Tschirch, and studying the problem specifically in relation to the camphor tree, Shirasawa [10] was able to show that a number of oil-containing cells occur in branches of the plant at an early stage of growth, and that, in the course of *several* years, a yellow essential oil develops and secretes in these glands. Gradually, this oil becomes lighter in color, much more mobile and volatile, and assumes the property of crystallizing and separating camphor. The mobile oil then penetrates into all woody parts of the tree, and by vaporization deposits crystalline camphor in the clefts and fissures of the wood.

Yahagi [11] conducted experiments with young camphor trees raised from seed, subjecting various parts of the plant, at various stages of growth, to

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[6] For a fuller discussion of this subject, the reader is referred to Vol. I of this work, p. 50 ff.

[7] *Arch. Pharm.* **240** (1902), 257.

[8] Tschirch calls this layer "resinogene Schicht."

[9] "Le Parfum chez la Plante," Paris (1908), 233.

[10] *Bull. Agr. Coll., Tokyo Imp. Inst.* **5** (1903), 373. *Chem. Zentr.* (1903), II, 892.

[11] *Sci. Papers Central Res. Inst. Govt. Monopoly Bureau Japan,* No. 23 (1928), Tokyo. Cf. Lehmann, "Planta," *Arch. wiss. Botanik* **1** (1925), 343. *Ber. Schimmel & Co.* (1927), 172.

biochemical analysis, in order to determine when and how the camphor and the oil are developed in the plant tissue. His observations indicate that, contrary to earlier belief, formation of camphor and camphor oil takes place *very early* in the plant's development (in the seedlings); and, further, that the inner walls of the oil glands are lined with a compound (probably an enzyme) which reacts like a peroxidase. Apparently minute droplets of oily matter are produced on contact with the oxydase; the droplets accumulate, until the oil gland is filled. Yahagi studied the formation of the oil in practically every part of the tree tissue, and especially in those parts lying directly under the cambium, where such formation is particularly heavy. The quantity of camphor and camphor oil thus formed depends upon the growth intensity of the plant. The largest amounts occur in those places which exhibit the heaviest growth.

Fujita [12] has done much work on young camphor trees grown from the seed of the Formosan Hon-Sho. The plants he examined ranged in age from twenty-six days to twenty-three months. He concludes that the process of oil formation may be divided into three stages, each independent of the others:

1. Formation of safrole and methyl eugenol. This process has no relation to the formation of other essential oil constituents in the plant; it seems rather to be in some way connected with the formation of lignin.
2. Formation of camphor. In the leaves this process is abrupt.
3. Formation of terpene alcohols. This takes place after the formation of the camphor, by assimilation. The alcohols are then converted into esters by reaction with acids, and into terpenes by dehydration.

Fujita and Yamashita [13] also studied the changes in specific gravity and optical rotation that take place as a result of maturation. The following figures were obtained in an investigation of the whole parts of young trees:

	26 Days after Germination	*190 Days after Germination*
Specific Gravity...........	1.0198	0.8914
Optical Rotation..........	+4° 30′	+34° 0′
Yield of Oil from Leaves and Stalks (%).............	0.63	0.69
Yield of Oil from Roots (%)	0.20	0.31

It will be observed that the specific gravity of the oil from very young plants is high. This appears to be due to the presence of a heavy content of

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[12] *J. Chem. Soc. Japan* **64** (1943), 595. *Chem. Abstracts* **41** (1947), 3509.
[13] *J. Chem. Soc. Japan* **64** (1943), 411.

safrole. As the percentage of other essential oil components increases, the specific gravity of the oil decreases. The increase in the optical rotation with age is undoubtedly the result of an increase in the percentage of camphor, which has a high optical rotation.

Analyzing oils derived from the leaves, the stalks, and from the roots, Fujita[14] identified the following constituents:

In the oil from the leaves and stalks: *Camphor*, *l*-linaloöl, α-terpineol, α-pinene, limonene, cineole, safrole, methyl eugenol, α-caryophyllene and sesquiterpenes of the eudalene and cadalene types.

In the oil from the roots: *Safrole*, camphor, limonene, cineole, terpene alcohols and their esters, methyl eugenol and small quantities of sesquiterpenes.

Although *camphor* is the chief constituent of the oil from the leaves and stalks, *safrole* is the most important constituent of the root oil.

Since linaloöl does not occur in the oil from mature Hon-Sho trees, its presence in the young tree is of considerable importance. To explain it, Fujita suggested that, of all terpene alcohols formed in the tree, linaloöl is formed first, being afterwards converted into terpineol, limonene, and cineole. Wherever linaloöl exists as a component of an essential oil derived from a camphor tree, the tree of origin may be assumed to be the Ho-Sho. (Hon-Sho and Ho-Sho are identical morphologically.)

As regards the inorganic chemical components of the camphor tree, they bear a direct biochemical relation to the growth of the tree. Mochida[15] analyzed the total ash of various parts of the tree, in various stages of growth:

Estimation of Total Ash (Percentage)

	1-Year-Old	*8-Year-Old*	*17-Year-Old*	*31-Year-Old*
Leaves	4.02	6.29	4.84	4.24
Branches	...	3.12	2.07	3.19
Trunk	...	1.39	1.03	1.04
Stump	...	1.84	1.11	0.91
Roots	...		1.15	0.78

These figures indicate that the ash content of the leaves and branches is high, and also that the ash content of the trunk, stump, and roots decreases as the plant matures. The ash was composed of:

SiO_2, SO_3, K_2O, Na_2O, Fe_2O_3, Al_2O_3, P_2O_5, Mn_3O_4, SrO, CaO, MgO

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[14] *Ibid.*, 1119. Cf. other papers of Fujita: *ibid.* **58** (1937), 1182; **63** (1942), 58; **64** (1943), 416.

[15] *J. Pharm. Soc. Japan* **59** (1939), 224.

Qualitative Assays.—The crude camphor and camphor oil carried by field producers to the collecting stations are subjected to the following simple tests:

Crude camphor.

(a) Test for moisture and solid impurities.

5 g. of the sample are placed in a graduated test tube, and petroleum ether (b. 40°–60° C.), saturated with water, is added until the volume of the mixture amounts to 15 cc. The mixture is then centrifuged, and the water and the solid deposit are measured.

(b) Test for oil content in crude camphor.

The camphor oil contained in a sample of crude camphor changes color on treatment with concentrated sulfuric acid. A simple colorimetric test (comparison with standard iodine solutions) is therefore employed to determine the percentage of camphor oil in any sample of crude camphor:

0.5 g. of the sample is placed in a regular test tube, and 10 cc. of concentrated sulfuric acid (J. Ph. d_{15} 1.84) are added. When the camphor has been completely dissolved by vigorous shaking, the color of the solution is compared with that of a series of iodine solutions, of different strengths. The percentage of camphor oil in the sample may be computed by means of the following tables:

A. *Standard iodine solutions*

$\frac{N}{8}$	$\frac{N}{9}$	$\frac{N}{10}$	$\frac{N}{12}$	$\frac{N}{15}$	$\frac{N}{18}$	$\frac{N}{20}$	$\frac{N}{24}$	$\frac{N}{30}$	$\frac{N}{35}$	$\frac{N}{40}$

B. *Percentage of camphor oil in the sample*

30.0	26.7	24.0	20.0	16.0	13.3	12.0	10.0	8.0	6.8	6.0

(The percentages of camphor oil represented in B refer to the respective figures for standard iodine solution in A directly above.)

The content of camphor oil in the sample is thus indicated by the closest match in color between the camphor-sulfuric acid mixture and the iodine solutions of known strength. (Normal iodine solution: 126.8 g. of iodine and 200 g. of potassium iodide are dissolved in 1,000 cc. of water.)

Rough standards of purity have been established for:

1. *Crude Hon-Sho Oil.* This should not contain any moisture or solid impurities. Its specific gravity at 25° C. should be higher than 0.920. On treatment with Denigès' reagent the oil should turn white or yellow, and in a short time precipitate a solid with the same color. (Denigès' reagent—mercuric sulfate solution—is prepared by dissolving 5 g. of mercuric chloride in the hot solution obtained when 20 cc. of concentrated sulfuric acid is added to 100 cc. of water.)

2. *Crude Ho-Sho Oil.* This should not contain any moisture or solid impurities. The specific gravity at 25° C. should be higher than 0.900. On

treatment with Denigès' reagent, the sample should exhibit a characteristic color reaction (due to the presence of linaloöl).[16] The following test is used:

> Ten cc. of Denigès' reagent are placed in a test tube, and an equal volume of the sample is added. The mixture is then shaken (at a temperature of about 20°), with resulting gradual precipitation. The contact layer between oil and water develops at first a rose color, which later changes to dark red. At the same time, the color of the solution changes from violet to brownish-violet and finally to dark gray, with increasing precipitation.

As regards the various types of camphor, the following standards of purity are applied:

Crude Camphor ("B" Camphor). This contains less than 2.5 per cent of water, less than 0.05 per cent of solid impurities, and less than 2.0 per cent of oily substances. Its purity is above 95 per cent.

Refined Camphor-2nd Class ("BB" Camphor). This contains no moisture or solid impurities, and less than 1.0 per cent of oily matter. Its purity is above 99 per cent.

Refined Camphor. This contains less than 0.5 per cent of oily matter as impurity. Hence its purity is above 99.5 per cent.

Quantitative Assays.—In 1940, the Association of Camphor Industry Engineers of Japan adopted certain methods of analysis for camphor and camphor oil. The salient points of the methods may be summarized as follows:

1. Determination of the purity of camphor.
A sample is placed in a test tube, and melted in an oil bath. The melted camphor is then transferred to a cooling bath, and the congealing point measured. By means of a complicated formula, involving the congealing point, the percentage of chemically pure camphor present in the sample can be determined.

2. Quantitative estimation of camphor in camphor oil.
The crude camphor is subjected to treatment with barium sulfate, concentrated sulfuric acid, and bromine, which has the effect of converting every component of the crude camphor sample, except the camphor itself, into nonvolatile substances. Since the camphor is not attacked, it may be distilled over with steam, extracted with toluene, and its purity determined by means of its optical rotation.

3. Quantitative determination of safrole in "Brown Camphor Oil."
Safrole forms an addition compound with 1,3,5-trinitrobenzene. When the latter is added to brown camphor oil, and the freezing point of the addition compound measured, the safrole content of the oil can be calculated, by reference to a table showing the relation between the safrole content and the freezing point of the safrole-trinitrobenzene addition compound.

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[16] An organic compound containing a vinyl group (such as linaloöl) exhibits a characteristic color reaction on addition of Denigès' reagent. Cf. Nagai, "Studies of Shiu (Ho) Oil" (1912).

4. Quantitative estimation of linaloöl in Ho-Sho oil.

(a) Methane gas (Grignard) method.

This represents an improvement upon the Zerevitinov[17] method. The Grignard reagent is added to the Ho-Sho oil. The action of the reagent upon the linaloöl present in the oil generates methane gas. Quantitative determination of the amount of gas generated indicates the percentage of linaloöl in the oil.

(b) Dehydration method.

The oil is treated with zinc chloride or phosphoric acid, whereby the linaloöl will be dehydrated. By determining the amount of water released, the linaloöl content of the oil can be calculated.

5. Quantitative estimation of cineole in "White Camphor Oil."

Cineole forms an addition product with ortho-cresol. The freezing point of this addition compound may be used to determine the cineole content of the oil. This procedure follows the method of cineole determination given in the British Pharmacopoeia (cf. Vol. I of this work, p. 294).

(For further methods the reader is referred to T. Ikeda and S. Takeda, "A New Method for the Determination of Linaloöl, Cineole and Terpineol," *J. Chem. Soc. Japan* **57** [1936], 442. *Chem. Abstracts* **30** [1936], 5907.)

PHYSICOCHEMICAL PROPERTIES OF ORIGINAL (NONRECTIFIED) CAMPHOR OILS

The physicochemical properties of camphor oils vary with every lot. In typical samples of nonrectified oils, the following values have been observed:

1. Oil of Kusunoki (*Cinnamomum camphora* Sieb.)

(a) Hon-Sho Oil

Specific Gravity at 25°	0.9543
Optical Rotation	+32° 24′
Refractive Index at 25°	1.4806
Acid Number	1.1
Saponification Number	4.1
Saponification Number after Acetylation	23.3
Alcohol Content, Calculated as $C_{10}H_{18}O$	6.5%
Camphor Content	50.5%

(b) Ho-Sho Oil

	From Northern Formosa	*From Southern and Middle Formosa*
Specific Gravity at 25°	0.9231	0.9306
Optical Rotation at 30°	+17° 14′	+21° 58′
Refractive Index at 25°	1.4692	1.4702
Alcohol Content, Calculated as $C_{10}H_{18}O$	36.8%	30.0%
Camphor Content	39.6%	44.0%

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[17] *Z. anal. Chem.* **50** (1911), 680. Cf. Vol. I of this work, p. 350.

(c) Ho-Sho Leaf Oil

Specific Gravity at 25°	0.8925
Optical Rotation at 25°	−11° 2′
Refractive Index at 25°	1.4659
Alcohol Content, Calculated as $C_{10}H_{18}O$	71.2%

(d) Yu-Sho Oil

Specific Gravity	0.942 (at 13°) to 0.972 (at 16°)
Optical Rotation	+18° 53′ to +29° 51′
Refractive Index	1.4746 (at 19°) to 1.4789 (at 20°)

The oil consisted mainly of cineole.

2. Sho-Gyu Oil (*Cinnamomum kanahirai* Hayata)

Specific Gravity at 9°	0.910
Optical Rotation at 9°	+23° 15′
Refractive Index at 20°	1.4748
Acid Number	0.63
Ester Number	0.65
Saponification Number after Acetylation	100.7
Alcohol Content, Calculated as $C_{10}H_{18}O$	30.05%

3. Ohba-Kusu or Pha-Chium Oil (*Cinnamomum micranthum* Hayata)

Specific Gravity at 20°/4°	1.089
Optical Rotation at 26°	−0° 14′
Refractive Index at 20°	1.5457
Acid Number	0.5
Ester Number	3.5
Saponification Number after Acetylation	5.7
Safrole Content	90% and more

Physicochemical Properties of Fractionated Camphor Oils

1. White Camphor Oil (Light Camphor Oil)

Boiling Range	160° to 185°
Specific Gravity at 15°	0.870 to 0.880
Optical Rotation	+15° 0′ to +20° 0′
Refractive Index at 25°	About 1.4663
Camphor Content	Below 2.5%
Cineole Content	20 to 25%

In addition, the oil contains dipentene, pinene, camphene, etc.

2. Brown Camphor Oil (Red Camphor Oil)

As the name implies, the oil has a reddish-brown color.

Boiling Range	210° to 250°
Specific Gravity	1.000 to 1.035

Optical Rotation	0° to +12° 0′
Refractive Index at 25°	About 1.5150
Camphor Content	Below 3.0%
Safrole Content	50 to 60%

The oil also contains α-terpineol.

3. Blue Camphor Oil (Green Camphor Oil)

This is a higher boiling fraction, and exhibits a blue color, as implied in the name.

Boiling Range	220° to 300°
Specific Gravity at 15°	Below 1.000
Refractive Index at 25°	About 1.5050
Camphor Content	Below 2.5%

The oil consists mainly of sesquiterpenes and sesquiterpene alcohols.

4. Ho Oil "A" (Extra Ho Oil)

This is the best quality of Ho oil produced by the prominent Nan-Mon distillery (Formosan Monopoly).

Specific Gravity at 25°	0.860 to 0.865
Optical Rotation	Above −14° 0′
Refractive Index at 25°	About 1.4613
Camphor Content	Below 0.7%
Linaloöl Content	94% and more (by the zinc chloride method)

5. Ho Oil "B" (Ho Oil)

This type of oil is used for the isolation of linalyl acetate.

Specific Gravity at 25°	0.860 to 0.865
Optical Rotation	Above −12° 0′
Refractive Index at 25°	About 1.4621
Camphor Content	Below 1.5%
Linaloöl Content	85 to 90% and higher (by the zinc chloride method)

The above-mentioned fractionated oils are further fractionated to produce several compounds important for export:

6. "Eucalyptus Oil" (Synthetic Eucalyptus Oil from Camphor Oil)

Boiling Range	170° to 175°
Specific Gravity at 15°	About 0.920
Optical Rotation	About +5° 0′
Refractive Index at 20°	1.460 to 1.465
Cineole Content	80 to 85% (by the ortho-cresol method)

7. White Oil "B" (White Camphor Oil with a lesser cineole content)

This oil is a by-product of the manufacture of "Eucalyptus Oil" from white camphor oil.

Boiling Range	160° to 170°
Specific Gravity at 15°	About 0.860
Optical Rotation	+20° 0′ to +30° 0′
Refractive Index at 20°	About 1.4680

The oil contains pinene, camphene, and about 5 per cent of cineole.

8. Safrole

Isolated by freezing from brown camphor oil, and by subsequent rectification *in vacuo*.

Boiling Range	230° to 235°
Specific Gravity at 15°	1.104 to 1.105
Optical Rotation	±0° to slightly dextro.
Refractive Index at 25°	About 1.5367
Congealing Point	+10° to +11°

9. "Sassafras Oil" (Synthetic Sassafras Oil from Camphor Oil)

Boiling Range	220° to 225°
Specific Gravity at 15°	1.070 to 1.085
Optical Rotation	Below +5° 0′
Refractive Index at 20°	About 1.5255
Safrole Content	About 80 to 90%

10. Yellow Camphor Oil

This is a by-product oil of the manufacture of safrole or sassafras oil from brown camphor oil. It is pale yellow in color:

Boiling Range	215° to 225°
Specific Gravity at 15°	0.97 to 0.99
Optical Rotation	+1° 0′ to +5° 0′
Refractive Index at 20°	About 1.5010

The oil contains about 20 per cent of safrole, the balance consisting of α-terpineol, camphor, sesquiterpenes, and sesquiterpene alcohols.

Chemical Composition of Individual Camphor Oils

Camphor Oil (Hon-Sho and Ho-Sho Oils)

Acetic acid, formic acid, propionic acid, isobutyric acid, isovaleric acid, *n*-caproic acid, *n*-caprylic acid, *n*-enanthic acid, citronellic acid, lauric acid, myristic acid, and piperonylic acid.

Acetaldehyde, propionaldehyde, isovaleraldehyde, *n*-hexylaldehyde, furfural, α-methyl furfural, α,β-hexenal, and pentenylaldehyde.

Camphor, piperitone, cineole, and safrole.

l-Linaloöl, geraniol, citronellol, borneol, cuminyl alcohol, dihydrocuminyl alcohol, α-terpineol, and terpinen-l-ol.

Cresol, ethyl phenol, ethyl guaiacol, carvacrol, eugenol, methyl eugenol, dihydroeugenol, and propyl pyrocatechol.

α-Pinene, β-pinene, camphene, fenchene, phellandrene, dipentene, and *d*-limonene.

Cadinene, α-caryophyllene, β-caryophyllene, bisabolene, camphazulene, α-camphorene, and β-camphorene.

Yu-Sho Oil

Furfural, camphor, cineole, safrole, α-terpineol, α-pinene, β-pinene, camphene, and dipentene.

Ohba-Kusu or Pha-Chium Oil (Oil of *Cinnamomum Micranthum* Hayata)

Caproic acid, piperonylic acid, and myristic acid.

Stearic aldehyde, decylaldehyde, pentadecylaldehyde, piperonal, piperonylacrolein, myristic aldehyde, and furfural.

Safrole, camphor, linaloöl monoxide, and cineole.

Linaloöl, α-terpineol, and borneol.

Laurol, microl, elemicin, methyleugenol, methylethyl phenol, eugenol, and carvacrol.

α-Pinene and camphene.

Micranene and micranol.

Sho-Gyu Oil (Oil of *Cinnamomum Kanahirai* Hayata)

Palmitic acid, cuminic acid, and piperonylic acid.

Terpinen-4-ol, geraniol, linaloöl, citronellol, α-terpineol, cineole, 1,4-cineole, and safrole.

Eugenol and carvacrol.

Sabinene, α-thujene, β-pinene, camphene, dipentene, α-terpinene, γ-terpinene, and *p*-cymene.

Cadinene, bisabolene, α-shogyuene, β-shogyuene, α-camphorene, and γ-camphorene.

CHEMICAL CONSTITUENTS OF CAMPHOR OILS

In the course of years a great many compounds have been identified by numerous investigators in the various types of camphor oil. They have been most competently reported in the classical work of Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, pp. 674–679, which appeared in 1929. Any newly discovered substances or data (since 1929) listed below are marked with an asterisk.

Acids

* Formic Acid

Found by Imoto[18] in a fraction of white camphor oil. Identified through the *p*-phenylphenacyl ester m. 71°.

* Acetic Acid

Found by Hirao[19] in white camphor oil. Identified by means of the *p*-phenylphenacyl bromide m. 110°–111°.

* Propionic Acid

Obtained from white camphor oil by Imoto.[20] B. 150°–156°, n_D^{16} 1.3968; *p*-bromophenacyl ester m. 56°–59°.

* Isobutyric Acid

Its presence in white camphor oil was confirmed by Imoto;[21] *p*-bromophenacyl ester m. 65°–68°.

* Isovaleric Acid

Found in white camphor oil by Imoto.[22] B. 170°–173°, n_D^{16} 1.4071; *p*-bromophenacyl ester m. 59°.

n-Caproic Acid

Rochussen[23] found small quantities of this acid in camphor oil. Analyzed as silver salt. Identified by means of the amide m. 100°. Converted to methyl amyl ketone; its semicarbazone melted at 122°–123°.

n-Caprylic Acid

M. 15°, b_4 113°–114°; analyzed by its calcium and silver salts.[24]

* *n*-Enanthic Acid

Obtained from brown camphor oil by Ono and Imoto.[25] It had the following properties: b. 215°–223°, d_4^{21} 0.9184, n_D^{21} 1.4268; amide m. 92°–94°.

dl-Citronellic Acid

Identified by Rochussen[26] through the amide m. 88°–90°; decomposed to β-methyladipic acid m. 94°–95°.

Lauric Acid

Kafuku[27] found this acid in the higher boiling fraction of camphor oil.

* Myristic Acid

Identified in blue camphor oil by Ono and Imoto,[28] m. 53°.

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[18] *Rept. Assocn. Camphor Ind. Eng. Japan* **8** (1940), 53.

[19] *Ibid.* **3** (1935), 144.

[20] *Ibid.* **8** (1940), 53.

[21] *Ibid.*

[22] *Ibid.*

[23] *J. prakt. Chem.* [2], **105** (1922), 120. *Ber. Schimmel & Co.* (1923), 12.

[24] *Ber. Schimmel & Co.,* October (1902), 22.

[25] *J. Chem. Soc. Japan* **58** (1937), 531. *Chem. Abstracts* **31** (1937), 7411.

[26] *J. prakt. Chem.* [2], **105** (1922), 130, 134.

[27] *J. Soc. Chem. Ind. Japan* **19** (1916), 815. *Chem. Abstracts* **10** (1916), 2960.

[28] *J. Chem. Soc. Japan* **58** (1937), 537. *Chem. Abstracts* **31** (1937), 7411.

* Piperonylic Acid

Kafuku[29] found this acid in a fraction of blue camphor oil, m. 226°-228°. Also identified in the trunk oil of Sho-Gyu (*Cinnamomum kanahirai* Hayata) by Ikedo and Naito.[30]

Aldehydes

Acetaldehyde

This aldehyde occurs in almost every essential oil. Usually it distills over (with steam) in the first fraction, particularly in the terpene fraction.

* Propionaldehyde

Found by Ono and Imoto[31] in white camphor oil; 2,4-dinitrophenylhydrazone m. 125°-137°.

* Isovaleraldehyde

Observed in white camphor oil by Ono and Imoto;[32] 2,4-dinitrophenylhydrazone m. 117°-118°.

* *n*-Hexaldehyde

Ono and Imoto[33] found this aldehyde in white camphor oil; 2,4-dinitrophenylhydrazone m. 102°-103°.

* Furfural

Presence in white camphor oil confirmed by Ono and Imoto;[34] 2,4-dinitrophenylhydrazone m. 219°-222°.

* α-Methyl Furfural

Occurs in white camphor oil; 2,4-dinitrophenylhydrazone m. 203°-204° (Ono and Imoto[35]).

* α,β-Hexenal

Identified in white camphor oil by Ono and Imoto;[36] 2,4-dinitrophenylhydrazone m. 137°-140°.

* Pentenylaldehyde

Found by Ono and Imoto[37] in white camphor oil, in combination with α,β-hexenal. B_{20} 50°-60°, d_4^{10} 0.9616, n_D^{15} 1.4614.

* Stearic Aldehyde

Ikeda[38] found this aldehyde in the oil of Ohba-Kusu, or Pha-Chium oil (*Cinnamomum micranthum* Hayata). M. 64°-66°; semicarbazone m. 105°-106°, oxime m. 73°-74°.

* Decylaldehyde

Found in the leaf oil of Ohba-Kusu (*Cinnamomum micranthum* Hayata) by Fujita and Yamashita;[39] 2,4-dinitrophenylhydrazone m. 104°, semicarbazone m. 100°-101°.

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[29] *J. Soc. Chem. Ind. Japan* **19** (1916), 815. *Chem. Abstracts* **10** (1916), 2960.

[30] *J. Chem. Soc. Japan* **59** (1938), 385. *Chem. Abstracts* **32** (1938), 8696.

[31] *J. Chem. Soc. Japan* **59** (1938), 1014. *Chem. Abstracts* **33** (1939), 2128.

[32] *Ibid.*

[33] *Ibid.*

[34] *Ibid.*

[35] *Ibid.*

[36] *Ibid.*

[37] *Ibid.*

[38] *J. Chem. Soc. Japan* **51** (1930), 335. *Chem. Abstracts* **25** (1931), 3438.

[39] *J. Chem. Soc. Japan* **65** (1944), 385, 591. *Chem. Abstracts* **41** (1947), 3509.

* Pentadecylaldehyde

The same authors found pentadecylaldehyde in the trunk oil of Ohba-Kusu (*Cinnamomum micranthum* Hayata); 2,4-dinitrophenylhydrazone m. 106°, semicarbazone m. 106°–107°, oxime m. 85°–86°.

* Myristic Aldehyde

Identified in the oil of Ohba-Kusu (*Cinnamomum micranthum* Hayata) by Ikeda et al.;[40] semicarbazone m. 106°.

* Piperonylacrolein

Obtained by the same authors; m. 85° to 86°.

Ketones and Oxides

Camphor

This is the most important component of camphor oil. The Hon-Sho oil contains about 50 per cent, the Ho-Sho oil about 40 per cent of camphor.

Piperitone

Identified by the Schimmel chemists;[41] semicarbazone m. 224°–226°, oxaminooxime m. 166°.

Cineole

White camphor oil contains 20 to 25 per cent of this oxide; it is the chief constituent of Yu-Sho oil. Isolated by means of the hydrobromide compound,[42] and the iodine compound.[43]

1,4-Cineole

S. Yamada and Masuda[44] isolated 1,4-cineole from Sho-Gyu oil (*Cinnamomum kanahirai* Hayata). It had the following properties: b. 172°–173°, d_4^{20} 0.8991, α_D ±0°, n_D^{20} 1.4494; terpinene dihydrochloride m. 51°, terpinene dihydrobromide m. 58°.

Safrole

First observed in camphor oil in 1885 by Bertram,[45] a Schimmel chemist. Next to camphor, safrole is the most important component of the oil. Brown camphor oil contains 50 to 60 per cent of safrole. Oil of Ohba-Kusu (*Cinnamomum micranthum* Hayata) contains 95 per cent of safrole.[46]

* Linaloöl Monoxide

Identified in Ohba-Kusu oil by Ikeda et al.[47] It had the following properties: b. 194°, d_4^{25} 0.9376, α_D^{27} $-5°\ 41'$, n_D^{25} 1.4493.

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[40] *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

[41] Observed in the laboratories of Schimmel & Co. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 676.

[42] *Ber. Schimmel & Co.*, October (1888), 8.

[43] *Ibid.*, October (1903), 41.

[44] *J. Chem. Soc. Japan* **52** (1931), 805. *Chem. Abstracts* **26** (1932), 5410.

[45] *Ber. Schimmel & Co.*, Sept. (1885), 7.

[46] *J. Chem. Soc. Japan* **51** (1930), 335. *Chem. Abstracts* **25** (1931), 3438. *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

[47] *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

Alcohols

* *l*-Linaloöl

A complete investigation has been carried out by K. Nagai[48] who obtained pure *l*-linaloöl from Ho-Sho oil and listed the following properties: b. 197.5°–199.5°, d_{15} 0.8710, α_D^{15} −17° 0′; phenylurethane m. 65°. Naito[49] mentioned the presence of linaloöl in Ho-Sho leaf oil: b. 196°–197°, d_4^{25} 0.8605, α_D^{19} −17° 35′, n_D^{25} 1.4592; phenylurethane m. 65.5°–66.3°.

* Geraniol

First observed by Nagai[50] in Ho-Sho oil. Phenylurethane m. 81°. Oxidation of the alcohol gave citral. Naito also found geraniol in Ho-Sho oil.[51]

Citronellol

B. 225°–227°. Oxidation gave citronellal; citronellyl naphthocinchoninic acid m. 225° (Schimmel chemists[52]).

d-Citronellol

Found in brown camphor oil by Ono et al.[53] B_{20} 119°–121°, d_4^{26} 0.8615, $[\alpha]_D^{23}$ +1° 12′, n_D^{23} 1.4582.

Borneol

M. 203°; semicarbazone m. 236°, oxime m. 118°–119° (Schimmel chemists[54]).

* *d*-Borneol

Identified by Ono et al.[55] in brown camphor oil, m. 202°, $[\alpha]_D^{30}$ +24° 0′; phenylurethane m. 138°–139°.

Cuminyl Alcohol

The higher boiling fraction of camphor oil is heated with phthalic anhydride, after which the ester is saponified. By this method the Schimmel chemists[56] obtained cuminyl alcohol b. 240°–248°, d_{15} 0.9634, n_D^{20} 1.49038. On oxidation with chromic acid and acetic acid, the alcohol gives cuminaldehyde; oxime m. 210°–212°. Oxidation with silver oxide yields cuminic acid m. 111°–113°.

* Dihydrocuminyl Alcohol

Found in brown camphor oil by Ono et al.[57] B. 240°–242°, d_4^{28} 0.9438, n_D^{28} 1.5000; oxidized with potassium permanganate to cuminic acid m. 109°–111°.

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[48] "Studies of Shiu (Ho-Sho) Oil," Monopoly Bureau of the Government of Formosa (1912), 118, 201 (Japanese Edition).

[49] *J. Chem. Soc. Japan* **64** (1943), 1125. *Chem. Abstracts* **41** (1947), 3776.

[50] "Studies of Shiu (Ho-Sho) Oil," Monopoly Bureau of the Government of Formosa (1912), 118, 201 (Japanese Edition).

[51] *J. Chem. Soc. Japan* **64** (1943), 1125. *Chem. Abstracts* **41** (1947), 3776.

[52] Observed in the laboratories of Schimmel & Co. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 675.

[53] *J. Chem. Soc. Japan* **57** (1936), 119. *Chem. Abstracts* **30** (1936), 4995.

[54] *Ber. Schimmel & Co.*, April (1904), 58.

[55] *J. Chem. Soc. Japan* **57** (1936), 119. *Chem. Abstracts* **30** (1936), 4995.

[56] Observed in the laboratories of Schimmel & Co. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 676.

[57] *J. Chem. Soc. Japan* **57** (1936), 119. *Chem. Abstracts* **30** (1936), 4995.

α-Terpineol

M. 35°; phenylurethane m. 112°, nitrolpiperidine m. 158°–159°.[58] Small quantities of caprylic and lauric esters have been observed in the red camphor oil (Ono [59]).

dl-α-Terpineol

Naito [60] found this alcohol in a fraction of Ho-Sho leaf oil; identified by means of the phenylurethane m. 112.5°–113.3°.

* *l*-α-Terpineol

According to Mochida,[61] *l*-α-terpineol occurs in a fraction of Hon-Sho oil. M. 34.8°–35°, b_{14} 103°–104°, d_4^{16} 0.9386, $[\alpha]_D^{16}$ −13° 18′, n_D^{16} 1.4855; phenylurethane m. 112°, nitrolpiperidine m. 149°–150°.

Terpinen-1-ol

Isolated by the Schimmel chemists;[62] on treatment with hydrochloric acid the alcohol gave terpinene dihydrochloride m. 50°–52°. Glycerol (1,3,4-trihydroxyterpane) m. 113°–115°. Oxidation yielded piperitone (1-*p*-menthen-3-one), semicarbazone m. 224°–225°.

* Terpinen-4-ol

Sho-Gyu oil (*Cinnamomum kanahirai* Hayata) contains about 30 per cent of terpinen-4-ol. Nagai [63] observed the following properties: b. 209°–209.5°, d_8 0.944, α_D^8 +26° 18′, n_D^{18} 1.4781; nitrosochloride m. 111°–112°, nitrolpiperidine m. 172°–174°, phenylurethane m. 71°–72°, naphthylurethane m. 105.5°–106.5°. Ikeda and Naito [64] also noted this alcohol in Sho-Gyu oil.

Phenols and Phenol Ethers

* Cresol and Ethyl Phenol

Ono and Imoto [65] acetylated brown camphor oil and obtained a fraction b. 213°–215°, d_4^{20} 1.0476, n_D^{20} 1.4989, which they assumed to be a mixture of cresyl acetate and ethyl phenol acetate.

Ethyl Guaiacol

$$C_6H_3 \cdot \overset{(1)}{C_2H_5} \cdot \overset{(3)}{OCH_3} \cdot \overset{(4)}{OH}$$

Isolated by Rochussen [66] in camphor oil; benzoate m. 59°, phenylurethane m. 107°.

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[58] *Ber. Schimmel & Co.*, April (1888), 9; April (1889), 8; Oct. (1903), 39.

[59] *Mem. Coll. Sci. Kyoto Imp. Univ.* **7** (1924), 99. *Chem. Abstracts* **18** (1924), 1659.

[60] *J. Chem. Soc. Japan* **64** (1943), 1125. *Chem. Abstracts* **41** (1947), 3776.

[61] *J. Soc. Chem. Ind. Japan* **36** (1933), 1091. *Chem. Abstracts* **27** (1933), 5891.

[62] Observed in the laboratories of Schimmel & Co. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 675.

[63] "Investigation of the Sho-Gyu and Yu-Ju Oils Produced in Formosa," Monopoly Bureau of the Government of Formosa (1914), 29 (English Edition).

[64] *J. Chem. Soc. Japan* **59** (1938), 213, 385. *Chem. Abstracts* **32** (1938), 8696. *J. Chem. Soc. Japan* **61** (1940), 303. *Chem. Abstracts* **36** (1942), 2686.

[65] *J. Chem. Soc. Japan* **58** (1937), 531. *Chem. Abstracts* **31** (1937), 7411.

[66] *J. prakt. Chem.* [2], **105** (1922), 120. *Ber. Schimmel & Co.* (1923), 12.

* Methyl Ethyl Phenol

$$C_6H_3\cdot OH\cdot CH_3\cdot C_2H_5$$

Oil of Ohba-Kusu (*Cinnamomum micranthum* Hayata) contains this phenol b_{60} 145°, d_4^{25} 0.9855, n_D^{25} 1.5205; phenylurethane m. 103°, α-naphthylurethane m. 100.5°, mol. refr.: obtained 42.0, calculated as $C_9H_{12}O$ 41.7. The positions of the side groups were not established (Ikeda and Takeda[67]).

Carvacrol

Found in the acidic substances of camphor oil by the Schimmel chemists.[68] Phenylurethane m. 136°. A higher boiling phenol was also found; its phenylurethane m. 85°–95°.

Eugenol

The presence of this phenol in camphor oil was detected as early as 1886.[69] It was later isolated by Nagai[70] in Ho-Sho oil; benzoate m. 69°.

* Methyl Eugenol

Fujita[71] noticed that this compound is formed in the young plant, together with safrole. Identified in the oil derived from camphor seedlings; mercuric oxychloride compound m. 117°–118°.

* Dihydroeugenol

Found by Ono and Imoto[72] in blue camphor oil b. 240°–243°, d_4^{32} 1.0565, n_D^{31} 1.5313; picrate m. 59°.

* Propyl Pyrocatechol (4-Propyl-1,2-catechol)

The same authors[73] also proved the presence of this diphenol in the blue camphor oil; identified by the hydroxyacetic acid derivative m. 142°–145°.

* Elemicin

Found in oil of Ohba-Kusu or Pha-Chium (*Cinnamomum micranthum* Hayata) by Ikeda et al.[74] It has the following properties: b. 275°, d_4^{20} 1.0648, α_D^{20} ±0°, n_D^{20} 1.5253; isoelemicin bromide m. 89°, mercuric oxychloride m. 110°.

* Laurol

$$C_6H_2\cdot (OCH_3)_2\cdot CH_3\cdot C_3H_5$$

Studying Ohba-Kusu oil, Ikeda[75] found a new phenolic substance m. 59°–60°, b. 274°, α_D ±0°; dibromide ($C_{12}H_{16}O_2Br_2$) m. 141°–142°, tetrabromide ($C_{12}H_{16}O_2Br_4$) m. 215°–217° (decomp.). Oxidation gave $C_{10}H_{12}O_4$ m. 182°–183°. Ikeda assigned to the compound the empirical formula $C_{12}H_{16}O_2$, and named it "Laurol." However, the position of the side groups was not determined.

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[67] *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

[68] *Ber. Schimmel & Co.*, October (1902), 21.

[69] *Ibid.*, April (1886), 5.

[70] "Studies of Shiu (Ho-Sho) Oil," Monopoly Bureau of the Government of Formosa (1912), 210 (Japanese Edition).

[71] *J. Chem. Soc. Japan* **63** (1942), 58. *Chem. Abstracts* **41** (1947), 3509.

[72] *J. Chem. Soc. Japan* **58** (1937), 537. *Chem. Abstracts* **31** (1937), 7411.

[73] *Ibid.*

[74] *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

[75] *J. Chem. Soc. Japan* **51** (1930), 335. *Chem. Abstracts* **25** (1931), 3438.

* Microl

$C_{13}H_{18}O_2$

In the course of the same investigation, Ikeda also found a new phenolic compound in Ohba-Kusu oil, b_4 133°–136°, d_4^{30} 1.0113, n_D^{30} 1.5252, mol. refr. 62.44; phenylurethane m. 101°, naphthylurethane m. 116°–117°. Ikeda named this new phenol "Microl."

Terpenes

α-Pinene

d-α-Pinene was observed in the forerun boiling below 160°. Nitrosopinene m. 130°,[76] nitrolbenzylamine m. 123°.[77]

β-Pinene

Isolated by the Schimmel chemists.[78] Oxidation gave nopinic acid; further oxidation yielded a ketone, nopinone, semicarbazone m. 187°-189°.

Camphene

First observed in camphor oil by Bertram and Walbaum.[79] M. 50°. Preparation of synthetic camphor from camphene via isoborneol.

* *l*-Camphene

Identified in Ohba-Kusu oil by Ikeda and Takeda;[80] d_4^{25} 0.8708, α_D^{20} −47° 6′, n_D^{25} 1.4686. Preparation of isoborneol m. 212°.

Fenchene

Identified by the Schimmel chemists[81] by conversion to isofenchone, semicarbazone m. 220°–222°. Isofenchone was prepared by the oxidation of isofenchyl alcohol. The latter was obtained from fenchene by the action of acetic acid and sulfuric acid.

Phellandrene

Very small quantities occur in camphor oil.[82] Identified by means of its nitrite m. 102°.

Dipentene

Identified by Wallach;[83] tetrabromide m. 124°, nitrolpiperidine m. 150°–152° (Schimmel & Co.[84]). Lallemand[85] obtained crude dipentene dihydrochloride m. 42° (pure derivative m. 49°–50°) from a camphor oil fraction b. 180°.

d-Limonene

Identified by preparation of the nitrolpiperidine m. 110°–111° (Schimmel & Co.—see above).

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[76] *Ber. Schimmel & Co.*, April (1889), 8.

[77] *Ibid.*, October (1903), 40.

[78] Observed in the laboratories of Schimmel & Co. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II. 674.

[79] *J. prakt. Chem.* [2], **49** (1894), 19.

[80] *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

[81] Observed in the laboratories of Schimmel & Co. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. II, 674.

[82] *Ber. Schimmel & Co.*, April (1889), 8.

[83] *Liebigs Ann.* **227** (1885), 296.

[84] *Ber. Schimmel & Co.*, April (1908), 23.

[85] *Liebigs Ann.* **114** (1860), 196.

* *p*-Cymene

Its presence in Sho-Gyu oil (*Cinnamomum kanahirai* Hayata) was confirmed by Yamada and Masuda;[86] *p*-hydroxyisopropylbenzoic acid m. 150°–157°.

* *d*-Sabinene

Found in Sho-Gyu oil by Ikeda and Naito.[87] The terpene had the following properties: b. 161°, d_4^{25} 0.8374, α_D^{30} +74° 5′, n_D^{25} 1.4648. Oxidation gave sabinenic acid m. 56°–57°.

* α-Terpinene

The same authors[88] found α-terpinene in oil of Sho-Gyu. Oxidation yielded α,α′-dihydroxy-α-methyl-α′-isopropyladipic acid m. 187°–189°.

* γ-Terpinene

Identified by Ikeda and Naito[89] in Sho-Gyu oil; γ-terpinene erithritol m. 234°–236°.

l-α-Thujene

Found by the same authors[90] in Sho-Gyu oil. The terpene had the following properties: b. 147°–149°, d_4^{25} 0.8341, α_D^{31} −26° 14′, n_D^{25} 1.4515. Identified by means of the semicarbazone of α-thujaketonic acid m. 182°–183°.

Sesquiterpenes

Bisabolene

A fraction of camphor oil b_5 97°–116° gave bisabolene trihydrochloride m. 79°-80°.[91]

Cadinene

When gaseous hydrogen chloride was conducted into the fraction b. 260°–270° of camphor oil, cadinene dihydrochloride formed in good yield, m. 117° (Schimmel & Co.[92,93]).

Caryophyllene

The nitrosate decomposed at 163°. Identified by conversion to caryophyllene hydrate m. 95°–96°. The latter was obtained by the action of acetic acid and sulfuric acid on caryophyllene (Simonsen and Ghose[94]). Kitajima[95] studied caryophyllene, which he obtained from camphor branch and leaf oil. He suggested new configurations for α- and β-caryophyllene different from those of Ruzicka et al.,[96] and Rydon.[97]

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[86] *J. Chem. Soc. Japan* **52** (1931), 805. *Chem. Abstracts* **26** (1932), 5410.

[87] *J. Chem. Soc. Japan* **59** (1938), 213. *Chem. Abstracts* **32** (1938), 8696. *J. Chem. Soc. Japan* **61** (1940), 303. *Chem. Abstracts* **36** (1942), 2686.

[88] *J. Chem. Soc. Japan* **59** (1938), 213. *Chem. Abstracts* **32** (1938), 8696.

[89] *Ibid.*

[90] *J. Chem. Soc. Japan* **59** (1938), 385. *Chem. Abstracts* **32** (1938), 8696.

[91] *Ber. Schimmel & Co.,* October (1909), 24.

[92] *Ibid.*

[93] *Ber. Schimmel & Co.,* April (1889), 9.

[94] *J. Soc. Chem. Ind.* **39** (1920), 296T.

[95] *Sci. Papers Central Research Inst. Govt. Monopoly Bur. Japan,* Tokyo, No. 80 (1948).

[96] *Helv. Chim. Acta* **14** (1931), 410; **19** (1936), 343.

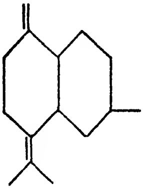
[97] *Chemistry Industry* **57** (1938), 123. *J. Chem. Soc.* (1939), 537.

* Camphazulene

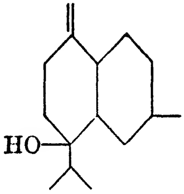
Kitajima[98] isolated this compound from camphor branch and leaf oil; picrate m. 120°, styphnate m. 112°–113°.

Incomplete Studies of Sesquiterpenes and Sesquiterpene Alcohols.—A number of sesquiterpenes and sesquiterpene alcohols observed in the various types of camphor oil are of such complex nature that their configuration has not yet been fully established. Suffice it, therefore, to report their physicochemical properties in Tables 2.5 and 2.6.

Komatsu and his collaborators[99] discussed the configuration of sesquiterpenes and sesquiterpene alcohols which they isolated, and assigned to them the following cadalene type formulas:

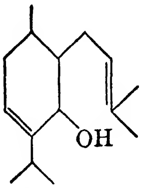


Sesquiterpene

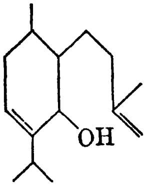


Sesquiterpene Alcohol

Kafuku et al.[100] advanced the following structural formulas for the sesquiterpene alcohol mentioned in literature reference 8, II, of Table 2.6.



(a)



(b)

The larger part of the sesquiterpene alcohol consisted of (a), but a fraction is isomerized to (b).

A tricyclic sesquiterpene alcohol $C_{15}H_{26}O$ was found in brown camphor oil by Ono et al.[101] who named the compound "Shojunol." M. 96°; phenylurethane m. 134.5°.

Diterpenes, $C_{20}H_{32}$

α-Camphorene

Found by Semmler and Rosenberg;[102] b_6 177°–178°, d_{20} 0.8870, α_D ±0°, n_D^{20} 1.5034, mol. refr. 90.60.

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[98] *Rept. Assocn. Camphor Ind. Eng. Japan* **4** (1936), 144.

[99] *Mem. Coll. Sci. Kyoto Imp. Univ.* **14** (1931), 149. *J. Chem. Soc. Japan* **50** (1930), 498. *Chem. Abstracts* **26** (1932), 719.

[100] *J. Chem. Soc. Japan* **54** (1933), 311. *Chem. Abstracts* **27** (1933), 3557.

[101] *J. Chem. Soc. Japan* **57** (1936), 119. *Chem. Abstracts* **30** (1936), 4995.

[102] *Ber.* **46** (1913), 773.

TABLE 2.5. SESQUITERPENES

(The asterisk in these tables refers to compounds discovered since 1929.)

Literature Reference	Investigator	B.p. in °C.	d	αD	nD	M.R. $(C_{15}H_{24}|_{2}^{=}=66.13)$	Origin	Remarks
1	Semmler..........	b_8 129–133	0.9015 (20°/4°)	+3° 0′	1.5006 (20°)	66.61		
2	Ono.............	b_{15} 140–141	0.9025 (20°/4°)	+25° 18′	1.5050 (20°)	66.74	Blue Camphor Oil	
3	Koike...........	b_{12} 122–125	0.9124 (21°/4°)	−28° 33′	1.5035 (21°)	...	Blue Camphor Oil	
4	Ruzicka and Stoll..	I b_{12} 127–128	0.8876 (15°/4°)	...	1.4955 (15°)	67.14		
		II b_{12} 131–134	0.8943 (14°/4°)	...	1.4974 (14°)	66.86		
5	Komatsu et al.....	* b_8 121–124	0.9100 (25°/4°)	+17° 42′	1.5046 (25°)	66.45	Formosan Blue Camphor Oil	
6	Ikeda and Takeda.	* b_1 110–115	0.9124 (20°/4°)	+26° 30′	1.5061 (20°)	66.51	Ho-Sho Blue Oil	"Ho-Sho Sesquiterpene"
7	Kafuku et al......	* b_{10} 127–129	0.9406 (30°/4°)	+26° 0′	1.5021 (30°)	...	Ho-Sho Blue Oil	
8	Ikeda...........	* b_5 123–124	0.9331 (20°/4°)	$[\alpha]_D^{19}$ −4° 6′	1.5169 (20°)	...	Ohba-Kusu Oil	Hydrochloride m. 106° Hydrobromide m. 124°–125° "Micranene"

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[1] *Ber.* **46** (1913), 769.

[2] *Mem. Coll. Sci. Kyoto Imp. Univ.* **8** (1925), 1.

[3] *J. Soc. Chem. Ind. Japan* **29** (1926), 214. *British Chem. Abstracts* (1926), A954.

[4] *Helv. Chim. Acta* **7** (1924), 264.

[5] *Mem. Coll. Sci. Kyoto Imp. Univ.* **14** (1931), 149. *J. Chem. Soc. Japan* **50** (1930), 498. *Chem. Abstracts* **26** (1932), 719.

[6] *J. Chem. Soc. Japan* **51** (1930), 177. *Chem. Abstracts* **26** (1932), 717.

[7] *J. Chem. Soc. Japan* **54** (1933), 311. *Chem. Abstracts* **27** (1933), 3557.

[8] *J. Chem. Soc. Japan* **51** (1930), 335. *Chem. Abstracts* **25** (1931), 3438. *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

TABLE 2.6. SESQUITERPENE ALCOHOLS

Literature Reference	Investigator	B.p. in °C.	d	α_D	n_D	M.R. $(C_{15}H_{26}O\,\vert\overline{1} = 68.15)$
1	Semmler et al.	b_9 150–155	0.9662 (20°/4°)	+50° 0′	1.5071 (20°)	68.39
2	Kafuku	b_5 130–133	0.9790 (18°/4°)	. . .	1.5035 (18°)	66.90
3	Ono	I b_{10} 160–163	0.9595 (14°/4°)	$[\alpha]_D^{17}$ +49° 18′	1.5075 (14°)	68.24
		II b_{10} 170–174	0.9692 (14°/4°)	$[\alpha]_D^{19}$ +66° 35′	1.5084 (14°)	68.39
4	Ruzicka and Stoll	I b_{12} 156–158	0.9568 (18°/4°)	+2° 12′	1.5045 (18°)	68.81
		II b_{12} 160–162	0.9720 (20°/4°)	−5° 12′	1.5066 (20°)	67.98
		III b_{12} 156	0.9665 (20°/4°)	. . .	1.5050 (20°)	68.21
5	Koike	I b_{18} 156–159	0.9654 (21°/4°)	+40° 54′	1.5011 (21°)	68.27
		II b_{18} 165–169	0.9590 (21°/4°)	+61° 42′	1.5017 (21°)	68.02
6	Komatsu et al.	* b_{12} 157–160	0.9501 (25°/4°)	+35° 30′	1.5040 (25°)	68.24
7	Ono et al.	I * b_3 116–120	0.9468 (23°/4°)	$[\alpha]_D$ +1° 54′	1.5019 (22°)	69.12
		II * b_7 138–140	0.9643 (18°/4°)	$[\alpha]_D$ +2° 30′	1.5026 (19°)	68.07
8	Kafuku et al.	I * b_{10} 170–173	0.9732 (30°/4°)	+45° 48′	1.5050 (30°)	67.66
		II * b_{10} 140–150	0.9333 (30°/4°)	+26° 0′	1.5050 (30°)	70.48
9	Ikeda and Takeda	I * b_2 125–130	0.9694 (18°/4°)	+34° 12′	1.5079 (18°)	68.37
		II * b_2 150–155	0.9382 (17°/4°)	±0° 0′	1.5065 (17°)	70.42
10	Ikeda	b_5 130–135	0.9655 (20°/4°)	. . .	1.5027 (20°)	68.00

[1] *Ber.* **46** (1913), 770; **47** (1914), 2074.

[2] *J. Soc. Chem. Ind. Japan* **19** (1916), 815. *Chem. Abstracts* **10** (1916), 2960.

[3] *Mem. Coll. Sci. Kyoto Imp. Univ.* **8** (1925), 1.

[4] *Helv. Chim. Acta* **7** (1924), 264.

[5] *J. Soc. Chem. Ind. Japan* **29** (1926), 214. *British Chem. Abstracts* (1926), A954.

[6] *Mem. Coll. Sci. Kyoto Imp. Univ.* **14** (1931), 149. *J. Chem. Soc. Japan* **50** (1930), 498. *Chem. Abstracts* **26** (1932), 719.

[7] *J. Chem. Soc. Japan* **57** (1936), 119. *Chem. Abstracts* **30** (1936), 4995.

[8] *J. Chem. Soc. Japan* **54** (1933), 311. *Chem. Abstracts* **27** (1933), 3557.

[9] *J. Chem. Soc. Japan* **51** (1930), 177. *Chem. Abstracts* **26** (1932), 717.

[10] *J. Chem. Soc. Japan* **51** (1930), 335. *Chem. Abstracts* **25** (1931), 3438. *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

β-Camphorene

Isolated by the same authors; b_7 170°–180°, d_{20} 0.930, $[\alpha]_D$ ±0°, n_D^{20} 1.518, mol. refr. 88.61.

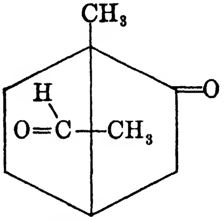
* Ho-Sho Diterpene.

From blue Ho-Sho oil Ikeda and Takeda[103] isolated a diterpene with the following properties: b_1 145°–150°, d_{20} 0.9079, α_D ±0°, n_D^{20} 1.5031, mol. refr. 88.66.

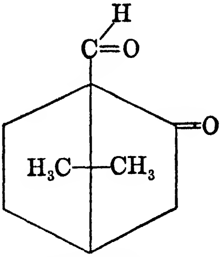
USE OF CAMPHOR AND CAMPHOR OILS

Years ago the Japanese Government prohibited the export of crude camphor oil, with the idea of manufacturing these isolates in Japan proper so that her newly established chemical industry could profit from Japan's dominating position in controlling the basic raw materials. Consequently, Japan's industry of synthetic perfumes, ore-flotation oils, solvents, insecticides, etc., has manufactured and utilized the constituents of camphor oil to the utmost and has made great progress in this direction during the last twenty years.

Camphor.—Camphor is a basic material in the manufacture of celluloid and films, and of medicinal and pharmaceutical preparations such as "Vita-Camphor" (*trans*-π-oxo-camphor), "Camphenal" (oxo-camphor), and "Bromo-camphor." Large quantities of camphor are exported to India, where the people use it as an incense in religious ceremonies. Camphor is employed also in mineral flotation, furthermore as a deodorizer and antiseptic, and in agricultural insecticides, with D.D.T.



"Vita-Camphor"
(*trans*-π-oxo-camphor)



"Camphenal"
(oxo-camphor)

White Camphor Oil.—Cineole is the principal component of this oil. A synthetic eucalyptus oil is made from white camphor oil; before the war, it competed with Australian eucalyptus oil. In addition to cineole, the oil contains a large percentage of terpenes. The oil is an excellent solvent, being superior to oil of turpentine and petroleum distillates. Employed in paints and lacquers as a thinner, as well as in polishes and in printing inks. Medicinally the oil is used in certain types of antiseptic and dis-

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[103] *J. Chem. Soc. Japan* **51** (1930), 177. *Chem. Abstracts* **26** (1932), 717.

TABLE 2.7. CAMPHOR AND CAMPHOR OIL PRODUCTION IN JAPAN AND FORMOSA

(In metric tons)

	Japan			Formosa				Total Quantities of Camphor (Japan and Formosa)
	Crude Camphor	Crude Camphor Oil	Total Camphor *	Crude Camphor	Crude Camphor Oil	Ho-Sho Oil	Total Camphor *	
1903	223	261	354	2,236	1,614		3,043	3,397
1904	380	429	595	2,024	1,629		2,839	3,434
1905	360	392	556	1,686	1,527		2,450	3,006
1906	441	510	696	1,850	1,900		2,800	3,496
1907	448	576	736	2,268	2,589		3,563	4,299
1908	502	619	811	2,135	2,779		3,525	4,336
1909	499	686	842	2,061	2,543		3,333	4,175
1910	633	998	1,132	3,405	3,870		5,340	6,472
1911	662	1,107	1,216	2,759	3,408		4,463	5,679
1912	586	1,012	1,092	2,483	3,232		4,099	5,191
1913	598	1,015	1,106	2,721	3,422		4,432	5,538
1914	670	1,186	1,263	2,850	3,847		4,774	6,037
1915	960	1,801	1,861	2,772	4,129		4,837	6,698
1916	941	1,820	1,851	2,970	4,789		5,365	7,216
1917	590	1,112	1,146	1,911	3,602		3,712	4,858
1918	239	422	450	1,405	2,933		3,372	3,822
1919	275	469	510	1,259	2,702		2,610	3,120
1920	544	919	1,003	1,262	2,395	1,347	2,998	4,001
1921	701	1,276	1,339	830	1,427	1,722	2,232	3,571
1922	358	657	686	764	1,618	2,398	2,532	3,218
1923	450	763	831	1,184	2,788	3,058	3,801	4,632
1924	862	1,505	1,615	1,012	2,478	2,451	3,231	4,846
1925	1,178	2,043	2,200	854	2,088	2,406	2,860	5,060
1926	943	1,684	1,785	766	2,107	3,191	3,096	4,881
1927	730	1,270	1,365	792	2,166	3,241	3,171	4,536
1928	651	1,096	1,199	793	2,285	3,515	3,342	4,541
1929	865	1,419	1,575	914	2,880	3,853	3,895	5,470
1930	1,291	2,068	2,325	791	2,592	3,181	3,851	6,176
1931	822	1,327	1,486	786	2,499	3,396	3,394	4,880
1932	736	1,190	1,331	473	1,681	2,135	2,169	3,500
1933	1,010	1,592	1,806	582	1,863	1,976	2,304	4,110
1934	1,319	2,086	2,362	892	2,455	2,058	2,943	5,305
1935	1,675	2,568	2,959	860	2,508	1,857	2,857	5,816
1936	1,695	2,652	3,021	794	2,583	1,772	3,295	6,316
1937	1,410	2,211	2,516	790	2,814	2,052	3,018	5,534
1938	1,020	1,623	1,832	793	2,820	2,017	3,010	4,842
1939	744	1,181	1,335	664	2,252	1,281	2,302	3,637
1940	894	1,362	1,575	638	2,100	1,440	2,264	3,839
1941	950	1,405	1,653	379	1,452	1,043	1,522	3,175
1942	806	1,193	1,403	247	939	712	1,002	2,405
1943	520	782	911	183	654	603	751	1,662
1944	566	772	952	149	539	449	598	1,550
1945	350	428	564	42	111	102	138	702
1946	643	745	1,016	. . .	. . .	. . .	. . .	1,016
1947	1,253	1,490	1,998	. . .	. . .	. . .	. . .	. . .

* Crude camphor + the camphor dissolved in crude camphor oil, or in Ho-Sho oil obtained by fractional distillation.

infectant preparations. In the refining of certain ores the oil is employed for differential flotation. The pinene fraction of the oil serves as the basic material for the synthesis of terpineol and borneol. From the cymene fraction, thymol and menthol may be synthesized.

EXPORTS OF CAMPHOR AND CAMPHOR OIL FROM JAPAN AND FORMOSA (IN KG.)

	Camphor *	*Camphor Oil* †	*Ho Oil* ‡
1926	2,538,740	1,807,920	5,560
1927	3,241,780	1,552,280	23,700
1928	3,510,360	1,236,250	47,430
1929	3,493,300	1,273,830	93,400
1930	1,941,420	692,400	12,330
1931	2,307,360	655,080	12,090
1932	2,347,560	1,132,460	82,010
1933	3,412,750	821,940	108,140
1934	2,897,580	652,560	150,030
1935	2,662,100	622,260	119,660
1936	2,665,660	678,010	183,520
1937	2,216,260	967,800	86,370
1938	1,543,560	753,530	86,170
1939	2,320,500	739,700	110,180
1940	1,129,580	684,650	100,060

* Includes refined camphor and "BB" camphor (refined camphor, second class).
† Includes safrole, sassafras oil, and yellow camphor oil.
‡ Includes Ho oil and linalyl acetate.

Heliotropin and borneol exports (in kg.) were as follows:

	Heliotropin	*Borneol*
1937	11,500	21,510
1938	7,330	34,740
1939	8,090	51,300
1940	4,340	27,670
1948	1,714	19,527

Since the end of World War II great efforts have been made to revive exports of the products derived from camphor and camphor oil in order to aid the reconstruction of Japan's national economy.

Brown Camphor Oil.—Of all the camphor oil fractions, this is the most important, because it serves as a base in the manufacture of many valuable derivatives.

Safrole—the chief component of brown camphor oil—is used for soap perfumes. In Japan a number of very important derivatives are prepared from safrole: isosafrole, heliotropin, and vanillin. Vanillin is synthesized from it, with protocatechualdehyde as intermediate. A synthetic sassafras oil is made from brown camphor oil. It contains more than 80 per cent of safrole and is employed for the scenting of soaps. Next to safrole, synthetic sassafras oil represents the most important camphor oil derivative exported from Japan. Aside from safrole, the oil contains terpineol. Terpin hydrate is used in medicines; terpineol and terpinyl acetate in perfumes. The residual oil (after separation of the safrole) is employed as an ore flotation agent, because the terpineol contained in it has strong foaming properties.

Blue Camphor Oil.—The oil contains sesquiterpenes and sesquiterpene alcohols. At the present time it has no wide use, being employed only as a disinfectant, in lacquers, and for the perfuming of cheap soaps. It is a good deodorant for mineral and lubricating oils. In the ore flotation process it serves as a collector, when mixed with coal tars. It appears likely that, with progress in the chemistry of sesquiterpenes, this oil will prove to be of considerable value.

Ho Oil.—Ho oil is produced only in Formosa. The loss of that island as a result of the war was therefore a heavy blow to the Japanese perfumery industry. Ho oil serves as a starting material in the manufacture of linaloöl, linalyl acetate, synthetic lavender oil and synthetic bergamot oil. Linaloöl may be oxidized to citral for the synthesis of ionones.

In conclusion, the writer wishes to express his hearty thanks to Dr. Tessaku Ikeda, former Chief of the Nan-Mon Factory, Government Monopoly Bureau of Formosa; Dr. Tsutomu Naito, former Chemical Engineer of the factory, and to Mr. Tatsuo Tejima, former Forestry Engineer of the Government Monopoly Bureau of Formosa, for their valuable suggestions about the entire manuscript and for the information they supplied on Formosan and Chinese camphor oils. The writer wishes to express his sincere thanks also to the Government Monopoly Bureau of Japan, and The Nippon Camphor Manufacturing Co., Ltd., through whose courtesy the writer was able to make a personal survey of the Kyu-Shu district—the center of Japan's camphor industry—and to study actual methods of production.

CHINESE CAMPHOR OIL

(The Camphor Oil Industry of China)

Introduction.—Natural camphor was first produced in China about 700 years ago. Throughout the centuries the industry there has remained primitive, the real progress in methods of production having been made in Japan and Formosa. However, since camphor trees grow most abundantly over vast regions of China, the Chinese industry could be greatly expanded if only technical progress could be made and, by proper fractionation, the camphor oil more fully utilized.

The camphor oil produced in China contains a smaller percentage of camphor than the oils produced in Formosa and Japan. The lower camphor content of the Chinese oil must be attributed to two features: (a) the primitiveness of the methods of production, and (b) more important, the fact that in China it is chiefly one variety of the true camphor tree—i.e., the so-called camphor *oil* tree (Yu-Sho)—which is exploited for the production of camphor and camphor oil.

Botany.—Camphor trees occur naturally over such enormous areas of semitropical and temperate Asia that there may well be some varieties which have eluded discovery and study by the botanist. At the present time only three varieties of the camphor tree (*Cinnamomum camphora* Sieb.) are known:

1. *Hon-Sho* (the *true* camphor tree). This, the most important variety as regards the production of camphor, is identical with that occurring in Formosa and Japan. On steam distillation the wood of the Hon-Sho tree yields about 2 per cent of camphor and camphor oil. In China, however, the Hon-Sho tree is very scarce, comprising only 2 to 3 per cent of all camphor trees growing there.
2. *Yu-Sho*[104] (the camphor *oil* tree). Although morphologically identical with Hon-Sho, the variety Yu-Sho differs from the former physiologically. On steam distillation the wood of the Yu-Sho yields an essential oil, the chief constituents of which are cineole and terpineol. No crystalline camphor separates in the distillate (as is the case with Hon-Sho). Thus the varieties Hon-Sho and Yu-Sho differ principally in regard to their content of camphor. In Japan the Yu-Sho tree does not exist at all; in Formosa it occurs only in the southwestern section; but in China about 90 per cent of all camphor trees belong to the variety Yu-Sho.
3. *Ho-Sho* (the *fragrant* camphor tree). Morphologically the variety Ho-Sho is identical with Hon-Sho and Yu-Sho, but physiologically it differs in that its essential oil contains linaloöl as chief constituent. As with Yu-Sho, no crystalline camphor separates from the distillate. In China only 4 to 5 per cent of all camphor trees belong to the variety Ho-Sho. It is very abundant in Formosa.

To summarize, there are three morphologically identical, but physiologically different varieties of the camphor tree (*Cinnamomum camphora* Sieb.):

1. Hon-Sho, the *true* camphor tree, occurring chiefly in Formosa and Japan, and yielding an oil which contains 50 and more per cent of camphor.

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[104] Yu-Sho is identical with Yu-Ju. Gildemeister and Hoffmann ("Die Ätherischen Öle," 3d Ed., Vol. II, 693) refer to this tree as Yu-Ju. In Japanese, *yu* means oil, *sho* means camphor, and *ju* means tree.

2. Yu-Sho, the camphor *oil* tree, occurring chiefly in China, and yielding an oil which contains cineole and terpineol as principal constituents, and only 30–40 per cent of camphor.
3. Ho-Sho, the *fragrant* camphor tree, occurring chiefly in Formosa, and yielding an oil which contains linaloöl as principal constituent, and only 30–40 per cent of camphor.

In China about 90 per cent of all camphor trees are of the variety Yu-Sho, and only about 10 per cent of the varieties Hon-Sho and Ho-Sho.

Producing Regions.—In China the camphor tree occurs south of latitude 32°, but more abundantly south of the Yangtse River. The principal growing regions are in the provinces of Kiangsi, Chekiang, Fukien, Hunan, Kwangtung, and Kwangsi. Recently, camphor has been produced also in Hupei and Anwei, north of the Yangtse River, and in Yunnan, Kweichow, and Szechwan, in the central and western parts of China.

Reliable figures as to the number of camphor trees, and the total area covered by them are, of course, unavailable, but on the basis of an actual survey of one large section[105] it may be assumed that the growing area of camphor trees in China comprises roughly 30 million hectares, the weight of camphor trees about 9.6 million metric tons, and the quantity of camphor oil stored in these trees approximately 150,000 metric tons. These are large figures, indeed!

In China all camphor trees grow more or less wild, and no program of large-scale or systematic reforestation has ever been undertaken. The trees have for ages been felled for use as fuel, and survive now chiefly in the vicinity of villages and graveyards, and along rivers and creeks; an ancient Chinese custom of deifying them in such locations has preserved them from destruction. As a result many very old trees can be seen near the habitations of the villagers. By natural seeding the number of camphor trees near villages and shrines thus increases.

Selection of Trees for Distillation.—For centuries the sole aim of the Chinese camphor producers was to extract camphor from the trees, and no attention was paid to the liquid part of the camphor oil. (The latter has been utilized in recent years only.) Of the three physiological varieties of camphor tree growing in China (see above), producers have always tried to select, for distillation purposes, the Hon-Sho (*true* camphor tree), which alone contains large quantities of camphor, rather than to exploit the Yu-Sho (camphor *oil* tree) which contains less camphor. To find and identify Hon-Sho trees the Chinese employ experts, who search the growing regions, and with the aid of small portable distillation equipment, test parts of a

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[105] N. Hirota, "Report of an Inspection of the Camphor Trees in Middle China" (1941), Monopoly Bureau of the Government of Formosa.

promising tree for oil from which camphor separates in crystalline form. Trees which yield oil containing sufficient camphor are then cut down and delivered to the distilleries. This sort of search for Hon-Sho trees is unnecessary and unknown in Formosa and Japan.

Because of the century-old practice of selecting only Hon-Sho trees for distillation, relatively few of these trees have been left in China, the numerous remaining camphor trees being mostly Yu-Sho (camphor *oil* trees).

With Yu-Sho it is necessary to determine whether the oils derived from the trees in a given section contain a sufficient quantity of camphor to render their exploitation profitable. Kawaguchi[106] examined numerous samples of Chinese camphor oils and found that there is some direct relationship between the rotatory power of a given oil and its content of camphor:

Optical Rotation α_D	*Content of Crude Camphor* (%)
Below +10°	Below 30
+10° to +15°	30 to 37
+15° to +20°	37 to 40
+20° to +25°	40 to 45
+25° and higher	45 to 50 and higher

Kawaguchi[107] determined the optical rotation of a great many lots of oil from several producing regions in China, collected between 1940 and 1942, and summarized his findings as follows:

Producing Region	*Hangchow*	*Sie Heing Chin* *	*Kiukiang*	*Nanchang*	*Total*
Total Quantity of Camphor Oil	26,374 kg.	4,797 kg.	7,679 kg.	6,800 kg.	45,649 kg.
Optical Rotation of the Oil					
+25° and over	2.0%	11.4%	16.3%	0	7.4 } 65%
+20° to +25°	26.0 } 84%	18.3 } 57%	38.7 } 62%	7.7 } 26%	22.6
+15° to +20°	58.2	38.7	23.1	18.7	34.7
+10° to +15°	11.0%	20.7%	8.7%	27.0%	16.8 } 35%
Below +10°	3.0%	10.9%	13.2%	46.7%	18.4

* Near Hangchow.

These figures give a good idea of the quality of camphor oil produced in various parts of China and show that the oils from Kiukiang and Hangchow are superior to others; the oils from Nanchang are of poorest quality.

To be suitable for the industrial isolation of camphor, an oil should contain at least 35 per cent of camphor; in other words it should have an optical rotation of +15° and higher. The above cited work of Kawaguchi also

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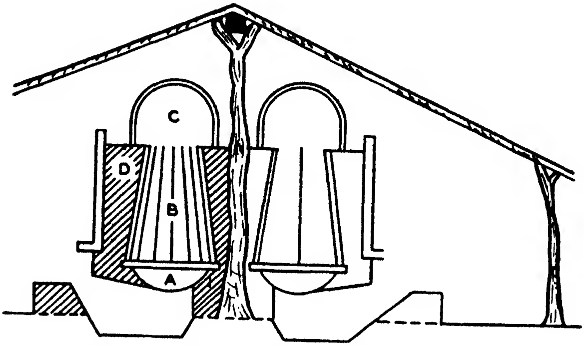
[106] *Rept. Assocn. Camphor Ind. Eng. Japan, Tokyo* **9** (1942), 39.

[107] *Ibid.*

proves that 65 per cent of all camphor oil produced in China lends itself to the recovery of camphor on an industrial scale.

Chinese Method of Distillation.—As has been pointed out, for many years the Chinese camphor industry aimed exclusively at the extraction of natural camphor from the wood of the tree. Even today the method of camphor recovery as practiced in some parts of China is based upon this principle. The operation is conducted so gently that no oil distills over. Only the camphor volatilizes. It then condenses in the form of crystals inside of the condenser which is cooled by air. In other words, this "distillation" of camphor from the wood is actually a process of sublimation.



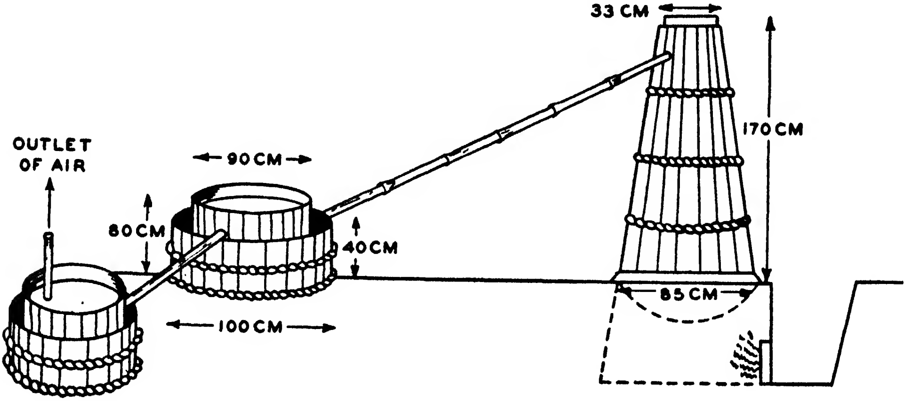
Chinese camphor distillery ("old bowl method").

A. Kettle.
B. Wooden barrel.
C. Porcelain bowl.
D. Insulation mass (mud).

A typical old-fashioned Chinese camphor distillation post consists of a hut which shelters two rows of "stills," each row containing five "stills." As shown in the drawing, a perforated wooden grid is placed on top of a kettle 38 cm. in diameter. Surmounting the grid is a small wooden barrel from which the top and bottom have been removed. The barrels are only 50 cm. high, 30 cm. in diameter at the bottom, and 17 cm. at the top. A porcelain bowl (45 cm. high and 35 cm. in diameter at the base) is then placed on top of the barrel. The camphor that volatilizes from the camphor chips in the barrel condenses by air cooling, and crystallizes on the inside walls of the porcelain bowl.

The wood of the tree is chipped by hand, and about 10 kg. of chips are charged into each barrel. In the remote regions of China the old "bowl method" of camphor recovery is practiced even today. Little is known about the yield of camphor obtained by this method. According to general report, ten stills operated for ten days produce about 18 kg. of camphor.

After Japan took possession of Formosa in 1895, the Japanese method of camphor distillation was gradually introduced not only into Formosa but into China as well. The Chinese method of camphor production has consequently improved substantially, and at present stills of the following construction are being popularized in China:



Chinese camphor distillery ("barrel method").

A wooden barrel from which the bottom has been removed is placed on top of a water kettle with a diameter of 85 cm. The barrel has a height of 1.7 m., and on top a diameter of 33 cm. A bamboo pipe leads from the upper side of the barrel into the receiver.

The receiver consists of two barrels, one of which is placed within the other. The bottom of the inner barrel is removed, but the top is concave so that it can be filled with water. The space between the outer and the inner barrel contains water which cools the inner barrel.

From 120 to 150 kg. of chips are charged into the wooden still and distilled for 20 hr. The yield of oil varies with the type of tree used. It may be as high as 3 per cent or even more, but it averages from 1.8 to 2.0 per cent.

A curious feature in the distillation of camphor wood as practiced in China is the necessity of employing a "water boy" who carries water from a pool or creek to the stills, which are always located on higher ground than the natural water supply.

The crude camphor obtained by the barrel method is usually of yellowish color, the result of the muddy water used in the retorts and condensers. The crude camphor is 80 to 85 per cent pure.

Compared with the capacity of equipment used in Formosa and Japan for the recovery of camphor from the wood, that of the Chinese barrel stills is small. The condensers are more primitive.

Development of the Chinese Camphor and Camphor Oil Industry.—In China the liquid portions of camphor oil were neglected for a long time, being used, indeed, only for fuel in lamps. In 1902, however, the isolation of camphor from camphor oil by means of fractional distillation was started in Foochow (province of Fukien) by a Japanese firm. According to Price,[108] in Foochow 133 lb. of camphor oil yielded 64 lb. of crude camphor and 27 lb. of liquid camphor oil. The so-called "Fukien" camphor gradually attained a wide reputation, and the province of Fukien became the center of the Chinese camphor industry. Later the center of production shifted to the neighboring provinces of Kiangsi and Chekiang. A camphor recovery factory was established in Kiukiang, subsequently transferred to Shanghai, and from 1917 on was managed by a Japanese firm. In 1920 the camphor recovery plant in Foochow, mentioned above, became the property of a Japanese firm which started refinement of the crude camphor produced in the plant. In 1940 the Chung-Hua Camphor Company was established in Shanghai by combined Japanese and Chinese interests. The plant had a capacity permitting the fractionation of 450 metric tons of oil, and the refinement of 300 tons of crude camphor per year. In the process employed in this plant the original crude oil yielded about 20 per cent of camphor. The factory was the largest of its kind in China, but World War II halted its operation.

The modern Chinese camphor industry may thus be said to have been founded in Foochow. The batches of crude camphor oil produced in the provinces of Fukien, Kwangtung, Kwangsi, and Yunnan were brought to Foochow for rectification and isolation of the camphor, which was then exported from Hong Kong. On the other hand, the batches of crude oil produced in the provinces of Kiangsi and Chekiang first went to Shanghai for rectification, and the products thus obtained were exported from there.

From the foregoing it can be seen that the history of the Chinese camphor industry is a long one, dating back to early times. China abounds with camphor trees, and large quantities of camphor and camphor oil could be produced. It is most unfortunate that the progress of the industry has been beset by successive political disturbances, particularly within recent years.

Exports of Camphor from China.—Reliable statistics regarding the quantities of camphor exported from China are not readily available, especially for the past twenty years. The following figures will give an idea of the amounts of camphor exported from China through 1928:

	Kilograms		*Kilograms*
1872	25,563	1906	933,000
1873	4,891	1907	1,631,820
1874	2,149	1908	914,760
1875	1,974	1909	576,120
1876	116	1910	379,140
...	...	1911	266,580
1888	5,291	1912	173,760

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[108] "On the Camphor Industry of Foochow," *Ber. Schimmel & Co.* (1926), 14.

	Kilograms
1889	1,946
1890	2,479
1891	14,993
1892	58,701
1893	76,809
1894	71,400
1895	114,900
1896	145,200
1897	64,680
1898	41,220
1899	86,880
1900	137,640
1901	98,280
1902	93,780
1903	135,360
1904	151,980
1905	358,740
1913	155,940
1914	162,540
1915	127,560
1916	181,680
1917	276,000
1918	356,460
1919	1,674,900
1920	2,066,640
1921	1,003,800
1922	778,560
1923	1,020,480
1924	630,480
1925	240,960
1926	181,560
1927	112,920
1928	80,820

Physicochemical Properties of Chinese Camphor Oil.—Kawaguchi[109] found that the properties of Chinese Hon-Sho oil (produced in Hangchow, province of Chekiang) closely resemble those of Hon-Sho oil produced on the island of Formosa. As was pointed out previously, the two oils are distilled from the same camphor tree variety.

	Chinese Hon-Sho Oil	*Formosan Hon-Sho Oil*
Specific Gravity	0.9101 (at 20°)	0.950 (at 25°)
Optical Rotation	+31° 23′	+30° 0′
Refractive Index at 30°	1.4751	1.5000
Camphor Content	51.33%	50.0%

Kitajima[110] reported on the properties of Yu-Sho oils produced in three different sections of China, comparing these oils with those of refined Hon-Sho oil produced in Japan:

	d_{25}^{25}	n_D^{25}	α_D	*A.N.*	*S.N.*	*S.N. after Acetylation*	*Camphor Content (%)*
Hangchow	0.9337	1.4719	+18° 48′	0.6	1.4	42.5	34.2
Kiukiang	0.9270	1.4704	+13° 36′	0.8	2.1	36.4	31.0
Nanchang	0.9328	1.4735	+7° 48′	0.9	2.2	47.9	27.0
Refined Japanese Hon-Sho Oil	0.9543	1.4806	+32° 24′	1.1	4.1	23.3	50.5

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[109] *Rept. Assocn. Camphor Ind. Eng. Japan, Tokyo* **9** (1942), 39.

[110] *Sci. Papers Central Research Inst. Govt. Monopoly Bur. Japan* **76** (1943).

Note that the saponification numbers after acetylation of the Chinese oils are higher than those of the Japanese oils. This means that the Chinese camphor oils contain a higher percentage of terpene alcohols than the Japanese oils do.

Kitajima[111] also studied the properties of Chinese Ho-Sho oil (produced in Hangchow, province of Chekiang), comparing them with those of the Formosan Ho-Sho oil:

	d_{25}^{25}	n_D^{25}	α_D	*A.N.*	*S.N.*	*S.N. after Acetylation*	*Camphor Content (%)*
Chinese Ho-Sho Oil	0.9088	1.4673	+0° 36′	0.4	0.9	56.7	12.5
Formosan Ho-Sho Oil	0.9231	1.4692	+17° 12′	...	...	121.7	39.6

Chemical Composition.—According to Kitajima,[112] Yu-Sho oils from China, Hon-Sho oils from Japan, and Ho-Sho oils from China and Formosa contain the following constituents:

	Yu-Sho Oil (China)			*Hon-Sho Oil*	*Ho-Sho Oil*	
	Hangchow (%)	*Kiukiang (%)*	*Nanchang (%)*	*Japan (%)*	*China (%)*	*Formosa (%)*
Monoterpenes	15.9	18.5	8.5	14.0	13.9	7.2
Cineole	19.0	21.6	14.3	4.6	14.5	4.1
Camphor	36.8	33.3	27.7	45.6	14.1	39.6
Terpene Alcohols	16.3	19.3	34.8	9.9	43.2	36.8
Safrole	2.9	0.8	1.7	18.1	0.2	7.8
Sesquiterpenes and Their Alcohols	6.3	3.0	7.8	6.2	6.6	2.0
Other Constituents	1.7	1.8	3.2	1.2	5.5	2.0
Resinous Matter	1.1	1.7	2.0	0.4	2.0	0.5

In conclusion it can be said that Chinese camphor oils (90 per cent of which is Yu-Sho oil) are particularly rich in cineole and terpene alcohols. The principal constituent of Yu-Sho oil is terpineol, whereas the chief component of Ho-Sho oil is linaloöl. The most serious deficiency of the Chinese camphor oil lies in its lack of safrole; in this respect the Chinese oil cannot compete with the Formosan and Japanese Hon-Sho oils. Nevertheless, the fact that the Chinese oils contain substantial quantities of cineole and terpineol renders them valuable for some purposes.

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[111] *Ibid.*

[112] *Ibid.*

Use.—The wide use of camphor in medicine and pharmacy, and in other branches of our industries, is so well known that it needs no detailed account here.

During the last war, camphor oil served also for the flotation of ores in Japan and Japanese controlled territories.

CHAPTER III

ESSENTIAL OILS OF THE PLANT FAMILY *BURSERACEAE*

OIL OF LINALOE, MEXICAN

Essence de Linaloé du Mexique *Aceite Esencial Linaloe del Palo*
Mexikanisches Linaloeöl *Oleum Linaloes*

Oil of Linaloe Wood

Botanical Origin.—Mexican linaloe oil is distilled chiefly from the wood and, to a small extent, from the fruit (seed), of closely related species of the genus *Bursera*. According to Holmes,[1] several species are employed for the purpose; principally *B. delpechiana* Poisson; probably also *B. aloexylon* (Schiede) Engl.; and perhaps *B. glabrifolia* (H.B.K.) Engl. and *B. fagaroides* Engl. var. *ventricosa*. The last variety possesses a caraway-like odor. These plants are trees or shrubs, native to tropical and subtropical America, and flourish on poor and stony soil, at altitudes of about 2,500 ft. Mexican producers, who call the trees linaloe or in vernacular "Copal limón," distinguish between wood with a very fine aroma, wood with a somewhat coarser odor, and wood with a caraway-like scent (see above). The Mexican linaloe oil is obtained from wild-growing trees and from trees planted in the natural linaloe forests (see below), but no effort has been made to domesticate the species in the form of plantations.

Producing Regions.—The producing regions of Mexican linaloe oil are now located chiefly in the southern part of the State of Puebla (the center there being Chiautla); the States of Guerrero, Morelos, and Oaxaca no longer supply the oil. Substantial quantities of oil used to be produced also in the State of Colima, but lately Colima has lost much of its importance.

General Conditions.—In the years following World War I, Mexican linaloe wood oil brought such high prices that the producers felled the trees indiscriminately and recklessly exploited the linaloe forests, in order to produce large quantities of oil. Not only were true linaloe trees cut down, but trees of other species and varieties, yielding an inferior oil, were also sacrificed for distillation purposes. Furthermore, the linaloe wood oil was frequently adulterated with linaloe seed oil. As a result, oils of such inferior quality were shipped under the label of linaloe wood oil that buyers lost confidence in the Mexican product and gave preference to the Brazilian oil of bois de rose, which is of similar chemical composition. Due to lack of interest, production of the Mexican oil thus fell off considerably, and for several years

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[1] *Perfumery Essential Oil Record* **1** **(1910), 57.**

amounted to not more than 10 metric tons annually. It was only with the outbreak of World War II, the ensuing difficulties in shipping from Brazil, and the lack of labor in the Amazon Basin (the available labor being used for the collection of natural rubber), that the Mexican linaloe wood oil came again into demand. The greatly reduced production of the Mexican oil in the years prior to World War II, however, had a most beneficial influence, in that the linaloe forests and trees were given a period of rest and an opportunity of being replenished by natural regrowth.

The trees grow mostly on privately owned land. The distillers lease such land and send out their own working crews to cut trees. A linaloe tree does not become oil-bearing until it is at least twenty years old, but the best oil originates from much older trees. Forest officials determine the number of trees which may be felled on each property, and Government regulations stipulate that for every cut tree four new ones must be planted. The ruling, however, has proved only partly successful, because the peons, too indolent to appreciate the reforestation program, frequently plant only one or two new trees, instead of four. Fortunately, the linaloe also propagates itself, either from dropped fruit (seed) or from young shoots developing on the extensive root system of the mother tree.

Since the wood of a healthy linaloe tree does not contain a sufficient amount of essential oil to make distillation worth-while, incisions have to be made on the trunk and on the branches of the live tree, to stimulate the development of oil, as a sort of pathological product. The development of oil is accompanied by a change in the color of the wood at the deepest point of the incision: spots of heartwood will be surrounded by a brown area which indicates the presence of oil. As an interesting feature it should be noted that the wounding of the trees is done in August or September, and in a night of full moon. This may seem like Indian superstition, but the author, during a survey of the linaloe oil producing regions, was told repeatedly by otherwise reliable and intelligent producers that, unless these conditions were observed, the trees would produce no oil. Either one of the following two methods may be employed to lacerate the wood of a live tree:

Vertical incisions are cut into the trunk in two successive seasons; oil will form in the second year. To stimulate the development of as much oil as possible, the lacerations made in the second year must be placed between those of the first year. The tree can then be felled in the following March or April.

The second method consists of making several step-like, horizontal gashes, one above the other. Depending upon the thickness of the trunk and branches, the gashes should be 2–3 cm. deep. The second method offers the advantage that the incisions need to be made only once and that the tree can be cut in the following March or April. This method, however, is more dangerous and requires considerable experience: if too severely hurt, the tree may die quickly.

Very hot weather during the dry season, and abundant showers during the rainy season (from June to October), favor a high yield of oil, but if the weather remains dry during the season of rains, the yield of oil will be low. The season for distillation of the wood is chiefly in March, April and May.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 28. Linaloe oil production in Mexico. A lacerated linaloe tree. The lacerations are made to stimulate development of oil in the tree.

Distillation.—Mexico's linaloe oil industry still operates on a very primitive basis in the interior of the above-mentioned states. Lack of roads prevents haulage of the cut trunks and heavier branches to centrally located distilleries, where the wood can be reduced to chips in saw mills or in power-driven grinders. All the work is therefore done by hand, around simple distillation posts set up along the banks of partly dried rivers, which supply the water necessary for distillation. Sitting beneath sun sheds, men and boys reduce the wood to chips with the help of hand saws, axes, and machetes.

So far as actual distillation and yield of oil are concerned, the reader will find a detailed account in Volume I of this work, p. 176. As most important feature it should be mentioned that today many of the stills, in which linaloe oil is produced, are provided with grids (perforated false bottoms) which support the chipped wood material. Thus, the latter does not remain, for hours and hours, in contact with the boiling water, which in the more primitive and old-fashioned stills causes almost complete hydrolysis of the esters, particularly linalyl acetate, originally present in the oil. The result of this slight improvement of the still construction has been a marked increase in the ester content of many lots of Mexican linaloe oil shipped abroad (see below).

Physicochemical Properties.—There has been a great deal of confusion, in literature, regarding the physicochemical properties of genuine Mexican linaloe wood oil, and many contradictory statements have been made, due partly to the difficulty of procuring authentic samples from the remote interior of Mexico. Because of the various factors which influence the physicochemical properties of this oil, it is today very difficult to evaluate a sample of Mexican linaloe wood oil by analytical figures, and careful organoleptic tests should be resorted to, in conjunction with chemical analysis.

The properties of Mexican linaloe wood oil are influenced by the following factors:

1. Plant Origin

Oils distilled from the wood of different *Bursera* species undoubtedly exhibit different properties, some of these oils being quite inferior to those derived from *B. delpechiana*, *B. aloexylon*, and closely related species (see above, "Botanical Origin"). Such inferior oils were frequently offered in the years following World War I. Unfortunately our knowledge regarding the botany of the true Mexican linaloe tree is still fragmentary.

2. Geographical Origin and Climatic Conditions

As was pointed out first by Gildemeister and Hoffmann,[2] and later confirmed by the author [3] on the basis of his own observations, the elevated and dry sections in the vicinity of Chiautla, Huachinantla, Huehuetlan el Chico and Ixcamilpan (State of Puebla), Chaucingo (State of Guerrero), and Huatla (State of Morelos) produce laevorotatory oils, whereas the State of Colima, with its moist tropical climate, produces oils which tend to be dextrorotatory. On several occasions it has been stated in literature that dextrorotation in a lot of Mexican linaloe oil must be attributed to admixture with linaloe seed oil (see below), which is dextrorotatory. In view of the explanation given above, such statements can no longer be accepted without qualification. Dextrorotation in a sample of Mexican linaloe wood oil may

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[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 170.

[3] *Drug Cosmetic Ind.* 49 (1941), 146.

be attributed either to adulteration with linaloe seed oil or to its origin in moist tropical lowlands, particularly from Colima. It should be kept in mind, however, that the quantities of linaloe wood oil produced in the State of Colima are very limited. That genuine linaloe wood oil may occasionally be dextrorotatory is evident from the fact that some lots of oil, distilled in Europe from imported logs, exhibited dextrorotation. Schimmel & Co.,[4] on steam distillation, thus obtained an oil (yield 8.1 per cent!) which had these properties:

Specific Gravity at 15°	0.8781
Optical Rotation	+8° 15′
Refractive Index at 20°	1.46072
Acid Number	1.5
Ester Number	47.5
Solubility	Soluble in 4.5 and more vol. of 60% alcohol

Fractionation of the oil proved that the oil contained 75 per cent of *d*-linaloöl (!).

3. Method of Distillation

As was said in the section on "Distillation," the method of distillation of the wood exerts a considerable influence not only upon the yield, but also upon the properties of the oil. Distilling imported linaloe logs, properly comminuted, with direct steam and in efficient stills, Schimmel & Co.[5] obtained oils which, in regard to their properties, particularly their specific gravity, differed substantially from the oils produced locally in Mexico. The oils (yield 6 to 11 per cent, against the 0.6 to 1.0 per cent, or rare 2 per cent, usually obtained in the primitive Mexican field stills) had these properties:

Specific Gravity at 15°	0.8842 to 0.900
Optical Rotation	−7° 2′ to −19° 24′
Saponification Number	8 to 9

The high specific gravity of the oils was caused by their high content of linaloöl oxide. The oils distilled by Schimmel & Co. contained substantial amounts of high boiling substances, whereas the usual Mexican oils contain chiefly linaloöl, as a result of hydrodiffusion in the old-fashioned types of primitive Mexican field stills (cf. Vol. I of this work, p. 114 ff.).

So far as the ester content of the oil is concerned, it is greatly influenced by the construction of the still (presence or absence of a perforated false bottom—viz., water *and* steam distillation, or water distillation). According to Simmons,[6] until about 1910, it was considered that the ester content

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[4] *Ber. Schimmel & Co.* (1927), 66.

[5] *Ibid.*, April (1908), 64.

[6] *Perfumery Essential Oil Record* **25** (1934), 378.

(calculated as linalyl acetate) of genuine linaloe wood oil should not exceed 10 per cent. Oils accepted as genuine at that time had properties which varied within these limits:

Specific Gravity at 15°	0.876 to 0.892
Optical Rotation	−3° 0′ to −15° 0′; rarely slightly dextrorotatory
Refractive Index at 25°	1.456 to 1.462
Ester Content, Calculated as Linalyl Acetate	1 to 8%
Alcohol Content, Calculated as Linaloöl	54 to 66%
Solubility	Soluble in 2 vol. of 70% alcohol

Until about 1910, dextrorotatory oils, in the experience of Simmons, were rare, and a dextrorotation was usually accompanied by a high ester content. From 1911 onward, however, the average ester content of linaloe wood oil has shown a marked increase (up to 14 to 16 per cent until 1914, then up to 20 per cent and more in 1915, until 25 to 30 per cent was occasionally noted in 1934).

The odor of the oil is not necessarily influenced by the ester content. The author of this work studied linaloe wood oils with a low ester content, ranging from less than 1 per cent to 6 per cent, and found that some of them possessed a very fine, delicate odor, whereas others had a somewhat harsh odor. The aroma of the oil seems to be affected by the botanical and geographical origin of the wood material and by the care exercised during distillation.

Age and Oxidation of the Oil.—The laboratories of Fritzsche Brothers, Inc., New York, examined linaloe wood oils with a refractive index (at 20°) as high at 1.4640, which was probably due to aging and autoxidation of the oil.

Adulteration with Linaloe Seed Oil.—Oils distilled from the seed of the Mexican linaloe tree usually exhibit dextrorotation (cf. "Linaloe Seed Oil," below). As Simmons[7] pointed out, the figures for the wood and seed oil, unfortunately, show a good deal of overlapping, but seed oils are generally more dextrorotatory and usually contain a higher percentage of esters. It is now extremely difficult to distinguish, by analysis, between a Mexican linaloe wood oil and a seed oil.

PHYSICOCHEMICAL PROPERTIES OF NORMAL OILS

In 1931, Gildemeister and Hoffmann[8] reported the following physicochemical properties of commercial linaloe wood oil:

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[7] *Ibid.*

[8] "Die Ätherischen Öle," 3d Ed., Vol. III, 169.

Specific Gravity at 15°	0.875 to 0.891
Optical Rotation	−14° 0′ to +8° 15′
Refractive Index at 20°	1.460 to 1.466
Acid Number	Up to 3.0
Ester Number	1 to 42; occasionally as high as 75. The oils with a high ester content could not be declared as adulterated; they had an odor suggesting the presence of linalyl acetate
Solubility	Soluble in 1.5 to 2 vol. of 70% alcohol; soluble in 4 to 5 vol. and more of 60% alcohol

The same authors [9] also described four authentic wood oils (I) which had been distilled, under supervision, in various parts of Mexico. Another oil (II), collected in Chiautla (State of Puebla), had been distilled from what was probably *Bursera aloexylon* Engl., and still another oil (III) in Tepecuacuilco (State of Guerrero). These oils had the following properties:

	I	*II*	*III*
Specific Gravity at 15°	0.8826 to 0.8869	0.8836	0.8869
Optical Rotation	−10° 6′ to −11° 35′	−10° 58′	−10° 6′
Refractive Index at 20°	1.46179 to 1.46426	1.46377	...
Acid Number	1.8 to 5.6	5.6	2.8
Ester Number	7.0 to 19.3	19.3	18.3
Solubility	All oils were soluble in 1.8 vol. and more of 70% alcohol		

Shipments of linaloe wood oils from Mexico, examined during the past twenty years by Fritzsche Brothers, Inc., New York, had properties which varied within these limits:

Specific Gravity at 15°/15°	0.883 to 0.889
Optical Rotation	−5° 25′ to −13° 8′
Refractive Index at 20°	1.4587 to 1.4612 (a refractive index below 1.4587 may indicate the presence of alcohol)
Acid Number	0.8 to 2.7
Ester Content, Calculated as Linalyl Acetate	14 to 27.1% (until about 20 years ago the ester content was considerably lower—see above)
Total Alcohol Content, Calculated as Linaloöl (Acetyl Chloride-Dimethyl Aniline Method [10])	85% and more
Solubility	Soluble in 4 to 5 vol. and more of 60% alcohol

Adulteration.—The Mexican producers, largely Indians, are not sufficiently experienced to adulterate linaloe wood oil in such a way as to render detection by routine analysis difficult. Additions of alcohol (from cane sugar)

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[9] *Ibid.* Cf. *Ber. Schimmel & Co.,* April (1908), 64.

[10] See Vol. I of this work, p. 277.

result in a lowered refractive index and can readily be proved (see Vol. I of this work, p. 338). Adulteration with linaloe seed oil decreases the usual laevorotation of the wood oil and may change it to dextrorotation (see above).

A form of sophistication much more difficult to detect consists in the addition of laevorotatory Japanese ho (shiu) oil, or of laevorotatory lots of Brazilian bois de rose oil (whenever the price of the latter oil is substantially lower than that of Mexican linaloe oil). The addition of laevorotatory ho oil or bois de rose oil will not materially change the properties of the linaloe oil, except that it will lower its ester content. The latter, however, has not much meaning, as the ester content of pure linaloe oils may be very low (see above). Several tests have been proposed, all based upon the identification of camphor, a minor natural constituent of ho oil and bois de rose oil, but absent in Mexican linaloe wood oil. Unfortunately such tests are time-consuming and not too reliable. In the evaluation of Mexican linaloe wood oil the expert should therefore be guided by careful organoleptic tests, the genuine oil being distinguished by a soft and sweet odor reminiscent of lily of the valley.

Total Production.—The total annual production of Mexican linaloe wood oil in the years from 1941 to 1947 was as follows:

	Kilograms
1941	14,760
1942	88,824
1943	39,255
1944	30,392
1945	14,273
1946	6,248
1947	5,258

From these figures it can be seen that production has declined substantially since the end of World War II.

Chemical Composition.—The following compounds, listed approximately in order of their boiling points, have been identified in Mexican linaloe oil:

Octylene(?) and Nonylene(?). Fractionating a large quantity of Mexican linaloe oil, Schimmel & Co.[11] separated a forerun b. 108°–170° (1–2 per cent of the total oil) which had a very low specific gravity (d_{15} 0.7727) and was almost optically inactive (α_D $+1° 46'$). Repeated fractionation over metallic sodium and combustion analysis showed this forerun to contain octylene b. 122°–125°, d_{15} 0.7396, α_D $\pm 0°$, n_D^{20} 1.41255, nonylene b. 139°–142°, d_{15} 0.7477, α_D $\pm 0°$, n_D^{20} 1.41808, and isomers thereof.

It is doubtful, however, whether these hydrocarbons are natural constituents of Mexican linaloe oil; they may have resulted from the addition of kerosene as adulterant, or from kerosene as contaminant in old drums.

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[11] *Ber. Schimmel & Co.*, April (1909), 61.

Myrcene(?). Further rectification of the forerun and removal of methyl heptenone gave a fraction b. 169°–173°, b_{16} 63°–65°, d_{15} 0.8243, α_D +0° 32′, n_D^{20} 1.46476. These figures in conjunction with combustion analysis pointed toward an olefinic terpene $C_{10}H_{16}$, probably myrcene. Hydration of this terpene with glacial acetic acid-sulfuric acid mixture yielded an alcohol which had the properties of myrcenol; reduction of the terpene produced a hydrocarbon which had the properties of dihydromyrcene. However, crystalline derivatives could not be obtained from any of these compounds.

A Terpene(?). The above-mentioned olefinic terpene (myrcene?) was accompanied by a terpene b_{16} 65°–72°, α_D +8° 41′, which, however, yielded neither a bromine derivative, a nitrosochloride, nor a nitrite.

Linaloöl Monoxide. The presence of epoxylinaloöl $C_{10}H_{18}O_2$, b. 193°–194°, b_{6-7} 71°–73.5°, b_4 63°–64° in Mexican linaloe oil was established by Schimmel & Co.[12] who prepared the phenylurethane m. 59°–60° (see also the monograph on "Linaloöl Monoxide," Vol. II of this work, p. 707).

Apparently the oils distilled in Europe (on rare occasions), from imported Mexican linaloe wood, contain a higher percentage of this oxide than the oils distilled in Mexico, probably for the reason that, during the long transport of the wood, the linaloöl is partly oxidized by air.

Methyl Heptenone. The same workers [13] also showed methyl heptenone to be a natural constituent of Mexican linaloe oil.

l-Methyl Heptenol. Isolated [14] from the foreruns b_{2-3} 57°–59° of the oil and purified by preparation of its acid phthalate. Saponification yielded methyl heptenol b. 178°–180°, b_3 58°–59°, d_{15} 0.8579, α_D −1° 34′. Identified by oxidation to methyl heptenone; semicarbazone m. 135°–136°.

Dimethyl Heptenol(?). Judging from the odor of a certain fraction, Barbier [15] ventured the opinion that Mexican linaloe oil also contains dimethyl heptenol.

Linaloöl. This, the main constituent of Mexican linaloe oil, was first observed by Morin [16] in French Guiana bois de rose oil (from a tree belonging to the family *Lauraceae*), and named licareol. Semmler [17] isolated this aliphatic terpene alcohol from Mexican linaloe oil and called it linaloöl. Barbier [18] first thought that licareol and linaloöl were different substances, but finally agreed that both alcohols were identical.

Mexican linaloe oil contains from 60 to 75 per cent of linaloöl. In the volatile oil derived from the wood, linaloöl appears most often as *l*-linaloöl, whereas in that distilled from the seed of the same tree linaloöl appears as the *d*-modification. More recent investigations, however, have led Schimmel & Co.[19] to the conclusion that the optical rotation alone is not necessarily a criterion as to whether an oil has been distilled from the wood or from the seed of the linaloe tree. On distilling the oil obtained from linaloe wood imported from Mexico, Schimmel

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[12] *Ibid.,* October (1912), 80.

[13] *Ibid.,* October (1894), 35.

[14] *Ibid.,* October (1908), 78.

[15] *Compt. rend.* **126** (1898), 1423.

[16] *Ibid.* **92** (1881), 998; **94** (1882), 733. *Ann. chim. phys.* [5], **25** (1882), 427.

[17] *Ber.* **24** (1891), 207.

[18] *Compt. rend.* **114** (1892), 674; **116** (1893), 883; **121** (1895), 168.

[19] *Ber. Schimmel & Co.* (1927), 66.

& Co.[20] found that it contained 75 per cent of *d*-linaloöl which was characterized by the preparation of its phenylurethane m. 65°.

It appears that the climate has a considerable influence upon the optical rotation of the linaloöl contained in the wood of the Mexican linaloe tree. The wood of trees growing in the dry highlands contains *l*-linaloöl, whereas the wood of trees growing in the humid lowlands of the Pacific coast contains the *d*-modification. The linaloöl present in the seed oil is almost always dextrorotatory.

α-Terpineol. In the course of their earlier work on Mexican linaloe wood oil, Schimmel & Co.[21] detected *d*-α-terpineol m. 35°, $[\alpha]_D^{20}$ +29° 45′, which they characterized by the preparation of its nitrosochloride m. 112°, and its nitrolpiperidine m. 151°–152°.

Investigating the above-mentioned dextrorotatory wood oil, the same authors [22] isolated *l*-α-terpineol m. 35° which gave a phenylurethane m. 112°.

Nerol. The same oil also contained nerol which was identified through its diphenylurethanes m. 51–53°. Nerol also seems to be present in laevorotatory wood oil.

Geraniol. Observed by Schimmel & Co.[23] in *d*- and *l*-rotatory wood oil. Diphenylurethane m. 82°.

Sesquiterpenes(?). According to Barbier and Bouveault,[24] and Schimmel & Co.,[25] Mexican linaloe oil contains about 3 per cent of a sesquiterpene and some other hydrocarbons which, however, have not been identified.

Use.—Mexican linaloe wood oil is an old established and highly valued perfumers' raw material, which has its place in numerous perfumes, lotions, cosmetics, and soaps. If pure, the oil possesses a suave lily of the valley odor, which blends well with lilac, jasmine, and most other floral bouquets.

Whenever its price is lower than that of Brazilian bois de rose oil, the Mexican products serve also for the isolation of linaloöl, one of the most important perfume and flavor ingredients.

Oil of Linaloe Seed

Harvest and Distillation.—The mature fruit of the linaloe tree consists of fleshy berries, the size of Spanish peas (chick peas or "Garbanzos"), greenish-red on the surface and red inside. Since the branches of the linaloe tree are quite brittle, the harvesters cannot climb into the crown of the tree and pick the berries by hand. Therefore the fruit must be collected by cutting off the ends of the branches.

The fruit matures in August and September and on distillation yields on the average 3 per cent of essential oil. Ample rainfalls during the period of

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[20] *Ibid.* Cf. *Ibid.*, October (1904), 56.

[21] *Ibid.*, October (1900), 43.

[22] *Ibid.* (1927), 66. Cf. *Ibid.*, October (1905), 44.

[23] *Ibid.*, April (1892), 24; October (1900), 43; October (1905), 44; (1927), 66.

[24] *Compt. rend.* **121** (1895), 168.

[25] *Ber. Schimmel & Co.*, April (1909), 61.

growth favor the development of sound fruit and an abundant crop, whereas a dry spell causes the fruit to shrivel up and drop off the trees prematurely. The total annual crop of berries, therefore, depends greatly upon the weather prevailing during the rainy season. Because the linaloe wood oil and the linaloe seed oil are produced at different periods of the year (the latter from August to October), the wood and the seed are never distilled together, contrary to statements occasionally made in literature. Under normal conditions the fruit is distilled without previous fermentation. However, during the peak of the harvest it may happen that large quantities of berries arrive at a distillation post, and cannot be processed immediately. Such fruit is then piled up inside of huts, or under sheds, where it may undergo slight fermentation. To what extent such partial fermentation influences the physicochemical properties and the odor of the oil is a problem which still needs to be investigated.

Physicochemical Properties.—Mexican linaloe seed oils are usually dextrorotatory, and contain a substantial amount of esters (chiefly linalyl acetate).

Simmons[26] recorded the following properties of a few typical oils submitted to him as distilled from seeds. The figures listed under (I) apply to seven dextrorotatory oils; oils (II) and (III) were laevorotatory:

	I	*II*	*III*
Specific Gravity at 15°......	0.8720 to 0.8901	0.8821	0.8820
Optical Rotation...........	+1° 36′ to +8° 24′	−1° 18′	−5° 48′
Refractive Index at 25°.....	1.4632 to 1.4669	1.4628	1.4627
Ester Content, Calculated as Linalyl Acetate..........	14.0 to 29.2%	14.2%	12.6%
Alcohol Content, Calculated as Linaloöl..............	51.0 to 65.9%	65.5%	58.2%
Solubility in 70% Alcohol...	Soluble in 2 vol.; one oil soluble in 3 vol.	Soluble in 2 vol.	Soluble in 1.5 vol.

A high ester content is associated with a high specific gravity.

Mexican linaloe seed oils examined by Fritzsche Brothers, Inc., New York, had properties which varied within these limits:

Specific Gravity at 15°/15°..	0.885 to 0.888
Optical Rotation...........	+2° 4′ to +3° 10′
Refractive Index at 20°.....	1.4641 to 1.4650
Acid Number..............	Up to 3.1
Ester Content, Calculated as Linalyl Acetate..........	13.9 to 18.6%
Solubility at 20°............	Soluble in 5 vol. and more of 60% alcohol

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[26] *Perfumery Essential Oil Record* **25** (1934), 378.

Total Oil Production.—Because of the restrictions placed upon the distillation of linaloe seed oil by the Mexican Forest Department, very little seed oil is now produced in Mexico. In 1948, for example, a great amount of seed was available for distillation purposes, but no seed oil was produced.

Chemical Composition.—The chemical composition of oil of linaloe seed closely resembles that of linaloe wood, except for the fact that the seed oil usually contains *dextrorotatory* linaloöl as chief constituent (cf. "Oil of Linaloe Wood—Chemical Composition")..

Use.—As has been pointed out on several occasions, in Mexico linaloe seed oil is occasionally employed as adulterant of linaloe wood oil. Since the odor of the seed oil is inferior to, and slightly harsher than that of the wood oil, it is not much used outside of Mexico, except occasionally in lower priced cosmetics and soaps.

OIL OF LINALOE INDIAN

Simmons [27] reported in 1934 that for some years prior to that date linaloe oils originating from southern India had appeared on the market. They were produced from the wood and seeds of trees grown from seeds originally introduced from Mexico. These oils usually differ from the Mexican linaloe oils in possessing a somewhat higher specific gravity, a lower refractive index, and particularly a substantially higher ester content. The optical rotation of the Indian linaloe oils is almost invariably dextro, usually lying between 0° and +2°; the ester content, calculated as linalyl acetate, ranges from 35 to 44 per cent.

Simmons [28] recorded the following properties for seven Indian linaloe wood oils and six seed oils:

	Wood Oils	*Seed Oils*
Specific Gravity at 15°	0.8887 to 0.8981	0.8885 to 0.8911
Optical Rotation	+1° 0′ to +2° 30′	−0° 18′ to +2° 18′
Refractive Index at 25°	1.4602 to 1.4628	1.4600 to 1.4623
Alcohol Content, Calculated as Linaloöl	73.3 to 76.1%	71.8 to 74.7%
Ester Content, Calculated as Linalyl Acetate	34.4 to 44.9%	31.5 to 44.1%
Solubility in 70% Alcohol	Soluble in 1.5 to 2.5 vol.	

Similar oils from India had been investigated, as far back as 1927, by Schimmel & Co.[29] who reported these properties for oils distilled partly from wood, partly from seed:

Specific Gravity at 15°	0.8886 to 0.8952
Optical Rotation	−0° 15′ to +2° 35′

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[27] *Perfumery Essential Oil Record* **25** (1934), 378.

[28] *Ibid.*

[29] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 170.

Refractive Index at 20°	1.4626 to 1.4662
Acid Number	Up to 2.2
Ester Content, Calculated as Linalyl Acetate	32 to 44.4%
Solubility	Soluble in 2 to 2.3 vol. and more of 70% alcohol; occasionally opalescent on further dilution

A sample examined in the Imperial Institute,[30] London, exhibited the following values:

Specific Gravity at 15.5°	0.8989
Optical Rotation at 20.5°	−4° 41′
Refractive Index at 20°	1.455
Acid Number	0.7
Ester Number	216.7 (= 75.8% Linalyl Acetate)
Solubility at 15°	Soluble in 3.3 vol. of 70% alcohol

Schimmel & Co.[31] distilled shells of the fruit, imported from Bangalore, India, and obtained 16.7 per cent of an oil with these properties:

Specific Gravity at 15°	0.9050
Optical Rotation	−6° 57′
Refractive Index at 20°	1.45182
Acid Number	0
Ester Number	270.7 (= 94.7% of Linalyl Acetate)
Solubility	Soluble in 5 vol. and more of 70% alcohol

Prior to the outbreak of World War II, the author of this work visited a plantation of linaloe trees in the vicinity of Bangalore, Mysore, comprising about 130 acres. The trees flourished well in that soil and climate. The seed had been brought from Mexico by an Englishman, Mr. P. J. Anderson, and was probably *Bursera delpechiana* Poisson. An examination of the trees showed that every part contained substantial quantities of essential oil. For actual distillation, however, only the shells of the fruit are used, after the matured fruit drops to the ground and is collected. Six pounds of mature fruit yield about 1 lb. of (dried) shells. The author also was told that the oil derived from fruit (shells) is of better quality than that distilled from the twigs and leaves. No oil is distilled from the wood itself.

Distillation of the fruit shells was carried out in simple stills, the comparative primitiveness of which probably accounts for the rather low ester content of the oil procured and analyzed by the author on that occasion:

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[30] *Bull. Imp. Inst.* **29** (1931), 182.

[31] *Ber. Schimmel & Co.* (1932), 44.

Specific Gravity at 15°	0.894
Optical Rotation	+1° 23′
Refractive Index at 20°	1.4629
Ester Content, Calculated as Linalyl Acetate	39.9%
Solubility in 70% Alcohol	Soluble in 2 vol. and more

As was proved by Schimmel & Co. (see above), the ester content of the oil derived from fruit shells can be increased substantially by distillation in modern steam stills. As in the case of lavender, rapid distillation with direct steam is required, otherwise part of the linalyl acetate will be hydrolyzed.

Except for occasional lots, Indian linaloe seed oil has not been exported. It is used chiefly by the soap and cosmetic industry of Mysore State and other parts of India. The oil is also known locally as "Indian Lavender Oil."

Narayan and Dutt[32] investigated a sample of oil, derived from *Bursera delpechiana* or *B. aloexylon,* which had these properties:

Specific Gravity at 20°	0.8952
Optical Rotation	+1° 30′
Refractive Index at 20°	1.4658
Acid Number	0
Saponification Number	130
Saponification Number after Acetylation	274

The oil had this composition:

	Per Cent
Methyl Heptenol	1.5
Linaloöl	47.7
Linalyl Acetate	40.8
Sesquiterpenes, Waxes and Resinous Substances	8.0

OIL OF MYRRH

(Oil of Heerabol-Myrrh)

Essence de Myrrhe *Aceite Esencial Mirra* *Myrrhenöl*
Oleum Myrrhae

Botanical and Geographical Origin.—Myrrh, also called heerabol-myrrh or bitter myrrh, is the gum-resin obtained from several species of *Com-*

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[32] *Indian Soap J.* **10** (1945), 47. *Chem. Abstracts* **42** (1948), 3535.

miphora (fam. *Burseraceae*), notably *C. abyssinica* (Berg) Engler, *C. schimperi* (Berg) Engler, and *C. myrrha* (Nees) Engler var. *molmol* Engler. The taxonomy of the tree which yields the commercial gum myrrh is rather confused, since the genus *Commiphora* comprises more than 60 species, all native to Africa and Arabia.

Commiphora myrrha is a small stunted tree, the trunk being covered with a whitish-gray bark. The rough branches terminate in spines. It grows in Somaliland, Eritrea, northern Abyssinia, and southern Arabia, in the form of dwarfish thickets interspersed among *Acaciae* and *Euphorbiae.*

In order to collect the gum, the natives make incisions into the bark, causing the exudation of a yellowish oleoresin. Exposed to the air, this dries, hardens and turns reddish-brown. A considerable proportion of the oleoresin accumulates in the schizogenous secretion reservoirs of the parenchym, and exudes spontaneously through fissures or cracks in the bark. The bulk of the drug originates from Somaliland, and before World War II was shipped to Trieste, occasionally via Aden.

Properties of the Gum.—Myrrh consists of rounded, irregular tears, or masses of agglutinated tears, brown-yellow or red-brown, and more or less covered with gray or yellow dust. The fracture is waxy, granular; the odor balsamic; the taste aromatic, bitter, and acrid. Myrrh yields not less than 30 per cent of alcohol-soluble extractive matter, and not more than 5 per cent of acid-insoluble ash. These are the United States Pharmacopoeia specifications, and, because of them, Arabian and Indian dealers in Aden before the war preferred to ship the gum to Europe rather than directly to the United States.

The alcoholic solution after filtration can be concentrated, preferably *in vacuo,* and yields the so-called "resinoid myrrh," a very viscous mass which, however, is soluble in high-proof alcohol and essential oils.

Myrrh is also partly soluble in water and in ether. Triturated with water, it forms an opaque yellowish or whitish emulsion which deposits a heavy precipitate on standing. The alcoholic tincture becomes opaque upon addition of water, but without precipitation.

The chemical composition of myrrh is little known and complicated; it contains from 25 to 45 per cent of resins, 30 to 40 per cent of gum, and 3 to 8 per cent of a volatile oil, which may be recovered by steam distillation.

It is possible to differentiate heerabol-myrrh from other gums by treating petroleum ether extracts of heerabol-myrrh with bromine vapors; this causes turbidity, a red color, and the separation of violet flocks in the extract. The same color reaction applies to the volatile oil distilled from the gum.[1]

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[1] Bonastre, *Buchners Repert. f. d. Pharm.* **34** (1830), 293. Ruickholdt, *Arch. Pharm.* **91** (1845), 10.

Since antiquity myrrh has served as a constituent of incense. Therapeutic values have been attributed to it, but myrrh is probably not more effective than any other resinous substance. The most important use of gum myrrh today is as an aromatic stimulant in mouth washes.

In the following we shall deal with the volatile, or essential, oil of myrrh extracted from the crushed gum by steam distillation.

Physicochemical Properties.—Oil of myrrh is a viscid liquid of yellow-brown or greenish color, possessing the characteristic odor of the gum.

According to Gildemeister and Hoffmann,[2] the oil has the following physicochemical properties:

Specific Gravity at 15°	0.988 to 1.024
Optical Rotation	−29° 0′ to −93° 0′
Refractive Index at 20°	1.5196 to 1.5274
Acid Number	0.8 to 6
Ester Number	16 to 40
Ester Number after Acetylation	32 to 78
Solubility	Soluble in 7 to 10 vol. of 90% alcohol; in a few cases with slight turbidity

Distilling imported myrrh in Southern France (Seillans, Var) the author obtained yields of oil ranging from 6 to 8 per cent. They had properties which varied between these limits:

Specific Gravity at 15°	0.986 to 1.006
Optical Rotation	−60° 32′ to −75° 26′
Refractive Index at 20°	1.5188 to 1.5229
Saponification Number	9.3 to 25.2
Solubility at 20°	Usually clearly soluble in 7 to 9 vol. of 90% alcohol, in some cases with haziness

Genuine oils of myrrh distilled by Fritzsche Brothers, Inc., New York, from imported myrrh had properties varying within the following limits:

Specific Gravity at 15°/15°	0.995 to 1.010
Optical Rotation	−62° 32′ to −83° 55′
Refractive Index at 20°	1.5211 to 1.5241
Acid Number	2.0 to 3.7
Saponification Number	16.0 to 35.5
Solubility	Soluble in 7.5 to 8.5 and more vol. of 90% alcohol

Chemical Composition.—The chemistry of myrrh oil (derived from heerabol-myrrh) was investigated almost simultaneously by Lewinsohn[3] and von

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[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 152.

[3] *Arch. Pharm.* **244** (1906), 412.

Friedrichs,[4] and more recently by Trost and Doro.[5] These authors established the presence of the following constituents:

d-Pinene. Identified by Lewinsohn who prepared the nitrosochloride m. 103°. Gildemeister and Hoffmann [6] maintain that pinene is a natural constituent of myrrh oil, despite an assertion of von Friedrichs [7] to the contrary.

Dipentene. Identified by preparation of the tetrabromide m. 124° (Lewinsohn [8]).

Limonene. Tetrabromide m. 104°–105° (Lewinsohn).

Another Terpene(?), $C_{10}H_{16}$. The same author observed in myrrh oil another terpene $C_{10}H_{16}$, $[\alpha]_D^{20}$ +80°, which yielded a tetrabromide m. 115°, and a monohydrochloride m. 6°, but did not succeed in elucidating the nature of this terpene.

Cuminic Aldehyde (Cuminaldehyde). According to Lewinsohn,[9] oil of myrrh contains up to 1 per cent of cuminic aldehyde b_{12} 116°, which gave an oxime m. 56°, and a semicarbazone m. 201°. Oxidation with permanganate yielded cuminic acid m. 114°–115°.

Cinnamic Aldehyde. The presence of cuminic aldehyde in oil of myrrh was confirmed by von Friedrichs,[10] who isolated the aldehydes by means of their bisulfite compounds and, aside from cuminic aldehyde, also identified cinnamic aldehyde.

Eugenol. So far as the phenols are concerned, Lewinsohn [11] found that the oil contains about 1 per cent of phenols. One-fourth of the phenols (0.23 per cent of the oil) consists of eugenol, which was identified by preparation of its benzoyl compound m. 69°.

Von Friedrichs,[12] who isolated the phenols from the oil with 5 per cent sodium hydroxide solution, did not observe any eugenol.

m-Cresol. According to von Friedrichs, the phenols contained in myrrh oil consist chiefly of *m*-cresol, which he identified by means of its tribromide m. 82°. Lewinsohn,[13] too, observed *m*-cresol in myrrh oil, but in very small quantities only.

Heerabolene. Several investigations of the high boiling constituents of myrrh oil (which exhibit a strong and characteristic myrrh odor) have been carried out, particularly of the sesquiterpenes. The results have not been very satisfactory, however. In the fraction b_{16} 130°–136°, d_{20} 0.943, α_D $-14° 12'$, n_D^{20} 1.5125, von Friedrichs [14] observed a probably tricyclic sesquiterpene (containing one ethylenic linkage), which he called heerabolene. It yielded a crystalline dihydrochloride m. 98°–99°. No characteristic bromide, nitrosate, or nitrosochloride could be obtained.

Cadinene(?). Lewinsohn [15] noted that on treatment with petroleum ether old myrrh oils separated a resin, which could be reduced to a hydrocarbon (probably cadinene) b_{12} 163°–168°, d_{20} 0.926, $[\alpha]_D^{20}$ +22° 45′. The crystalline hydrochloride melted at 115°–117°.

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[4] *Ibid.* **245** (1907), 432.

[5] *Ann. chim. applicata* **26** (1936), 126.

[6] "Die Ätherischen Öle," 3d Ed., Vol. III, 153.

[7] *Arch. Pharm.* **245** (1907), 432.

[8] *Ibid.* **244** (1906), 412.

[9] *Ibid.*

[10] *Ibid.* **245** (1907), 432.

[11] *Ibid.* **244** (1906), 412.

[12] *Ibid.* **245** (1907), 432.

[13] *Ibid.* **244** (1906), 412.

[14] *Ibid.* **245** (1907), 432.

[15] *Ibid.* **244** (1906), 412.

A Sesquiterpene(?). Another sesquiterpene b_{15} 151°–154°, d_{21} 0.911, $[\alpha]_D$ +30° 24′, isolated by Lewinsohn, was not identical with any sesquiterpene known at that time.

A Bicyclic Sesquiterpene(?), $C_{15}H_{24}$, and a Tricyclic Sesquiterpene(?), $C_{15}H_{24}$. More recently Trost and Doro[16] investigated two samples of myrrh oil, and observed the presence of a bicyclic sesquiterpene b_1 88°–89°, and of a tricyclic sesquiterpene b_1 94°–95°. With simultaneous splitting of the ring, this gave a dihydrochloride, and, on dehydrogenation, yielded small quantities of an azulene. Both sesquiterpenes displayed the characteristic color reaction of myrrh.

Formic Acid, Acetic Acid, and a Nonvolatile Acid(?). Treating oil of myrrh with a sodium bicarbonate solution, von Friedrichs[17] isolated formic and acetic acid, and a nonvolatile acid m. 159°, which probably originated from an ester. Nothing is known of its nature.

Myrrholic Acid(?). Freeing the oil first from acids, phenols and aldehydes, and saponifying the remaining oil with alcoholic potassium, the same author obtained an acid ester $C_{16}H_{21}O_3 \cdot COOH$, which crystallized in the form of small yellow crystals m. 236°; to this compound von Friedrichs assigned the name myrrholic acid.

Palmitic Acid. According to Lewinsohn,[18] oil of myrrh contains palmitic acid m. 62°. In old oils both this acid and acetic acid occur free, whereas in freshly distilled oils they are present as esters.

Use.—Oil of myrrh is a most valuable ingredient in perfumes of the oriental type. Its suave balsamic, heavy odor blends well with that of opopanax, olibanum, sandal, vetiver, patchouly, and geranium.

Resinoid of myrrh is a useful fixative. The odor is similar to that of the volatile oil but less pronounced, and it imparts lasting tonalities to perfume compounds.

SUGGESTED ADDITIONAL LITERATURE

David I. Macht and Hilah F. Bryan, "The Pharmacology of Myrrh, Krameria and Eriodictyon," *Am. J. Pharm.* **107** (1935), 500. *Chem. Abstracts* **30** (1936), 1868.

J. Small, "Asafoetida and Myrrh," *Food,* May (1943), 154.

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[16] *Ann. chim. applicata* **26** (1936), 126.

[17] *Arch. Pharm.* **245** (1907), 432.

[18] *Ibid.* **244** (1906), 412.

OIL OF OPOPANAX

(Oil of Bisabol-Myrrh)

Essence d'Opopanax *Aceite Esencial Opopónaco* *Opopanaxöl*

Botanical Origin.—In the past "true" opopanax meant the concrete juice or oleo-gum-resin of *Opopanax chironium* Koch. syn., *Pastinaca opopanax* L. (fam. *Umbelliferae*), a plant closely allied to the common parsnip and native to the warm countries of the Levant. Wounding the stem at its base caused exudation of a juice which, after drying in the sun, constituted the opopanax of commerce.

This type of opopanax, however, is no longer available; it has become a rarity, found here and there in the collections of importers, druggists, and perfumers.

Today's commercial gum opopanax, also called bisabol-myrrh or sweet myrrh, is the sun-dried exudation from the bark of *Commiphora erythraea* var. *glabrescens* Engler (fam. *Burseraceae*), a tall tree growing in the western parts of Somaliland. The gum is collected by the natives, sold on the market of Berbera and shipped to Aden, from where it is exported to Europe, India, and China. In the Far East the gum is employed widely as a constituent of incense.

Properties of the Gum.—Gum opopanax is partly soluble in high-proof alcohol. The alcoholic solution, after filtration, can be concentrated, preferably *in vacuo,* and yields the so-called resinoid opopanax, a very viscous mass which, however, is soluble in alcohol and essential oils.

According to Tucholka,[1] the gum opopanax (bisabol-myrrh) can be distinguished from the lower-priced gum myrrh (heerabol-myrrh) by the following color reaction:

> Six drops of gum opopanax petroleum ether extract (1:15) are mixed with 3 cc. of glacial acetic acid and carefully poured upon 3 cc. of concentrated sulfuric acid. If the gum is opopanax, the layer of contact between the two liquids turns pinkish red, and shortly thereafter the entire acetic acid layer assumes a pink color. If the gum is myrrh, the layer of contact turns green and the whole acetic acid layer assumes only a very faint pink color.

The volatile oil of opopanax dissolved in petroleum ether (1:40) gives the same color reaction, but much more weakly. Oil of myrrh does not show any color reaction at all, if treated under the same conditions.

The typical odor of gum opopanax is due to the presence of a volatile or essential oil, which can be recovered by steam distillation.

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[1] *Arch. Pharm.* **235** (1897), 289.

Distillation.—It is advisable to crush the gum prior to distillation. According to Gildemeister and Hoffmann,[2] the yield of oil varies from 5 to 10 per cent. According to the author's own experience, it ranges from 3.5 to 8 per cent.

Physicochemical Properties.—Oil of opopanax (bisabol-myrrh) is a liquid of greenish-yellow color possessing the characteristic balsamic odor of the gum. When exposed to air it resinifies easily.

According to Gildemeister and Hoffmann[3] the oil has the following physicochemical properties:

Specific Gravity at 15°.	0.870 to 0.905
Optical Rotation......	−8° 0′ to −14° 0′
Refractive Index at 20°	1.489 to 1.494
Acid Number.........	Up to 3.7
Ester Number........	7 to 20
Ester Number after Acetylation.........	37 to 55
Solubility.............	Soluble in 1 to 10 vol. of 90% alcohol; sometimes with opalescence or turbidity

In recent years the properties of opopanax oil have undergone certain changes, for unknown reasons. According to Schimmel & Co.,[4] the properties now vary within the following limits:

Specific Gravity at 15°..............	0.8835 to 0.9170
Optical Rotation....................	−12° 11′ to −19° 28′
Refractive Index at 20°.............	1.49039 to 1.49535
Acid Number......................	0.6 to 2.6
Ester Number......................	5.6 to 16.8
Ester Number after Acetylation......	29.9 to 57.9

Oils distilled by Fritzsche Brothers, Inc., New York, from imported gum had these properties:

Specific Gravity at 15°/15°....	0.880 to 0.904; in one case 0.920
Optical Rotation.............	−11° 33′ to −17° 30′
Refractive Index at 20°.......	1.4902 to 1.4952
Acid Number................	1 to 4
Saponification Number........	6.5 to 15.1
Solubility at 20°.............	Usually soluble in 8 to 10 vol. of 90% alcohol; in some cases hazy to turbid in 10 vol. of 90% alcohol

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[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 156.

[3] *Ibid.*

[4] *Ber. Schimmel & Co.* (1939), 59.

Igolen[5] reported the following properties of an oil distilled from true (see above, "Botanical Origin") opopanax (yield 3 per cent):

Specific Gravity at 15°	1.006
Optical Rotation	±0° (in a 25% alcoholic solution)
Refractive Index at 20°	1.5165
Acid Number	3.08
Ester Number	173.95
Solubility	Soluble in 10 vol. of 70% alcohol and in 2 vol. of 75% alcohol

The oil had the typical odor of true opopanax which resembles a mixture of foenugreek, lovage oil, costus root oil, and licorice. The properties of this oil differ considerably from those of the present commercial oils described above.

Chemical Composition.—Surprisingly little is known, at this writing, about the chemical composition of this interesting oil. As a matter of fact, the compounds which are chiefly responsible for the strong and peculiar odor of opopanax oil have not yet been identified.

More than fifty years ago, Tucholka[6] investigated an oil of bisabol-myrrh (opopanax oil) and, conducting gaseous hydrogen chloride into a solution of the oil in ether, obtained 6.5 per cent of a hydrochloride m. 79.3°, from which he regenerated a sesquiterpene $C_{15}H_{24}$; it was called *bisabolene.* The presence of bisabolene in opopanax oil was confirmed by Schimmel & Co.[7] who obtained a trihydrochloride m. 80°, and later by Ruzicka and van Veen[8] who reported for their bisabolene fraction, after distillation over metallic sodium, b_{12} 130°–135°, d_4^{15} 0.875, n_D^{20} 1.493 (cf. the monograph on "Bisabolene," in Volume II of this work, p. 84).

In order to identify any sesquiterpene alcohols which may be present in the oil, Schimmel & Co.[9] warmed the viscous brown distillation residue to 100° with phthalic anhydride. When processed in the usual way, the reaction product yielded an acid phthalic ester which, on saponification with alcoholic alkali, gave an alcohol very sparingly volatile with steam. Fractionated (b_2 135–137°), the alcohol yielded a small quantity of a colorless, viscous oil which possessed an odor characteristic of opopanax. The melting point of a crystalline phenylurethane could not be obtained constant, despite repeated recrystallization. The chemists of Schimmel & Co. then concluded that the alcohol thus obtained consisted of a mixture of several alcohols.

Use.—Oil of opopanax is a most valuable perfume ingredient. Its warm, balsamic, and exotic odor blends into bouquets of oriental character. If

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[5] *Parfums France* **14** (1936), 302.

[6] *Arch. Pharm.* **235** (1897), 289.

[7] *Ber. Schimmel & Co.,* October (1904), 69.

[8] *Liebigs Ann.* **468** (1929), 137.

[9] *Ber. Schimmel & Co.,* October (1904), 69.

skillfully employed, oil of opopanax produces peculiar but very attractive tonalities, which harmonize with myrrh, olibanum, sandal, vetiver, and patchouly.

The oil was formerly employed as an antispasmodic and deobstruent, but is now rarely used in pharmacy.

Resinoid of opopanax is a very useful fixative. Its odor is similar to that of the oil, but less pronounced, imparting strength and lasting tonalities to perfume compounds.

OIL OF OLIBANUM

(Oil of Frankincense)

Essence d'Oliban *Aceite Esencial Olíbano* *Weihrauchöl*
Oleum Olibani

Botanical Origin.—Olibanum, the frankincense of the ancients, is derived from *Boswellia carterii* Birdw. and other species of the genus *Boswellia* (fam. *Burseraceae*), small trees growing in Somaliland and southeast Arabia. The regions of production in the order of their importance are: Italian Somaliland, British Somaliland, and French Somaliland, the latter producing only very small quantities of frankincense.

The bark of the tree contains schizogenous gum-oleoresin reservoirs. To collect the gum the natives incise the bark, causing exudation of a white emulsion, which after a time congeals into yellowish tears and drops. The tears can be picked off the bark or from the ground. The gum is collected all year round, except in the rainy, monsoon months (from mid-June to September), when the natives are busy with agricultural work.

Producing Regions.—Prior to World War II Italian Somaliland levied an export duty on all frankincense, except that destined for Italy. For this reason Trieste was the leading port for transshipping gum olibanum to other parts of Europe and to the United States. The product of French Somaliland went mostly to Marseilles, while that of British Somaliland and parcels smuggled out of Italian Somaliland were shipped on Arabian dhows to Aden, main port of Arabia.

With the outbreak of the war, Basra, on the Persian Gulf, became a transshipping port of gum olibanum to the United States, and a few parcels seem to have reached ports of the eastern Mediterranean, probably on small coastal steamers or native sailing craft.

Grading of the Gum.—In Aden the gum was assorted into three qualities:

1. Grade I (tears): The best and most carefully selected grade, of white color, employed chiefly in church or temple incense.
2. Grade II (reddish): A mixed white and reddish quality, which contains also some particles of bark.
3. Grade III (dust and siftings): Because of its low price, the most suitable quality for oil distillation.

By assorting the crude gum about 33 per cent of each of the three grades is obtained. The unassorted gum, as it comes from the producing regions, might be considered another, or fourth quality.

Properties of the Gum.—Gum olibanum consists of yellowish, somewhat translucent, roundish tears, irregular reddish lumps or agglutinated masses. Because of friction the tears are usually covered with a whitish powder; their texture is brittle, the fracture dull and waxy. The odor is aromatic, balsamic, and the taste slightly bitter and acrid. When triturated with water, olibanum forms a milky emulsion; alcohol dissolves about 75 per cent of the gum. The alcoholic solution, after filtration, can be concentrated, preferably *in vacuo,* and yields the so-called resinoid of olibanum. This is a transparent, viscous, almost solid mass, soluble, however, in high-proof alcohol and essential oils.

Yield of Oil.—The essential or volatile oil can be extracted from the gum by steam distillation, the yield varying from 5 to 9 per cent. Distilling gum olibanum of own importation in Southern France (Seillans, Var), the author obtained oil yields ranging from 6 to 7 per cent.

Physicochemical Properties.—The oil possesses an agreeable, balsamic odor, with a slight lemon-like by-note.

According to Gildemeister and Hoffmann,[1] the properties of olibanum oil vary within the following limits:

Specific Gravity at 15°	0.872 to 0.892
Optical Rotation	The oils distilled prior to 1903 were laevorotatory, up to $-17°$; since then the oils are dextrorotatory, up to $+35°$
Refractive Index at 20°	1.471 to 1.482
Acid Number	Up to 3
Ester Number	5 to 16
Ester Number after Acetylation	28 to 48
Solubility	Soluble in 3.5 to 6 vol. of 90% alcohol, sometimes with slight turbidity

In recent years the properties of olibanum oil have undergone certain changes. The cause is not clear; perhaps the gum is collected from a dif-

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[1] "Die Ätherischen Öle," 3d Ed., Vol. III, 158.

ferent plant variety, or in regions which previously had not been exploited, or perhaps it reaches the market faster.

Chiris[2] reported on an oil of somewhat abnormal constants. The specific gravity and the alcohol content were very high, the solubility good, the odor fine.

Specific Gravity at 15°	0.9404
Optical Rotation at 20°	+44° 06′
Refractive Index at 20°	1.4849
Acid Number	2.52
Ester Number	12.63
Ester Number after Formylation	165.53
Solubility	Soluble in 1 vol. of 80% alcohol

In 1939 Schimmel & Co.[3] reported that the constants of olibanum oils (yield 3.3 to 10.4 per cent) had changed, during the previous years, and suggested that the limits, therefore, should be modified as follows:

Specific Gravity at 15°	0.8652 to 0.8862
Optical Rotation	−26° 3′ to +34° 37′
Refractive Index at 20°	1.46954 to 1.47740
Acid Number	Up to 1.9
Ester Number	3.7 to 16.8
Ester Number after Acetylation	21 to 47.6
Solubility	Soluble in 4 to 6.2 vol. and more of 90% alcohol

Oils distilled within recent years by Fritzsche Brothers, Inc., New York, from imported gum olibanum had the following properties:

Specific Gravity at 15°/15°	0.875 to 0.895, in one case 0.917
Optical Rotation	+25° 2′ to +34° 50′
Refractive Index at 20°	1.4710 to 1.4784
Acid Number	1.9 to 2.4
Saponification Number	4.7 to 30.0
Solubility at 20°	Soluble in 0.5 to 5 vol. and more of 90% alcohol

Early in 1950, the same company had occasion to examine several lots of imported gum olibanum, of excellent appearance, which, on distillation, yielded *laevo*-rotatory oils (−6° to −11°). The odor of these oils showed a characteristic phellandrene note. Nothing is known as yet as to the reason for this variation.

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[2] *Parfums France* **15** (1937), 147.

[3] *Ber. Schimmel & Co.* (1939), 88.

Chemical Composition.—The chemistry of the laevorotatory type of olibanum oil, which used to be produced prior to 1903, has not been thoroughly investigated, except perhaps in regard to the terpenes present in that oil. The following hydrocarbons have been identified:

l-α-Pinene. First called "olibene" by Kurbatov,[4] this terpene was identified as *l*-α-pinene by Wallach.[5] It occurs in the fraction b. 157°–160° of the oil and yields a nitrosochloride which, on boiling with alcoholic potassium, is readily converted into nitrosopinene m. 130°.

Dipentene. Wallach [6] identified dipentene in the fraction b. 177°–179° by preparing the tetrabromide m. 124°–125°.

Phellandrene. According to Gildemeister and Hoffmann,[7] laevorotatory oil of olibanum gives the typical phellandrene reaction with sodium nitrite and glacial acetic acid.

Cadinene. Observed by Wallach [8] in the high boiling fractions of laevorotatory olibanum oil.

So far as the dextrorotatory type of olibanum oil (produced since 1903) is concerned, its chemical composition is better known, particularly in regard to the oxygenated components. Years ago, Haensel [9] reported that the oil contains a strongly laevorotatory alcohol $C_{26}H_{44}O$, which he named "olibanol." Fromm and Autin,[10] and Fromm and Klein [11] described an α-, β-, and γ-"olibanol" of the molecular formula $C_{10}H_{16}O$, the configuration of which they could not elucidate. More recently Blumann and Schulz [12] arrived at the conclusion that the "olibanol" of Fromm and Autin is in reality a mixture of verbenone, verbenol, and some other terpene alcohols, including most likely *d*-borneol. According to Blumann and Schulz [13] the designation "olibanol" can be maintained only for the alcohol $C_{26}H_{44}O$ originally described by Haensel (see above).

In the light of these and earlier findings, the dextrorotatory type of olibanum, produced since 1903, contains the following constituents:

dl- and *d*-α-Pinene. Identified in the fraction b. 156°-157° of the oil by Schimmel & Co.[14] who prepared the nitrosochloride and the nitrolpiperidine m. 118°. Oxidation yielded pinonic acid b_7 170°–175°; the optically active acid melted at 69°–70°, the inactive at 104°.

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[4] *Liebigs Ann.* **173** (1874), 1.

[5] *Ibid.* **252** (1889), 100.

[6] *Ibid.*, 101. Cf. *Ber. Schimmel & Co.*, April (1914), 96.

[7] "Die Ätherischen Öle," 3d Ed., Vol. III, 159.

[8] *Liebigs Ann.* **271** (1892), 297.

[9] *Chem. Zentr.* (1908), I, 1837; (1908), II, 1437.

[10] *Liebigs Ann.* **401** (1913), 253.

[11] *Ibid.* **425** (1921), 213.

[12] *Ibid.* **478** (1930), 303.

[13] *Ibid.*

[14] *Ber. Schimmel & Co.*, April (1914), 96.

Camphene. Identified by the same workers in the fraction b. 158°–164°. Hydration yielded isoborneol m. 210°–211°.

Dipentene. Tetrabromide m. 124°.

p-Cymene. On oxidation with potassium permanganate, the last fraction of the terpenes gave *p*-hydroxyisopropyl benzoic acid m. 156°.

The six kilograms of olibanum oil investigated by Schimmel & Co.[15] yielded 4.71 kg. of terpenes and 1.29 kg. of higher boiling constituents. The terpene fraction contained 99 per cent of α-pinene and camphene, and only 1 per cent of dipentene and *p*-cymene. The terpene fraction boiled as follows:

156°–161°	92%
161°–163°	ca. 5%
163°–181°	ca. 4%

β-Pinene, phellandrene and terpinene were not present.

d-Borneol. Fromm and Autin[16] first expressed the opinion that oil of olibanum contains *d*-borneol in ester form. This was later confirmed by Blumann and Schulz.[17]

Verbenone. These workers treated the united high boiling fractions of the oil with sodium sulfite and sodium bicarbonate, and in the regenerated ketones identified *d*-verbenone d_{15} 0.980, α_D +172° 40′ by means of its semicarbazone m. 201.5°–203°. The optical rotation of this verbenone was not as high as that of the verbenone obtained by autoxidation of turpentine oil. (Cf. the monograph on "Verbenone," Vol. II of this work, p. 444.)

Verbenol. In order to separate the small quantities of high boiling terpene and sesquiterpene alcohols from high boiling hydrocarbons, Blumann and Schulz[18] employed the boric acid method and indirectly proved the presence of verbenol: on distillation, the borate of verbenol lost water and yielded verbenene which could be identified by the preparation of its dibromide m. 71°–72°.

Olibanol(?), $C_{26}H_{44}O$. Haensel[19] observed in the oil of olibanum a substance of pleasant olibanum odor which was viscous in a freezing mixture, and not congealing. Haensel declared it to be an alcohol, $C_{26}H_{44}O$, which he named olibanol. It had these properties:

b_{751}	333°–334°
b_{17}	205°–212°
d_{20}	0.9570–0.9596
α_D	−65° 3′ to −71° 30′

Use.—Oil of olibanum is used in all sorts of perfumes, especially of the oriental type, to which it imparts a rounding-out effect and alluring tonalities, the origin of which is difficult to identify.

The alcohol-soluble resinoid of olibanum possesses much greater fixation properties than the distilled (volatile) oil, and represents one of the best fixatives employed in perfume work. Its odor is soft, reminiscent of frankincense.

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[15] *Ibid.*

[16] *Liebigs Ann.* **401** (1913), 253.

[17] *Ibid.* **478** (1930), 303.

[18] *Ibid.*

[19] *Chem. Zentr.* (1908), I, 1837; (1908), II, 1437.

OIL OF ELEMI

(Manila Elemi Oil)

Essence d'Elémi *Aceite Esencial Elemi* *Elemiöl* *Oleum Elemi*

Introduction, Botany, and Origin.—Gum elemi is the soft, whitish or yellowish, aromatic, turpentine-like, pathological exudation of the tree *Canarium luzonicum* (Miq.) A. Gray,[1] which grows wild in the southern part of the district of Tayabas in the Philippine Islands. (Locally the tree is called "Pili.") On contact with air the resin slightly hardens, assuming on the surface a wax-like consistency and a yellowish color. To stimulate the flow of gum, the trunk of the tree must be lacerated by incisions. However, the tree will produce gum only at the beginning of the rainy season when the leaves begin to develop. During the dry season the tree is in a dormant stage, devoid of leaves, and does not produce any resin.

The tapping of the trees and the collection of the gum are effected in a very crude and primitive way. Instead of making proper incisions into the bark, or collecting the gum in buckets attached to the tree (as is done with rubber latex or turpentine), the natives simply hack into the trunk of the live tree with a "bolo." The exuded gum trickles down the bark toward the ground. After a few days or a week the natives come around again and, by scraping with a knife, collect the gum which in the interim has hardened slightly. Obviously, any gum gathered from the trunk and the base of the tree will contain pieces of broken bark, leaves, earth and all sorts of other impurities.

According to Bacon,[2] a fully grown tree yields from 4 to 5 kg. of gum per year; one very tall tree produced 22 kg. of gum within two months.

The natives sell the crude gum to dealers (usually Chinese) in the nearest village; from there the gum finally reaches the exporters in Manila. Most of the gum offered in Manila has been packed by Chinese intermediaries and contains substantial amounts of impurities at the bottom of the containers. Every can in any lot, therefore, ought to be examined individually before the lot can be bulked.

In Manila the gum is offered in two qualities:

1. "Primera" or cleaned gum. Cleaning is effected simply by scooping up the gum with a metal ladle and picking out the coarser impurities by hand. The gum is seldom strained or filtered.

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[1] Merrill, *Govt. Lab. Pub., Manila* **29** (1905), 51.

[2] *Philippine J. Sci.* **4** (1909), A 93.

2. "Secunda" or crude (uncleaned) gum. It is darker than "Primera" and contains such impurities as pieces of bark, earth, etc. The price differential between the two qualities is usually small.

On distillation with steam, gum elemi yields from 20 to 30 per cent of a volatile oil which possesses an odor typical of phellandrene.

Physicochemical Properties.—Gildemeister and Hoffmann,[3] reported the following properties for the essential (volatile) oil distilled from Manila elemi gum:

Specific Gravity at 15°	0.870 to 0.914
Optical Rotation	+35° 0′ to +55° 0′
Refractive Index at 20°	1.479 to 1.489
Acid Number	Up to 1.5
Ester Number	4 to 8
Solubility	Soluble in 0.5 to 5 vol. of 90% alcohol; usually soluble in 5 to 10 vol. of 80% alcohol

On storage, the optical rotation of the oil changes, usually decreasing by a few degrees. For example, the rotation of an oil distilled by Schimmel & Co. decreased from +36° 40′ to +34° 14′ within four years and eight months (cf. the monograph on "Phellandrene" in Vol. II of this work, p. 41).

Oils distilled from Manila elemi gum by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.880 to 0.910
Optical Rotation	+40° 50′ to +64° 0′
Refractive Index at 20°	1.4800 to 1.4880
Solubility	Soluble in 0.5 to 1 vol. of 90% alcohol; opalescent to turbid with more

The properties of some (pure) oils exceeded the limits indicated above. These deviations were caused by the distillation technique employed, or by variations in the raw material used (see below).

On treatment with sodium nitrite and glacial acetic acid the oils gave a strong phellandrene reaction.

Chemical Composition.—The first reliable investigations of the volatile oil derived from Manila elemi gum were undertaken about sixty years ago by Wallach,[4] who identified some of the chief constituents of the oil, viz.: *d*-α-phellandrene and dipentene. Years later the chemical composition of the oil—particularly its oxygenated components (see below)—was studied further by a number of workers, among them Schimmel & Co., Semmler, and Ruzicka et al.

[3] "Die Ätherischen Öle," 3d Ed., Vol. III, 178.

[4] *Liebigs Ann.* **246** (1888), 233; **252** (1889), 102.

The following compounds have been identified in the volatile oil distilled from Manila elemi gum:

d-*α*-Phellandrene. In the fraction boiling below 175°; identified by Wallach.[5]

Dipentene. The same author observed substantial quantities of dipentene in the fraction b. 175°–180°. He identified dipentene by means of its tetrabromide m. 125° and by preparing the nitrosochloride which could be converted to carvoxime m. 93°. (Regarding other terpenes present in Manila elemi oil, see below.)

Elemicin. So far as the oxygenated components of Manila elemi oil are concerned, Schimmel & Co.[6] obtained a fraction b. 277°–280°, which was optically almost inactive and which, on oxidation, yielded an acid m. 170°.

Investigating the same fraction, Semmler [7] found that its main constituent was a phenolic ether, viz., elemicin (cf. the monograph on "Elemicin" in Vol. II of this work, p. 534).

A Sesquiterpene Alcohol(?). The same fractions also contained small quantities of a sesquiterpene alcohol which was not identified.

Elemol. This monocyclic, tertiary sesquiterpene alcohol m. 51°–52° has been investigated by a number of workers, particularly by Schimmel & Co.,[8] Semmler and Liao,[9] Jansch and Fantl,[10] Ruzicka and Pfeiffer,[11] and Ruzicka and van Veen [12] who succeeded in establishing its configuration. (For details see the monograph on "Elemol" in Vol. II of this work, p. 262.)

Dihydroxyphellandrene, $C_{10}H_{18}O_2$. Years ago Clover [13] observed in the volatile oil of Manila elemi a substance $C_{10}H_{18}O_2$, which he believed to be an oxidation product of phellandrene. Later Mladenovic [14] arrived at the conclusion that this compound is dihydroxyphellandrene m. 168°, $[\alpha]_D^{20}$ +32° 27′ (in chloroform). On hydrogenation it adds 2 mols of hydrogen.

To refer again to the oxygenated constituents of Manila elemi oil: Schimmel & Co.[15] acetylated an oil sample and obtained a fraction b_3 82°–83.5°, acetylation number 196.5, which had an odor suggestive of spearmint oil. The opinion that the compound giving this odor was dihydrocuminyl alcohol could not be confirmed, as no characteristic naphthylurethane could be prepared. Yet, on saponification of the ester fraction, Schimmel & Co. obtained an oil b. 220°–230°, the odor of which resembled that of dihydrocuminyl alcohol.

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[5] *Ibid.*

[6] *Ber. Schimmel & Co.*, October (1896), 95; April (1907), 30. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 179.

[7] *Ber.* **41** (1908), 1768, 1918, 2183, 2556.

[8] *Ber. Schimmel & Co.* (1916), 17.

[9] *Ber.* **49** (1916), 794; **50** (1917), 1286.

[10] *Ibid.* **56** (1923), 1363.

[11] *Helv. Chim. Acta* **9** (1926), 841.

[12] *Liebigs Ann.* **476** (1929), 70, 88.

[13] *Am. Chem. J.* **39** (1908), 640.

[14] *Monatsh.* **64** (1934), 177. Cf. *Deut. Parfümerieztg.* **21** (1935), 54.

[15] *Ber. Schimmel & Co.*, April (1907), 30.

Apparently not all lots of Manila elemi oil contain the same terpenes (see above). For example, Clover[16] collected, and distilled, the gums from 31 trees which were identified as *Canarium luzonicum.* In ten of the oils, the terpene fraction consisted of pure *d-limonene;* nine oils contained *phellandrene;* the terpene fraction of one oil was almost pure *terpinene* (nitrite m. 155°), whereas that of another oil was almost pure *terpinolene* (tetrabromide m. 116°). Clover ventured the opinion that the almost pure terpinolene (of particularly low boiling point) originally present in the oil, on standing for several weeks, was transformed into dipentene, *d*-phellandrene, and a laevorotatory, unknown terpene.

Similar investigations were carried out by Bacon,[17] who collected 62 samples of elemi gum from trees growing in Calaog (District Tayabas) which were identified as *Canarium luzonicum.* Distilling the oils from these gums, Bacon found that only two oils contained *d-limonene;* all the others contained *phellandrene.* Of nine oils from gums originating from another section six contained *limonene.* Other samples of elemi gum (from Culion and from the island of Mindanao) gave terpene fractions which consisted almost exclusively of *pinene.* Bacon suggested that oil of elemi contains three different types of phellandrene, with the following boiling points: 165°–169°, 173°–175°, and 175°–178°.

Bacon also investigated changes in the optical rotation of phellandrene and limonene under the influence of sunlight and heat and found that the action of sunlight lowers the rotation of phellandrene much more than the action of heat does. The rotation of limonene, on the other hand, is very little affected by light.

Our description of the chemical composition of Manila elemi oil applies to the volatile oil only and does not include the components of the gum, which does not fall within the realm of this work. The reader interested in the chemistry of the gum will find ample literature on the subject.

Use.—Oil of elemi is not used widely in the perfume industry. Occasionally it finds application in the scenting of soaps and low-priced technical preparations. However, the oil is a suitable starting material for the isolation of α-phellandrene, which is used for the compounding of certain artificial (imitation) essential oils.

The gum has been employed for a long time in pharmaceutical plasters and ointments, and to impart toughness to varnishes.

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[16] *Philippine J. Sci.* **2** (1907), A1. *Am. Chem. J.* **39** (1908), 613.

[17] *Philippine J. Sci.* **4** (1909), A93.

CHAPTER IV

ESSENTIAL OILS OF THE PLANT FAMILY *MYRTACEAE*

OIL OF MYRTLE

Essence de Myrte *Aceite Esencial Mirto* *Myrtenöl* *Oleum Myrti*

Myrtus communis L. grows as an evergreen bush, wild and profusely in poor soil on sunny hillsides of countries bordering the Mediterranean. Since antiquity the aromatic leaves have been highly esteemed, and used for the flavoring of culinary preparations. The leaves and flowers contain an essential oil which can be extracted by steam distillation. Oil of myrtle is thus produced in Southern Spain, Southern France, Corsica, Algeria, Morocco, Southern Italy, Sicily, and Sardinia. Yield and quality of the oil depend greatly upon the region of production, the season of harvest, the nature of the plant material (leaves alone, leaves and flowers, or leaves and twigs), the method, and particularly the length, of distillation. Distillation of fresh leaves and flowering tops, without the heavier woody branches, yields the best oils. The oils most appreciated for their quality are those originating from Corsica.

In the following we shall describe briefly the various types of oil produced in Mediterranean countries:

Spanish Myrtle Oil

As in other countries bordering the Mediterranean, the myrtle bush in Spain grows wild and abundantly on the arid slopes of the coastal mountain ranges, particularly in the province of Huelva (southern Andalusia). In fact, Huelva is the only section in Spain which produces this oil.

The plant bears flowers from the end of February to June, May and June being the best months for distillation. During the summer months the plant loses moisture and volatile oil by evaporation and gives a very low yield of oil; distillation is therefore stopped until the end of August. From then until October the yield increases again to normal, and distillation is resumed during these months. The Spanish distillers use only freshly cut plant material, as the dry leaves contain very little oil. The distillation material consists of the fresh branches with their leaves attached, and, in the blooming season, with the flowering tops. Distillation is carried out in the usual type of field stills described in Vol. III of this work (cf. "Spanish Oil of Spike Lavender," "Rosemary," "Thyme," etc.). Under normal conditions, distillation of one batch of myrtle lasts 7 hr.; but this time may have to be extended for another 2 hours if the myrtle bushes are old. Old plants give not only a lower yield, but also a poorer quality of oil, containing a lower percentage of myrtenol. If cut from old plants, 450 to 550 kg. of branches and leaves are required to yield 1 kg. of oil.

The fact that the Spanish producers prolong distillation to 7, or even 9, hr. is probably responsible for the usually high specific gravity and high myrtenol content (ester number after acetylation) of the Spanish myrtle oils. As this oil is produced in only one region, and by the identical method, any variations in the physicochemical properties within different lots of Spanish myrtle oil must be due to different seasons of production. However, the problem has not yet been sufficiently studied to warrant any definite conclusions.

Gildemeister and Hoffmann[1] reported the following properties for myrtle oils produced in Spain:

Specific Gravity at 15°	0.913 to 0.929
Optical Rotation	+21° 0′ to +26° 15′
Refractive Index at 20°	1.466 to 1.470
Acid Number	Up to 2.7
Ester Number	63 to 92
Ester Number after Acetylation	85 to 117
Solubility	Soluble in 1 to 2 vol., seldom up to 5 vol., of 80% alcohol

A few lots of genuine myrtle oils distilled under the author's supervision in Spain had properties ranging within these narrow limits:

Specific Gravity at 15°	0.911 to 0.914
Optical Rotation	+22° 10′ to +23° 50′
Refractive Index at 20°	1.4660 to 1.4670
Acid Number	1.2 to 2.1
Saponification Number	44.7 to 58.8
Ester Number after Acetylation	80.3 to 84.6
Solubility	Soluble in 1.5 to 2 vol. of 80% alcohol; occasionally hazy or slightly opalescent

Most of the myrtle oil sold in the United States originates from Spain, which country now produces 300 to 400 kg. yearly. Prior to the outbreak of the Civil War in 1936 Spain produced yearly about 500 kg. of myrtle oil, the bulk of which went to Germany.

FRENCH MYRTLE OIL

The plant grows wild on the slopes of the coastal mountains bordering the Mediterranean, particularly in the Esterel and Maures Mountains extending

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[1] "Die Ätherischen Öle," 3d Ed., Vol. III, 260.

from Grasse toward Toulon. Production is in the hands of a few small-scale operators, who collect the plant material and distill it in simple field stills of the same type as those used for the distillation of lavender oil. In the late spring and summer 400 to 500 kg. of fresh plant material yield 1 kg. of oil; in the winter 500 to 600 kg. are required to give the same amount of oil. Distillation of one batch lasts from one to several hours. The best time for distillation is in the period of blooming—in the spring and early summer. At that time, however, the farmer-producers are busy with other, more important work; hence they produce the oil chiefly during the winter months, when they have little else to do. Production of myrtle oil in Southern France has been quite irregular, depending chiefly upon demand. At one time it amounted to several hundred kilograms per year; but it has fallen off as a result of competition from the lower-priced Corsican, Spanish, and North African oils. Years ago, some myrtle oil of very good quality was produced in the modern distilleries of Grasse (A. M.), from plant material growing in the Esterel and Maures Mountains, but the transport of the plant material from these areas to Grasse proved a prohibitive factor in the cost calculation of the oil.

Gildemeister and Hoffmann [2] suggest the following physicochemical properties for myrtle oils produced in Southern France:

Specific Gravity at 15°	0.890 to 0.904
Optical Rotation	+15° 0′ to +25° 0′
Refractive Index at 20°	1.464 to 1.468
Acid Number	Up to 1.8
Ester Number	19 to 47
Ester Number after Acetylation	38 to 70
Solubility	Soluble in 0.5 vol. of 90% alcohol. Most oils are soluble in 5 to 10 vol. of 80% alcohol

If genuine, French myrtle oils are of good quality; but, as has been said, their prices are high. Today very little of that type of oil is produced.

CORSICAN MYRTLE OIL

The oil of myrtle originating from the island of Corsica has always been esteemed for its fine quality.

Gildemeister and Hoffmann [3] indicated these properties:

Specific Gravity at 15°	0.883 to 0.887
Optical Rotation	+22° 0′ to +27° 0′
Refractive Index at 20°	1.464 to 1.470

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[2] *Ibid.*

[3] *Ibid.*

Acid Number	Up to 1.7
Ester Number	13 to 25
Ester Number after Acetylation	30 to 38
Solubility	Not soluble in 10 vol. of 80% alcohol; soluble in 1, occasionally only in 2.5 vol. of 90% alcohol

Chiris[4] reported on two Corsican myrtle oils which had an ester number after acetylation of 50.4 and 53.2, respectively.

MOROCCAN MYRTLE OIL

Production of myrtle oil in Morocco is comparatively recent, having been started only a few years prior to the outbreak of World War II. Morocco could produce large quantities of this oil, provided demand should warrant it, as the myrtle plant grows abundantly and wild over wide areas of the Riff and Atlas Mountains. The oil is distilled in movable field stills, centers of production being Ouezzane, Terroual, and Zoumi.

In Morocco the distillation material consists of leaves only, occasionally including fruit. Distillation of one batch lasts 2 to 2½ hr., and, depending upon the moisture content of the material, yields 0.2 to 0.25 per cent of oil.

Two lots of myrtle oil distilled under the author's[5] supervision in the Riff Mountains (I), and in the Atlas Mountains (II) in August (I) and June (II) 1937 had these properties:

	I	*II*
Specific Gravity at 15°	0.912	0.900
Optical Rotation	+24° 40′	+24° 40′
Refractive Index at 20°	1.4669	1.4671
Saponification Number	58.8	49.5
Solubility in 80% Alcohol	Hazy in 4.5 vol., almost clearly soluble in 10 vol.	Soluble in 7 and more vol.

The odor and flavor of these two oils were excellent.

ALGERIAN MYRTLE OIL

Algeria has been producing myrtle oil for quite some time.

Gildemeister and Hoffmann[6] (I), and Chiris[7] (II, III) reported these properties of Algerian myrtle oils:

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[4] *Parfums France* **8** (1930), 334.

[5] Guenther, "Moroccan Essential Oils," *Drug Cosmetic Ind.* **42** (1938), 304, 439.

[6] "Die Ätherischen Öle," 3d Ed., Vol. III, 260.

[7] *Parfums France* **8** (1930), 334; **10** (1932), 315.

	I	*II*	*III*
Specific Gravity at 15°	0.881 to 0.894	0.9185	0.9196
Optical Rotation	+23° 20′ to +27° 30′	$\alpha^{18°}$ +25° 38′	$\alpha^{18°}$ +24° 24′
Refractive Index at 20°	1.464 to 1.468	1.4702	1.4703
Acid Number	0.3 to 1.1	7.7	7.9
Ester Number	17 to 26	28	28
Ester Number after Acetylation	39.2 to 57	75.5	74.9
Solubility	Soluble in 0.5 vol., occasionally only in 2.5 vol. and more of 90% alcohol	Soluble in 9.5 vol. and more of 80% alcohol; soluble in 0.8 vol. and more of 85% alcohol	Soluble in 11.8 vol. of 80% alcohol; soluble in 1.5 vol. and more of 85% alcohol

Odor and flavor of the Algerian myrtle oils are normal.

ITALIAN MYRTLE OIL

Small quantities of myrtle oil are produced in Calabria, Sicily and Sardinia. A summary of the physicochemical properties of Calabrian and Sicilian oils has been given by Cancer[8] whose figures will be found in the Table No. 4.1. It includes the reports of Chiris[9] on Sicilian oils produced from 1925 to 1935, and the findings of Gildemeister and Hoffmann,[10] and of Vodret[11] on Sardinian myrtle oils.

According to Cancer[12] the content of cineole (by volume) in Sicilian myrtle oils is 22 per cent, whereas the Sardinian oil investigated by Vodret[13] contained 17 per cent of cineole, determined by the resorcinol method.

CHEMICAL COMPOSITION OF OIL OF MYRTLE

The following compounds have been observed in oil of myrtle:

α-Pinene. In the fraction b. 158°–160°; identified as nitrosochloride by Jahns.[14]

Camphene(?). Hydrating the same fraction (α_D +36°), according to the method of Bertram and Walbaum, Schimmel & Co.[15] obtained a mixture of borneol and iso-

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[8] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **14** (1939), 158. Cf. La Face, *ibid.* **2** (1927), No. 9. Pellini and Morani, *Ann. chim. applicata* **13** (1923), 97.

[9] *Parfums France* **13** (1935), 239.

[10] "Die Ätherischen Öle," 3d Ed., Vol. III, 260.

[11] *Ann. chim. applicata* **18** (1928), 421.

[12] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **14** (1939), 158.

[13] *Ann. chim. applicata* **18** (1928), 421.

[14] *Arch. Pharm.* **227** (1889), 174.

[15] *Ber. Schimmel & Co.,* April (1907), 81.

TABLE 4.1

Origin of Oil	Yield of Oil (%)	Specific Gravity at 15°	Optical Rotation	Refractive Index at 20°	Acid Number	Ester Number	Ester Content, as Myrtenyl Acetate (%)	Ester Number after Acetylation	Free Alcohol Content, as Myrtenol (%)	Total Alcohol Content, as Myrtenol (%)
Calabrian Oils										
La Face	0.19	0.9044	+21° 12′	1.4650	1.8	72.80	29.22	112.0	14.24	34.0
La Face	0.22	0.911	+22° 48′	1.4670	2.4	85.87	29.74	132.53	16.86	40.16
Cancer	0.1 to 0.125	0.9955	+18° 40′	1.4690	2.06	73.79	25.85	...	...	35.37
Sicilian Oils										
Pellini and Morani	0.112 to 0.220	0.9057 to 0.9258	+19° 38′ to +30° 5′	1.4666 to 1.4687	Up to 2.4	84 to 133	29.1 to 46.28	116.2 to 155.1	5.99 to 14.07	34.35 to 42.18
Luisi	...	0.8794	+17° 36′	1.4680	1.02	...	17.20	...	20.16	...
Chiris	...	0.8792 to 0.8912	+24° 30′ to +28° 48′	1.466 to 1.469	Up to 2.8	42.7 to 59.5	...	83.3 to 105.7	...	...
Sardinian Oils										
Gildemeister and Hoffmann	...	0.886 to 0.896	+18° 0′ to +21° 0′	1.465 to 1.470	0.4 to 1.36	18.7 to 23	...	32 to 53	...	...
Vodret	0.5	d_{10} 0.8961	α_D^{10} +18° 24′	1.4702	1.36	21.44	...	53.10	...	...

borneol, which indicates that the oil contains a compound similar to camphene, and perhaps still another hydrocarbon yielding also borneol on hydration.

Cineole. When passing gaseous hydrogen chloride or bromide through the fraction b. 176°, Jahns[16] obtained the corresponding addition products from which, by the action of water, pure cineole could be regenerated.

Dipentene. Identified in the fraction b. 180° by preparation of the tetrabromide m. 125°.

d-Myrtenol (mainly as Acetate). Investigating the higher boiling fractions of myrtle oil, von Soden and Elze[17] observed a new terpene alcohol $C_{10}H_{16}O$ which they named myrtenol and which occurs in the oil chiefly as acetic ester. The alcohol was isolated by saponification of the ester fraction with alcoholic potassium hydroxide and by conversion of the alcohol into the acid phthalate m. 116°. This method also permitted the separation of accompanying other alcohols, *geraniol* and *nerol* for example.

After purification *d*-myrtenol, a colorless viscous oil with an odor reminiscent of myrtle, had these properties:

b_{751}	220°–221°
$b_{3.5}$	79.5°–80°
d_{15}	0.985
α_D	+49° 25′

(For further details the reader should consult the monograph on "Myrtenol," Vol. II of this work, p. 233.)

l-Myrtenol. Examining a myrtle oil of Spanish origin, Paolini[18] isolated, aside from *d*-myrtenol $[\alpha]_D$ +49° 68′, acid phthalate m. 115°–116°, *l*-myrtenol which had these properties:

b.	220°
d_{15}	0.981
$[\alpha]_D$	−3° 50′

According to Pellini and Morani,[19] Sicilian myrtle oil contains 40 per cent of total alcohols, about half of which consists of myrtenol.

Aldehydes(?). The same authors observed in their oil also 1.8 per cent of aldehydes (determined by the neutral sulfite method).

Geraniol and Nerol. Small quantities of these terpene alcohols were isolated from myrtle oil by Elze[20] (see above).

Use.—Oil of myrtle is used to great advantage as a replacement for the dried leaves in all kinds of flavoring compositions for culinary purposes, particularly for table sauces. The oil is employed also in toilet waters, especially eaux de Cologne, to which it imparts an agreeable spicy note.

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[16] *Arch. Pharm.* **227** (1889), 174. Cf. *Ber. Schimmel & Co.*, April (1889), 29.

[17] *Chem. Ztg.* **29** (1905), 1031. Elze, *ibid.* **34** (1910), 857.

[18] *Gazz. chim. ital.* **63** (1933), 666.

[19] *Ann. chim. applicata* **13** (1923), 129.

[20] *Chem. Ztg.* **34** (1910), 857.

OIL OF PIMENTA

(Oil of Pimento; Oil of "Allspice")

Essence de Piment *Aceite Esencial Pimiento* *Pimentöl*
Oleum Amomi seu Pimentae

There are two types of pimenta oil on the market: (a) the oil distilled from the berries. This has a finer odor and flavor, characteristic of the spice, and therefore is higher priced than (b) the oil distilled locally from the leaves. Both types of oil will be described in the following pages.

Botany and Occurrence.—The pimenta tree, *Pimenta officinalis* Lindley (*Myrtus pimenta* L.; *Eugenia pimenta* D.C.), a native of the West Indian islands and adjacent parts of Central and South America, grows most abundantly on the British island of Jamaica. Indeed the bulk of the "allspice" (dried pimenta berries), and most of the pimenta leaf oil sold on the market, originates in Jamaica. Berries from other islands or from Central and South America seem to be derived from a different *Pimenta* species, and differ from the Jamaica product in size, appearance, and aroma. The same is true of the volatile oil distilled from these berries, and of the leaf oil.

The term "pimenta" has its origin in the belief of the early Spanish explorers that the berries of this tree were a sort of pepper; thence also the English expression "Jamaica pepper" and the German "Nelkenpfeffer." The designation "allspice" frequently employed in North America came into use probably because the odor and flavor of pimenta berries suggest a mixture of clove, pepper, cinnamon, and nutmeg. For the same reason the French use the term "Quatre épices."

The tree, an evergreen, grows to a height of about 30 ft.; it flourishes on poor, calcareous, well-drained soil, and from the age of seven to twenty years bears sufficient fruit to make harvesting worth-while.

Planting.—In Jamaica the pimenta tree does not have to be planted. It has escaped cultivation long ago and is spontaneously propagated by birds and by the "rat bat," which relish the fruit and, in flight, drop the seed. Seedlings thus are distributed and grow over wide areas, forming whole forests of pimenta trees in some mountainous sections. The only care required consists in the clearing of underbrush and in keeping the trees about 20 ft. apart.

Producing Regions.—The principal producing regions lie in the parish of St. Ann in the northern part of central Jamaica, in the parish of Manchester in the southern section of central Jamaica, and in a few other parishes—for example, Elizabeth in the southwest, Westmoreland in the west, and Hanover in the extreme northwest of the island. Most pimenta forests grow on the slopes of hills and mountain ranges.

Harvest of Pimenta Berries and Leaves.—The planters on whose land the trees grow employ native labor for the harvesting of leaves and berries, and pay accordingly. Leaves may be harvested throughout the year, but this is usually done when there is a demand for oil. The period of the berry harvest varies with the parishes. In general, the berry harvest lasts from September to March, beginning in the western parishes (Elizabeth) and gradually moving eastward. Heavy rain showers in October and November sometimes damage the crop by beating the berries off the trees. The natives harvest leaves and berries by climbing into the trees and breaking the branches off by hand. This procedure is not harmful to the trees—in fact, it has the effect of pruning. Bush knives (machetes) should not be used because of the presence, in the branches, of tannic acid, which reacts with the iron and seems to have such a poisonous effect upon the trees that they may perish after two years.

The broken-off branches are thrown to the ground where the berries are either beaten off with sticks or lashed off with whips. It is important to harvest the berries when they have attained full size, but are still green, because, when fully ripened, the fruit loses some of its aroma.

The berries are subsequently dried in the sun, usually on concrete platforms (barbecues), for four to ten days, depending upon the sunshine. They should be spread out in a thin layer and turned occasionally in order to avoid fermentation. Light rains are not harmful, especially not in the beginning of the drying, but if the showers become too heavy the drying must be continued beneath a shelter.

The berries are marketed as two different types:

1. The so-called "settlers' berries," which come from the smaller producers and are usually of somewhat inferior appearance and smaller size. About 40 per cent of the total crop of pimenta berries consists of "settlers' berries."
2. The so-called "planters' sifted berries," which originate from larger estates. On the larger plantations the drying and handling of the berry material are usually done more carefully.

There is no appreciable difference between "settlers'" and "planters'" berries in regard to flavor and, therefore, the "settlers'" berries are well suited for distillation. Sometimes there is very little difference even in the appearance of the two types of berries, some of the smaller settlers taking just as much care in the handling of their products as the larger plantations do.

The larger producers sell their berries directly to the exporters in Kingston, while the smaller settlers usually sell through native intermediaries in the various villages. The dried berries are exported in sacks holding 175 to 180 lb.

Description and Use of Pimenta Berries.—Dried pimenta berries of commerce are 4 to 7 mm. in diameter, of sub-globular shape, and reddish brown color. They have a rough surface, caused by protuberant, minute oil glands. The odor and flavor of the berries are due to the volatile oil present, chiefly in the shells (pericarps). The dried berries contain from 3 to a little more than 4 per cent of essential (volatile) oil, more than 8 per cent of quercitannic acid (whence the astringent taste), a soft resin with a burning taste, up to 25 per cent of crude fiber, some fixed oil, proteins, about 3 per cent starch, and traces of an alkaloid.

The bulk of the Jamaica pimenta berries is exported to the United States and to Europe. Prior to World War II Germany used to be a very important buyer of Jamaica berries, most of the imports being transshipped to other central European countries. Since then, however, the United States and Great Britain have emerged as the principal users of "allspice."

The berries are used as a condiment, as a flavoring ingredient in catsups, soups, sauces, pickles, canned meats, sausages, etc.

The essential oil, which in many culinary preparations, baked goods, etc., has replaced the ground spice to great advantage, is isolated from the spice by steam distillation. This work is done in a few local distilleries in Jamaica, or—to a much larger extent—in North American and European essential oil factories.

The average annual total production of pimenta berries in Jamaica amounts to 60,000 sacks, one sack holding 175 to 180 lb. of dried berries. The yearly production, however, varies considerably with weather conditions and with the demand from abroad.

Description and Use of Pimenta Leaves.—The leaves of the pimenta tree are opposite, oval-oblong, 4 to 6 in. long, and glandular-dotted beneath. The leaves, too, contain an essential oil which can be isolated by steam distillation. The leaf oil has a higher content of eugenol than the berry oil, but the odor and flavor of the leaf oil are not as fine as those of the berry oil.

The leaves are not exported from Jamaica, and the leaf oil is produced exclusively in a number of local distilleries. In 1946 Jamaica exported a total of 62,190 lb. of pimenta leaf oil, 54,891 lb. of which went to the United States.[1] Since then, exports to the United States have declined sharply, falling to 29,167 lb. in 1948, and 12,761 lb. in 1949.

[1] Private communication of Messrs. George and Branday, Ltd., Kingston, Jamaica.

PIMENTA BERRY OIL

Distillation and Yield of Oil.—In Jamaica only about five distilleries produce pimenta berry oil. The same installations also distill pimenta leaf oil. In general, the local production of berry oil in Jamaica is limited and irregular, the distillers producing berry oil only when they have firm export orders for the oil. As has been mentioned, the bulk of pimenta berry oil is distilled in North American and European essential oil factories, from imported berries. Owing to the more efficient equipment available in these distilleries, the European and North American distilled oils are usually superior to the locally (Jamaica) produced berry oils.

The distillation of pimenta berries resembles that of cloves (see "Oil of Clove"), and requires considerable attention. Prior to distillation the berries should be crushed. They are then charged into the still immediately. Distillation is usually carried out with direct steam, and lasts about 10 hr., the time required, however, depending upon the quality of the steam, the condition of the berries (crushed or whole), the method of charging the still, etc. The distillation waters may contain a considerable amount of oil (partly in emulsified form), and are, therefore, cohobated.

The total yield of volatile oil from pimenta berries ranges from 3.3 to 4.3 per cent.

Physicochemical Properties.—Oil of pimenta berry is a colorless to yellow or yellow-reddish liquid, darkening with age, and possessing the characteristic odor and flavor of "allspice."

Gildemeister and Hoffmann[2] reported the following limits for pimenta berry oil:

Specific Gravity at 15°	1.024 to 1.055
Optical Rotation	−0° 32′ to −5° 0′
Refractive Index at 20°	1.525 to 1.536
Phenol Content (Determined with 3% Sodium Hydroxide)	65 to 89%
Solubility	Soluble in 1 to 2 vol. and more of 70% alcohol; occasionally with opalescence to turbidity on dilution

Genuine pimenta berry oil, distilled by Fritzsche Brothers, Inc., New York, N. Y., in the course of many years, had these properties:

Specific Gravity at 25°/25°	1.021 to 1.042
Optical Rotation	−0° 20′ to −6° 0′
Refractive Index at 20°	1.5267 to 1.5329
Phenol Content (by Volume)	67.5 to 83.0%
Solubility	Soluble in 1 vol. and more of 70% alcohol

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[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 263.

(Details concerning the assay of the phenol content will be found in Vol. I of this work, p. 293.)

The phenols contained in pimenta berry oil and pimenta leaf oil consist chiefly of eugenol.

It is interesting to note that the phenol content of some pure oils distilled by Fritzsche Brothers, Inc., has been slightly lower than that of the oils described by Gildemeister and Hoffmann.[3] Nevertheless, the odor and flavor of these oils (with a phenol content below 65 per cent) were equally good, if not better, than those of oils with a high phenol content. As a matter of fact, the odor and flavor of the latter type of pimenta berry oil approach that of pimenta leaf oil (see below).

Adulteration.—Pimenta berry oils found on the market are frequently adulterated. The simplest adulterant is the much lower priced pimenta leaf oil. The addition of leaf oil to berry oil results in a higher phenol content and higher specific gravity. Another adulterant is clove oil, or certain fractions of it. It is sometimes very difficult, if not impossible, to identify such additions chemically, especially when they are cleverly made. The best criterion for purity is, therefore, the odor and flavor of the oil.

Chemical Composition.—The following constituents have been identified in the volatile oil derived from pimenta berries:

Eugenol. The main component of the oil, first noted by Bonastres,[4] and by Oeser [5] who found that it is identical with the chief constituent of clove oil. Schimmel & Co.[6] identified this phenol by the preparation of its benzoyl compound m. 69°–70°.

Fractionating the nonphenolic constituents of the oil *in vacuo*, the same workers [7] isolated these further constituents of pimenta berry oil:

Cineole. In the lower boiling fraction b_5 40°–50°. The iodol compound of cineole melted at 112°. Oxidation of the fraction b. 170°–180° with potassium permanganate, according to the method of Wallach and Gildemeister,[8] yielded cineolic acid m. 202°–203°.

l-α-Phellandrene. Identified in the next, somewhat higher boiling fraction, α_D $-36° 36'$, by the preparation of a nitrite m. 119°–120°. This nitrite was dextrorotatory, $[\alpha]_D$ $+95°$ in 10 per cent chloroform solution, which indicates *l*-phellandrene as parent substance.

Caryophyllene. When treating the fraction b_6 120°–125° with Bertram and Walbaum's sulfuric acid—glacial acetic acid mixture,[9] the Schimmel chemists [10] obtained caryophyllene alcohol m. 97°, which was characterized by the preparation

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[3] *Ibid.*

[4] *J. pharm.* **11** (1825), 187; **13** (1827), 466. Cf. *Trommsdorffs Neues J. pharm.* **11,** I (1825), 127.

[5] *Liebigs Ann.* **131** (1864), 277.

[6] *Ber. Schimmel & Co.*, April (1904), 79.

[7] *Ibid.*

[8] *Liebigs Ann.* **246** (1888), 268.

[9] *J. prakt. Chem.* [2], **49** (1894), 1.

[10] *Ber. Schimmel & Co.*, April (1904), 79.

of its phenylurethane m. 136°–137°. The nitrosate of caryophyllene melted at 159°, the nitrolpiperidine at 146°–147°.

Eugenol Methyl Ether. The fraction b_6 120°–125° possessed a high specific gravity (d_{15} 0.941), which indicated the presence of an oxygenated compound. Oxidation of the fraction b. 248°–260° with potassium permanganate yielded veratric acid m. 179°–180°. Using Zeisel's[11] method of methoxy group determination, Schimmel & Co.[12] calculated a content of 9.6 per cent of eugenol methyl ether in the (total) pimenta berry oil which they investigated.

Palmitic Acid. The same workers noted the presence of palmitic acid m. 60°, in the distillation residues of those constituents of the oil which were soluble in a 3 per cent aqueous solution of sodium hydroxide.

Terpene Alcohols(?). The oil probably also contains small quantities of terpene alcohols which, however, were not further investigated by the above-named authors.

Use.—Pimenta berry oil is used widely for the flavoring of all kinds of food products (meats, sausages, canned goods, table sauces, pickles, confectionery, etc.) in which the oil replaces the ground spice to great advantage, as the oil is of more uniform quality and can be dosed more easily and with greater accuracy.

Pimenta Leaf Oil

While pimenta berry oil has been known and commercially used for many years, the production of the leaf oil is of more recent date, having been started in Jamaica about 1916.

Distillation, Yield, and Quality of Oil.—For the purpose of distillation the leaves of both the "female" and the much scarcer "male" tree are used; as the latter is nonbearing, its leaves give a higher yield and better quality of oil. The leaves may be harvested throughout the year, but as a rule the oil is produced only when there appears to be some demand. The distillers in Jamaica obtain the necessary leaf material either from their own property or buy it from neighboring lands. Distillation is carried out in fairly large stills with direct steam generated in a separate steam boiler. One batch is distilled for 3 to 10 hours, the exact length of time depending upon the size of the still, the steam pressure applied, and the condition of the leaves.

During distillation of one batch, two fractions of oil are obtained, one lighter than water and one heavier than water. The latter has a very high phenol content. The runs between the two fractions consist of a milky emulsion and are difficult to separate clearly. Large settling tanks, or specially designed smaller vessels are employed in which the emulsions break up into oils lighter than water, and heavier than water. Distillation completed, the two fractions of oil are bulked.

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[11] *Monatsh.* **6** (1885), 989.

[12] *Ber. Schimmel & Co.,* April (1904), 79.

The phenols contained in oil of pimenta leaves consist chiefly of eugenol.

The phenol content of pimenta leaf oils varies largely as a result of three factors:

1. The method of distillation. Prolonged distilling gives oils of higher phenol content. Oils of too low phenol content must be redistilled and fractionated.
2. The quality of the leaf material. Leaves from branches on which the berries have been harvested give an oil with a phenol content of only 30 to 40 per cent, whereas leaves from "male" trees give a very high phenol content.
3. The place of origin of the leaf material. In the higher altitudes and on the southern part of the island, growth of the trees is inclined to become stunted. The yield of oil from such leaves is lower (about 8 oz. of oil per 100 lb. of leaves), but the phenol content of the oil is high. This lower yield of oil and higher phenol content may be caused by the greater rate of evaporation of the more volatile terpenic constituents. In the central part of the island the yield of oil may be as high as 16 oz. per 100 lb. of leaves, but the phenol content of the oil often amounts to only about 52 per cent. In the northern sections 100 lb. of leaves yield about 14 oz. of oil, which has a phenol content of 60 to 65 per cent.

By fractionating and bulking lots of different phenol content, two commercial types of pimenta leaf oil are obtained for export, viz., an oil of about 83 per cent phenol content, the other an oil of about 62 per cent phenol content.

The bulking is usually done by the producers, on receipt of orders from exporters, who specify a particular type. The oil is shipped in drums of 500 lb. net. The exporters, as a rule, do not control the quality of the oil analytically; they depend upon the word of the producers, who guarantee a certain phenol content. However, in cases of doubt the exporters have the lot analyzed by the Government chemist in Kingston.

Physicochemical Properties.—Gildemeister and Hoffmann[13] reported the following properties for pimenta leaf oil:

Specific Gravity at 15°	1.026 to 1.065
Optical Rotation	Inactive to −5° 30′
Refractive Index at 20°	1.530 to 1.540
Eugenol Content	65 to 96%
Solubility	Soluble in 1 to 2 vol. of 70% alcohol

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[13] "Die Ätherischen Öle," 3d Ed., Vol. III, 265.

The numerous lots of genuine pimenta leaf oils imported and analyzed by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 25°/25°	1.031 to 1.050
Optical Rotation at 25°	−0° 8′ to −3° 0′
Refractive Index at 20°	1.5303 to 1.5358
Phenol Content	67.5 to 90%, occasionally as high as 91%
Solubility	Soluble in 1 to 2 vol. and more of 70% alcohol

High-grade commercial oils should have a specific gravity of not less than 1.040 at 25°, and a phenol content of not less than 81 per cent.

(For assay of the phenol content see "Pimenta Berry Oil.")

The odor and flavor of pimenta leaf oil are coarser than those of the berry oil.

Adulteration.—Pimenta leaf oil is occasionally adulterated with clove oil, or with the lower priced clove stem and clove leaf oils, or combinations and fractions of these. It is difficult to discover such adulteration chemically, and the analyst must depend mainly upon his knowledge of the odor and flavor of the genuine oil.

Chemical Composition.—Kemp[14] investigated a pimenta leaf oil distilled in Jamaica and found that it contained:

Eugenol. 95.5 per cent in free form, 96.6 per cent as total eugenol. The determination was carried out according to the benzoyl chloride method of Thoms.[15]

In the nonphenolic portions of the oil Kemp[16] identified:

Caryophyllene. B_{17} 132°–138°, which yielded a blue nitrosite m. 112°, and a nitrosate m. 159°.

An Unsaturated Acid(?), $C_{13}H_{14}O_4$. Solid, m. 78°.

An Unsaturated, Dibasic Acid(?), $C_{10}H_{14}O_4$. Not identified.

An Aldehyde or Ketone(?). In very small quantities.

Use.—Pimenta leaf oil is employed as a substitute for the more expensive berry oil. When prices are sufficiently low, the leaf oil may be used also for the isolation of eugenol.

SUGGESTED ADDITIONAL LITERATURE

John B. Wilson, "Report on (the analysis of) Flavors and Nonalcoholic Beverages," *J. Assocn. Official Agr. Chem.* **19** (1936), 407. *Chem. Abstracts* **30** (1936), 7235.

H. S. Redgrove, "Spices and Condiments," Sir Isaac Pitman and Sons, Ltd., London (1933).

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[14] *Arch. Pharm.* **263** (1925), 12.

[15] *Ibid.* **241** (1903), 592.

[16] *Ibid.* **263** (1925), 12.

OIL OF BAY

Essence de Bay   *Aceite Esencial Bay-Malagueta*   *Bayöl*
Oleum Myrciae

Producing Regions.—The bay or bay rum tree, *Pimenta racemosa* (Mill.) J. W. Moore, occurs wild, semiwild and cultivated on several of the West Indian islands, chiefly Dominica (B. W. I.), and Puerto Rico (U.S.A.); and to a lesser extent the Virgin Islands (U.S.A.), St. Lucia and Montserrat (B. W. I.).

Years ago the best quality of oil was produced on St. Thomas and St. John (Virgin Islands), but production has now shifted to Dominica and Puerto Rico. As a result of the high cost of labor prevailing in Puerto Rico, the island is now faced with difficulties in competing with Dominica where wages are substantially lower. Between 1936 and 1946 Dominica exported from 20,000 to 50,000 lb. of bay oil annually. Puerto Rico and Dominica have about equal productive capacities. Bay oil and bay rum exports from all of the islands, however, vary considerably from one year to the next.

Oil produced on some of the West Indian islands is exported to neighboring islands for processing into bay rum. Jamaica and Puerto Rico, for example, may receive oil from the Virgin Islands or other islands for processing with local alcohol, and for use locally, or for exportation to the United States and Europe. The United States is the largest consumer of bay oil; large quantities of oil also are consumed in and near the production areas in the West Indies. In Puerto Rico, the export figures show only 10,000 to 20,000 lb. of oil exported annually, although probably some 60,000 lb. or more are produced in some years (based on a survey of the distilleries in 1946–1947). Thus, over half the oil produced in Puerto Rico is used locally.

The oil is obtained by distillation of the leaves of the bay tree (usually cultivated) and is the most important active ingredient in bay rum, popular in the West Indies and in the United States.

Botany.—The wide variability within, and the similarity between the genera *Pimenta* and *Myrcia* (fam. *Myrtaceae*) has led to much confusion regarding the taxonomy of the plant, the leaves of which serve for the distillation of bay oil. The confusion has extended even to official standard works.

The commercial designation bay oil, itself, is somewhat ambiguous, because it may suggest "bay laurel," *Umbellularia californica* (the California mountain laurel), or "sweet bay," *Laurus nobilis*, the common laurel used in culinary preparations. Nevertheless, we shall retain the term "oil of bay," since, after many years of use, it has become firmly established in commerce and is now generally applied to the West Indian product.

According to the classification of the American Joint Committee on Horticultural Nomenclature,[1] the correct botanical name for the West Indian bay tree is *Pimenta racemosa* (Mill.) J. W. Moore.

Other botanical names have been assigned to the plant at one time or another, among them *Pimenta acris* Wight (*Eugenia acris* Wight et Arnott), *Myrcia acris* D.C., *Myrtus pimenta* Ortega, *Myrtus acris* Sw., *Myrtus caryophyllata* Jacq.

Common names are: bay-berry, wild cinnamon, "guayavita," "ausu," and "malagueta," the latter term being commonly used in Puerto Rico.

The species consists of many races differing mainly in the amount and quality of the oil content, but also in shape, size, and color of the leaves, and shape of the fruit.

Within some bay sections in the West Indies there is a tree (*Pimenta citrifolia, Amomis caryophyllata grisea*) closely resembling the true bay tree. It is considered highly undesirable because of the poor quality of the oil which has an odor of lemon or anise. Seedling trees of this undesirable species may sometimes occur in bay plantations. They should be removed in order to avoid contamination, adulteration, and lowering of the quality of the bay oil during the harvesting and distillation process. In Puerto Rico and other Spanish-speaking countries this tree is known as "lemoncillo," "cinnamon bush," or "false" bay rum tree.

Careful producers do not use leaves of the "lemoncillo" for distillation and are on guard against their admixture to normal leaf material. The "lemoncillo" tree can easily be recognized by its weak, stunted appearance, the true bay tree being strong and vigorous. There may be marginal cases, however, where these characteristics do not hold, and where the nose is not sufficiently sensitive to detect the lemon-anise odor of the "lemoncillo" leaves. For such cases Hendricksen[2] devised a colorimetric method permitting differentiation between leaves of the "lemoncillo" and the true bay tree. For details the reader is referred to the original literature.

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[1] "Standardized Plant Names," 2d Ed. (1942), 204, 483, J. Horace McFarland Co., Harrisburg, Pa.

[2] "A Chemical Test for the Identification of Lemon-Scented Bay Leaves," *U. S. Dept. Agr., Mayaguez, Puerto Rico, Agr. Notes* **58** (1931). Cf. Childers, et al., "Bay Oil Production in Puerto Rico," Federal Experiment Station in Puerto Rico, *U. S. Dept. Agr., Mayaguez, Puerto Rico, Circ.* No. 30 (1948).

BAY OIL PRODUCTION IN PUERTO RICO

Introduction.—According to Childers, Robles and Loustalot,[3] who made a detailed study of Puerto Rico's bay oil industry, there is considerable acreage of steep and rolling land in Puerto Rico that is for the most part either lying idle or yielding little or no profit. The bay rum tree, *Pimenta racemosa* (Mill.) J. W. Moore, can be grown successfully on much of this type of land. Several groves and scattered clumps of bay rum trees are already well established in Puerto Rico with a total area approaching 1,000 acres. These groves are located in the central and southern portion of the island, mainly in the southeast section near Guayama.

In the region of Guayama, it is estimated that about 3,500,000 lb. of bay leaves are distilled annually, yielding between 1.0 and 2.0 per cent of bay oil, or from 35,000 to 40,000 lb. of bay oil. Near Adjuntas there is a planting of about 120 acres. Above Ponce there is another planting of about 50 acres, whereas near Cabo Rojo the trees are mostly scattered with but few trees systematically planted. Trees in the latter region were not harvested for several years beginning shortly after 1940, due to the death of a local distiller and to a temporary suspension of interest.

During periods of a generally low price level in the United States the amount of bay oil that the market absorbs has been limited, but during periods of prosperity and high prices, as following World War II, the demand for bay oil far exceeded the supply in Puerto Rico. Thus, during unfavorable economic conditions, overproduction of bay oil, a more or less luxury item, may be experienced unless a definite sales program is initiated to increase consumption.

Climatic Conditions.—Bay trees are one of the few crops in Puerto Rico that will succeed under relatively low rainfall conditions of 30 to 50 in. annually. The most productive and largest plantings, however, are located in medium to heavy rainfall areas of 70 to 100 in. Near Cabo Rojo under rainfall conditions of 40 to 50 in., bay trees grow slowly but satisfactorily. The bay groves in the Virgin Islands are largely located in regions receiving an annual rainfall of between 35 and 55 in. At Mayaguez, bay trees thrive under an annual rainfall of about 82 in. falling chiefly during the months of April to October, inclusive. Low rainfall of 1 to 2 in. per month, or less, may occur between December and March, inclusive, during which time drought has resulted in death of young seedlings, but the total loss has not exceeded 5 per cent.

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[3] The author wishes to express his gratitude to Dr. Kenneth A. Bartlett, Director, and to Mr. Arnaud J. Loustalot, Acting Director of the Federal Experiment Station in Mayaguez, Puerto Rico, for permission to quote this comprehensive material freely.

The insular climates found in the Caribbean area are apparently ideally suited to bay culture inasmuch as the industry, for this or other reasons, has shown little spread to other areas during the past 100 years. The mean temperature in Puerto Rico varies between a high of 79.9° F. at Guayama (sea level) to a low of about 72° F. at Maricao and Aibonito (about 2,000 ft.). In general, the temperature is about 5° F. warmer at sea level than at an altitude of 1,500 ft., above which few bay rum trees are found. During the warmest month (August) the average temperature rarely exceeds 95° F., or drops lower than 58° F. There is an abundance of sunshine almost every day throughout the bay-growing districts.

Soil Conditions.—Bay rum trees are found growing for the most part on relatively heavy clay on hilly and rolling land. A rooting depth of 3 ft. or more appears desirable. Hillsides with heavy outcroppings of rocks and a thin covering of soil of low fertility are undesirable for bay trees. Soils in bay plantations in Puerto Rico vary in reaction from very acid (pH 4.5) to almost neutral. It is not known if the crop will succeed well on alkaline soil.

Bay rum trees are usually planted on land which is too steep for the cultivation or growing of other economic crops. The slope may reach 60 per cent or more. In the drier region near Cabo Rojo, however, many bay trees are found growing on moderately rolling land.

Bay rum trees usually produce better at the base of a slope than at the top. Also, size of the trees and general vigor are usually greater in the concave than in the convex areas of the slope. This may be due to more fertile soil and better moisture conditions in the concave areas.

Propagation by Seed.—Plantings in the Virgin Islands and to some extent those in Puerto Rico are sometimes established by cutting away the forest trees and underbrush and allowing the voluntary bay seedlings to take over gradually. After a year or two these seedlings are thinned to a distance of about 6 by 9 ft.

Most bay groves in Puerto Rico are planted systematically from propagated seedlings. The seeds are usually collected in August when the drupes are hard ripe. The drupes are opened and the seed is washed and planted *immediately* in flats or specially prepared seedbeds similar to those used for growing vegetable seedlings. These beds are raised about 6 to 8 in., 3 to 4 ft. wide, and of a convenient length. A mixture of rich soil, rotted manure, sand, and leaf mold in about equal parts makes an excellent seedbed mixture. Manure is the most important ingredient and should be used freely if available. The seeds are planted in rows about 6 to 8 in. apart, and sown ¼ to ½ in. deep at the rate of about 10 seed per linear foot. The seedbed should be located in partial but not heavy shade, and irrigated during dry periods. Germination of 50 per cent or more is reported by growers; as high as 98 per cent germination has been obtained under laboratory conditions at Mayaguez.

When about 3 to 5 in. high, the seedlings are transplanted to nursery beds or to 1- or 2-qt. cans. The beds are 3 to 4 ft. wide, any convenient length, and with aisles about 2 ft. wide between beds. The beds should be located with a northern exposure along a creek bank where it is moist and cool. The seedlings are grown for approximately one year in these nursery beds; then the tap roots are severed about 3 in. below ground in order to induce a more fibrous root system. The seedlings are usually ready for transplanting to the field after a year and a half to two years in the nursery. The seedlings vary widely in type and vigor; only the sturdy plants should be used.

No nurseries in Puerto Rico handle bay seedlings. Some growers occasionally have trees in excess of their planting needs which are offered for sale. The usual practice is to dig these seedlings from the nursery beds with part of the soil attached to the root system at the beginning and during the rainy season. The trees are placed in quart tin cans, and additional rich soil is packed moderately around the roots. The potted trees are shaded and watered frequently until trucked to their destination.

Planting.—Bay seedlings should be transplanted to the field at the beginning or during the rainy season. Planting distances vary; a common distance is 5 to 6 ft. between trees in rows, with the rows spaced 8 to 10 ft. apart.

The trees should be dug from the nursery after a rain and shortly before or preferably on the day they are planted. The roots can be surrounded with moist peat moss, sawdust, or similar organic debris and wrapped in burlap in order to prevent the roots from drying during the transplanting process. If the roots are allowed to lie in the sun and dry, the percentage survival and vigor of the trees will be greatly reduced the first year after planting. Survival and early growth are usually better if a handful or more of soil is left attached to the root system.

Planting is facilitated by first clearing the area and letting the hay and debris lie for later use as mulch around the young trees. Trees are planted at the same depth they grew in the nursery. Top soil should be packed well around the roots in order to avoid large air spaces in the soil which allows soil to dry too rapidly. After planting, about one-third of the top of the seedling is removed with a machete or pruning shears, in order to reduce the top in proportion to the roots. It is suggested that a shovel-full of rotted manure, when available, be placed in the planting hole to stimulate early vigorous growth.

Training of the Bay Tree.—Although the bay rum tree will attain a height of 60 ft. or more if allowed to develop normally, the commercial tree is usually not permitted to attain a height of more than 10 to 15 ft. to facilitate management. The pruning is performed at harvest when the leaves and limbs are removed. One or two central leader trunks with many side branches are more convenient to harvest than a bushy tree with many spindly trunks. While the young tree is developing, a vigorous leader should be selected and encouraged, and any smaller competing leaders either should be removed or subdued by heavily cutting back to a strong lateral limb to give the tree a spreading habit.

Bay trees will live for many years in spite of rather heavy and regular pruning at harvest. When old trees become poorly shaped, gnarled, and low in vigor, it may be desirable to encourage a young leader from the base of the tree to gradually take over, after which the old section of the tree is removed entirely.

Cover Crops.—Voluntary weeds and grass comprise the only cover crop used in bay plantings in Puerto Rico and the Virgin Islands. This cover is cut once or twice a year with a machete, and particularly preceding the harvest period in order to facilitate traffic in the grove. The possibility of growing a permanent legume cover should be given further study. Legumes are known to furnish nitrogen to crops growing in combination with them. Legumes showing promise in Puerto Rico are Tropical Kudzu, Trailing Indigo, *Indigofera endecaphylla*, and *Crotalaria spectabilis*.

Fertilization.—Nitrogen is the element most frequently lacking in Puerto Rican soils. Phosphorus is also important, particularly in the hill sections. Benefits from applications of potassium have not been clearly demonstrated. Thus, it appears that nitrogen is the element which should give the most response per unit weight of fertilizer and should be given first consideration in fertilization of the bay plantation.

Mulching.—Most of the bay prunings and a large quantity of the spent leaves are used in the boiler furnace to produce steam for distillation of the bay oil. However, some distilleries have large quantities of spent leaves and ashes left over during and after the distillation season. A grower near Guayama hauls these leaves to the grove and distributes them beneath the trees to a depth of 4 to 6 in., which is a wise practice. Grass cut between the trees should be gathered and also placed about the base of the trees, forming a ring of mulch about 2 ft. wide and 6 to 12 in. deep. Mulching has several advantages: it conserves moisture, reduces the temperature of the soil about the roots, provides organic matter to the soil, and supplies nutrients to the tree roots.

Insects and Diseases.—Bay trees have relatively few insects and diseases, the only insect causing moderate damage to the leaves being the sugar cane weevil (*Diaprepes abbreviatus,* L.), commonly called "vaquita" in Puerto Rico.

No specific disease organisms have been identified in bay plantations insofar as the literature shows. Young bay seedlings in the station plantations have been noted to suddenly die after a period of several months of growth following transplanting. The leaves become light green to yellowish, then turn brown and adhere to the tree. Death of the tree appears to be due to a root rot; drought may also be a cause as death frequently occurs during the dry season.

Harvest and Oil Content of the Leaves.—The principal harvesting season in Puerto Rico lasts from January to June, but some harvesting is performed throughout the year near Guayama. Growers claim that the bay oil content in leaves is higher during the relatively dry season from January to June than during the rainy season. Preliminary results have shown that a charge of 550 lb. of mature bay leaves yielded 2,270 cc. of oil, whereas a similar charge of immature leaves yielded 1,950 cc. of oil. Growers are of the opinion that leaves coming from trees in high altitudes contain relatively less oil than those grown near sea level.

A survey conducted by the Federal Experiment Station in Puerto Rico[4] on the oil content of 120 bay leaf samples from different regions in Puerto Rico and St. John, Virgin Islands, indicated that rainfall is an important factor influencing the growth of bay trees and the production of bay oil. The oil content seemed to vary inversely with the amount of rainfall.

In Puerto Rico the percentage of oil ranged from 1.03 to 2.76 per cent, whereas the oil content from bay leaf samples from the Virgin Islands ranged from 1.32 to 3.40 per cent. The average oil content in 120 leaf samples was 2.02 per cent.

While a high percentage of oil in the leaves is desirable, the factor of most interest to growers is high production of oil per acre over a period of several years. A tree yielding a high percentage of oil may not necessarily produce well on an acre basis and over a period of years. In a dry region such as near Cabo Rojo, growth is probably slower and the interval between harvests is somewhat longer, which may account for the higher percentage of oil. It has not been established, however, if the net profit will be higher in dry regions where oil content is relatively higher and harvesting less frequent than in moist regions where the oil content is lower and harvesting practiced more often.

The peak periods of harvest will vary depending upon the urgency of duties with other crops, and upon the rate of leaf development which is affected by many factors such as soil type, fertility, moisture, and cultural care. Intervals between harvest may extend from nine months to two years, but if the leaves are left longer than two years they tend to drop, especially during the dry season. During years of high prices, the leaves may be harvested at intervals of about twelve months. Fourteen to eighteen months,

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[4] *Ibid.*

however, is considered an average harvest interval in normal times in Puerto Rico.

Harvesting Methods.—Two methods of harvesting are employed. In one method leaves are stripped from the trees, with few limbs or shoots being removed except those at the top, which are pruned to keep the tree low. In the other method both shoots and leaves are removed and tied in bundles for transportation to the distillery, or the shoots and limbs may be tossed into a pile where women paid on a low hourly basis pull the leaves and place them in burlap bags which are carried by animals down the steep slopes. In recent years, a jeep with a trailer has proved economical and rapid for transporting bay leaves, provided the slopes are not too steep. The "deshooting" method is used both near Ponce and in the Guayama region, whereas the method of removing mostly leaves and but few limbs is used near Adjuntas. The deshooting method is simple, more convenient, and requires less labor. Also, it tends to keep the tree within bounds and the center of the tree free from barren twigs. However, this heavy removal of limbs, shoots, and leaves may lengthen the harvest intervals and tend to reduce yield per tree. It has not been experimentally established which of these methods is the most profitable from the standpoint of oil produced over a period of years.

The harvesting crew may consist of a dozen men who are paid either by the day or by the hundredweight of leaves harvested. The men may then be subdivided into groups of three men organized with two men cutting the limbs and the other making the bundles. Where the harvesters are paid by the 100 pounds, the average man can harvest between 700 and 800 lb. a day, some men harvesting as much as 1,500 lb. Men paid by the hundredweight require less supervision, and there is frequently a desire on their part to work faster in order to obtain a higher daily income. Inasmuch as the harvesting can be spread over several months, there is no need for hiring large numbers of men to do the job in a relatively short time; the work can be spread over a period of six months or more if necessary. Also, the still can accommodate only a certain quantity of leaves and it is not good practice to accumulate large quantities of bay leaves awaiting distillation.

In the region of Guayama where there is one large bay distiller and the groves or clumps of bay trees are scattered over a rather large area, the bay distiller hires one or two reliable men on a salary basis who contact the various farmers having bay leaves for sale. A price is agreed upon by buyer and seller on the basis of 100 lb. bundles of leaves, including shoots and stems. The grower may harvest his own bay leaves, or the bay distiller may furnish the men who perform the harvesting, and pay a base rate to the owner of the property for the leaves obtained. The bay distiller also supplies a truck that tours the regions where harvesting is in progress, collects the bundles, and makes cash payments to the growers.

Yield of Leaves.—From 10,000 to 30,000 lb. of fresh bay leaves may be obtained per acre. Puerto Rican growers in general report around 15,000 lb. per acre. As stated previously, however, yields may vary considerably with frequency of harvest, rainfall, and soil fertility.

Storage of the Leaves.—Bay leaves may be processed immediately upon arrival at the distillery, or they may be stored for a short period after the harvest in a well aerated bin. Storage for about three days in such bins is thought by the growers to increase the yield of oil and facilitate the handling of the leaves. Also, more leaves can be packed into the distilling vat, thus making it possible to obtain more oil per distillation.

The leaves are first comminuted to small pieces by passing through a chopper which should be conveniently located above the distilling vat so that the crushed leaves fall down the shoot directly into the still where they are packed moderately.

Distillation.—The distillation of bay leaves is simple and requires precautions only in the process of separating the oil, as the condensate flows off in two fractions, the first fraction containing oil lighter than water, and the second fraction containing oil heavier than water. The two types of oil—which after completion of the distillation must be mixed to obtain the complete oil—can be collected in the type of oil separator described in Vol. I of this work, pp. 138 and 139.

The stills used in Puerto Rico operate on the principle of water *and* steam distillation, or direct steam distillation.

In the case of water *and* steam distillation, salted fresh water (or distillation water from the previous operation), or sea water[5] (⅓ sea water to ⅔ fresh water) is placed in the bottom of the still below the grating, the bay leaves are packed into the vat above the grating, the lid is tightly closed by bolting with winged tip nuts, and the distillation conducted by placing a fire beneath the vat. In experiments performed at the Federal Experiment Station in Puerto Rico, Arrillaga and Jones[6] have shown that distillation from salt solution (25 per cent sodium chloride) gave a higher yield of oil and a higher phenol content than the distillation without salt.

By placing the condenser and the oil separator at a sufficient elevation, it is easy to arrange the process so that the condensed water may return directly to the still (automatic cohobation). This arrangement has several advantages: it reduces the amount of water necessary, it obviates the danger of the still being injured owing to all the water being boiled away with the consequent "burning" of the plant material, and it has the additional advan-

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[5] Sea water contains about 5.0 per cent salt (sodium chloride).

[6] *Am. Perfumer* **43**, Dec. (1941), 29; **44**, August (1942), 25; **44**, Sept. (1942), 29; **44**, October (1942), 25.

tage of returning any oil to the still which may escape with the waste water, thus permitting its recovery by redistillation (cohobation).

One of the main disadvantages of this type of still consists in the inconvenience of discharging the spent leaves after completion of the distillation. This difficulty may be overcome by generating the steam in a separate boiler (direct steam distillation) so that the vat containing the leaves can be opened both at top and bottom, thus permitting it to be charged from the top and discharged from the bottom; or similar operations can be carried out by placing the still on a pivot (tilting stills). In the case of distillation with live steam (from a steam generator) the distillation water cannot be returned to the still automatically.

Distillation of one batch usually lasts 9 hr. and can be shortened considerably by higher steam pressure, or in the case of direct fire distillation by the use of salt water beneath the grating. Previous reduction of the leaf material also shortens distillation time.

As has been pointed out, the oil comes over in two fractions which are usually collected separately. In the first fraction, the oil is lighter than water, and has a phenol content of about 50 per cent and higher. In the second fraction which is smaller, the oil is heavier than water and consists almost exclusively of phenols. By mixing the two fractions an average phenol content of 60 per cent and even higher is obtained. Variations in the proportions of these two fractions are attributable, at least in part, to the relative freshness of the leaves and the season in which they are collected. These proportions in turn influence the phenol content and specific gravity of the complete final oil. The yield of final oil obtained in the process ranges from 0.75 to 1.25 per cent, this percentage being considered about normal.

At the time of this writing (1949), there are five bay oil distilleries in Puerto Rico. Each distiller uses his own method of distilling, some operating with direct live steam generated in a separate boiler, others with direct fire stills (water *and* steam distillation). The fuel consists of exhausted, sun-dried bay leaves and wood alone or mixed with coconut husks or other materials. In general, the distilleries are rather primitive; one is quite modern. Their construction, the methods, and especially the length of distillation greatly influence the phenol content which in oils of best quality may be as high as 65 per cent. The altitude, soil, season, and weather conditions also are thought to influence the phenol content of the oil. Even more important is the age of the leaves which, as pointed out earlier, are often left on the tree for thirteen or fourteen months before being collected. A yearly harvest of the leaves results in a somewhat lower phenol content but greater yearly yield of oil. According to local producers, the best quality of oil is contained in the green stems of the leaves and flowers, but these are rarely used for commercial production of bay oil. One bay oil distiller near

Guayama, Puerto Rico, is in a position of producing as much as 1,000 lb. of oil per week. His method of distillation consists of generating steam in a large boiler and passing it through two or three distillation vats at the same time, each vat containing 450 to 500 lb. of fresh leaves. With this system he is able to distill 4 to 6 batches of leaves per day. The oil is collected with the Florentine flask system, but instead of returning the distillation water to the still, it is transferred to a large settling tank where the heavy portions settle to the bottom and are drawn off at intervals. These heavy oils are high in phenol content and are used to fortify the lower boiling fractions when their phenol content drops below 55 per cent. With this system, the distiller is in a position to offer a more uniform oil assaying between 55 and 60 per cent phenol, which consequently finds a ready market.

Summary on Bay Oil Production in Puerto Rico.—1. According to Childers, Robles and Loustalot,[7] the bay oil industry is a small but old enterprise in Puerto Rico. Total acreage approaches 1,000 acres, most of which is located in the southeastern section. Annual bay oil production in Puerto Rico ranges from 25,000 to 50,000 lb.

2. Bay rum trees are grown for the most part on the heavier slightly acid clay soils which may be rocky, relatively steep, and unsuited for most agricultural crops.

3. The seedling trees are germinated and grown in nurseries by a special technique and transplanted to the field at distances of 5 to 6 ft. apart in rows 9 ft. apart. Harvesting of leaves can begin in four to five years after planting. Sod cut once or twice a year is the usual soil management program; nitrogen fertilizer has shown definite response where used in commercial groves.

4. Bay trees will grow satisfactorily in regions of 35 to 50 in. of rainfall annually, but growth and production are better in regions receiving from 75 to 100 or more inches. Temperatures encountered from sea level to 1,500 ft. appear to be most favorable, with apparently better growth from sea level to 500 ft.

5. Bay trees are trained to one or two main trunks with numerous side branches. Tree height is maintained at about 10 to 12 ft. by heavy pruning of the top.

6. Two harvesting methods are used: first, the leaves may be stripped from the limbs with little pruning of branches, or second, the small and medium size branches may be removed with leaves intact, after which the leaves are either pulled and bagged in the field, or the limbs are tied in bundles and transported to the shed.

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[7] "Bay Oil Production in Puerto Rico," Federal Experiment Station in Puerto Rico, *U. S. Dept. Agr., Mayaguez, Puerto Rico, Circ.* No. 30 (1948).

7. Bay rum trees have few insects and diseases, all of which are of minor importance.

8. Interval of harvest ranges from twelve to eighteen months, depending upon growing conditions, labor available, still capacity, and market conditions. Bay leaves may yield from 1 to 2 per cent of oil upon distillation, but leaves from occasional trees assay as high as 2.75 to 3.40 per cent. Yields of fresh bay leaves may vary from 10,000 to 30,000 lb. per acre, with an average of around 15,000 lb.

9. Bay oil may be shipped directly to large consuming centers in tins weighing up to 50 lb., or it may be made into bay rum and sold locally, or sent to distant markets.

10. The bay oil industry might undergo some expansion but it should be accompanied by a strong technical research program in finding new uses for the oil, and by an organized and effective advertising program for the products.

Bay Oil Production in Dominica

Producing Regions.—The bay tree flourishes on the windward side of the island (i.e., in the south, east, and parts of the north), at altitudes ranging from sea level to about 2,000 ft. The windward parts of the island are kept humid by the steady trade winds, which carry clouds from the Atlantic. These, in the form of heavy rain and light drizzle, are deposited on the steep and towering volcanic mountain sides, covering the magnificent scenery with tropical vegetation.

Most of the bay trees are cultivated, being planted from seeds and from young wild trees. However, there are also many wild trees growing spontaneously from fallen fruit or from seed dropped by birds. Some of the plantations are quite extensive, others small and scattered widely throughout the windward parts of the island.

Harvest and Distillation.—Collection of the leaves takes place from September to the middle of December, and from January to March, but small quantities of oil are produced all year around. The leaves are harvested by breaking small branches (with attached leaves) off the trees, or by cutting them off with machetes. The collected leaf material is left to dry for a few days near the distillation posts, during which time it loses part of its moisture content and can be distilled more easily.

There are about thirty or forty bay oil distilleries—all of small size—on Dominica. Exact figures are not available because a bay oil distillery requires no operating license.

The stills are, in general, very primitive. The smallest hold 200 to 300 lb. of leaves, the largest from 800 to 2,000 lb. Made of copper or sheeted iron, they are provided with a rough wooden grid above which the leaf material is charged. The stills are heated with open fire, wood from the dense tropical forests of Dominica serving as fuel. The exhausted leaves are much in demand as excellent mulching material for lime trees.

As a rule, the leaves are not triturated prior to distillation, which lasts about 9 hr. for one charge. The yield of oil averages 1 per cent. The distillation waters are used again for the following charge of leaves, after salt or sea water has been added.

The phenol content of the oil depends upon:

1. The condition of the leaf material. Young leaves are claimed to give not only a low yield of oil but also oil of low phenol content. The same is true of leaves containing much moisture, for which reason distillation is stopped during the rainy season (from June to August).
2. The method of distillation. Prolonged distillation gives a correspondingly higher phenol content. Some producers, therefore, distill up to 24 hr. and more. Previous trituration of the leaves would help to shorten the distillation time, but this is seldom done because of the primitive state of the bay oil industry in Dominica, which is mainly in the hands of small native producers.
3. The locality of production. Because of the more frequent rainfall, leaves originating from the higher altitudes contain much moisture and little oil. The altitude also seems to affect the composition of the oil.

In general, the phenol content of bay oil in Dominica ranges from 50 to 60 per cent (from 55 to 60 per cent in better grade oils). It may run as high as 64 per cent, but lots of oil containing such a high percentage are rare, and usually small. Only the few distillers who work very carefully can obtain oils with a phenol content of more than 60 per cent. The majority produce oils containing about 56 per cent of phenols; in order to reach a higher phenol content, these oils are redistilled with a new charge of leaves.

The native producers in the interior sell their small parcels of bay oil in Roseau, the shipping port of Dominica, where the exporters bulk and ship the lots with a guaranteed phenol content, usually assayed by the government chemist in Roseau.

Physicochemical Properties of Bay Oil

The principal constituents of bay oil being phenols (chiefly eugenol, and some chavicol), the quality of an oil is generally evaluated by its phenol content (cf. Vol. I of this work, pp. 291 and 293).

It has been suggested in literature that bay oils with a low phenol content possess as good an odor as those with a high phenol content, and that the phenol content of a bay oil should not, therefore, be taken as a criterion of its quality.[8] In the author's opinion, this view is open to question, since it must be kept in mind that bay oil is employed mainly in bay rum, which owes its medicinal value chiefly to the presence of phenols. The laboratories of Fritzsche Brothers, Inc., New York, have examined natural bay oils, undoubtedly pure, which possessed a phenol content as low as 43.4 per cent. Such oils, in fact any bay oil, with a phenol content lower than 50 per cent should be considered sub-standard. Oils containing 50 to 55 per cent of phenols may be regarded as of good quality; oils containing 55 to 65 per cent of highest quality. Steam distilling imported dried leaf material in efficient stills, Fritzsche Brothers, Inc., obtained bay oils containing as much as 65 per cent phenols. As was pointed out above, the distillers in the West Indian islands are in a position to produce oils with a phenol content of 50 to 60 per cent or even more. A phenol content of higher than 66 per cent is suspicious, and indicates adulteration with clove stem or clove leaf oil.

The specific gravity (at 25°) ranges from 0.950 to 0.990, and depends upon the phenol content of the oil. Exceptions may be attributed to slight variations in the amount of methyl eugenol or methyl chavicol present.

The higher the phenol content, the lower the optical rotation of a bay oil. The refractive index increases with the phenol content of the oil.

So far as the solubility in alcohol is concerned, freshly distilled oils are clearly soluble; but after a short time of standing, particularly under the influence of air and light, the solubility decreases and the oils dissolve in alcohol with opalescence or slight turbidity. This is caused by myrcene (see Vol. II of this work, p. 8), an olefinic terpene, which readily polymerizes in the presence of air and light.

Gildemeister and Hoffmann[9] reported the following properties of bay oil:

Specific Gravity at 15°	0.960 to 0.985; in oils of lower quality as low as 0.951
Optical Rotation	Laevorotatory up to −2°, seldom up to −3°
Refractive Index at 20°	1.506 to 1.520
Phenol Content (Eugenol and Chavicol), Determined with 3% Sodium Hydroxide Solution	57 to 66%; in oils of poor quality as low as 40%
Solubility	Freshly distilled oils are soluble usually in 1 to 2 vol. of 70% alcohol. The solubility decreases rapidly, however, and after a short time the oils, even in 90% alcohol, dissolve clearly only in concentrated solution[10]

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[8] *Perfumery Essential Oil Record* **13** (1922), 12.

[9] "Die Ätherischen Öle," 3d Ed., Vol. III, 271.

[10] Upon further dilution with 90% alcohol, the solution usually becomes cloudy—The author.

Genuine bay oils imported and examined by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 25°/25°	0.957 to 0.988 in oils of best quality. 0.952 to 0.957 in oils of good quality. As low as 0.939 in an oil which contained only 43.4% of phenols. Oils from Dominica often exhibit a lower specific gravity than oils from Puerto Rico, even though their phenol content is high. For example, an oil d_{25} 0.953 contained 55.5 per cent of phenols.
Optical Rotation	−0° 44′ to −2° 56′.
Refractive Index at 20°	1.5075 to 1.5170.
Phenol Content (Eugenol and Chavicol)	55 to 65% in oils of best quality. 50 to 55% in oils of good quality. As low as 43.4% in oils which must be considered substandard
Solubility	Soluble or slightly opalescent in equal volumes of alcohol. Polymerization of myrcene causes the oils to become less soluble with age

The dark color frequently found in direct shipments from the West Indies is due largely to the presence of heavy metals, most of the oils being produced in iron stills. By eliminating the heavy metals according to the usual methods, a considerably lighter color can be obtained.

Adulteration.—Bay oil shipped from the West Indies occasionally contains small quantities of added kerosene or alcohol, the latter being readily obtainable from low-priced rum. Every shipment of oil should therefore be tested for the presence of kerosene and alcohol (cf. Vol. I of this work, pp. 332 and 338).

A much more skillful form of adulteration—and one difficult to detect—consists of the addition of limited quantities of clove stem oil, clove leaf oil, or their terpenic fractions. If cleverly made, such additions cannot readily be detected, and a suspected oil will have to be fractionated, after the phenols have been removed by means of potassium hydroxide solution (cf. Vol. I of this work, pp. 291 and 293). This obviously entails a good deal of work, and the evaluation of the fractions thus obtained requires considerable experience on the part of the analyst.

Careful odor and flavor tests may be of help where analytical means fail.

It should be pointed out that adulteration of the "skillful" type is not practiced on the islands, because the oils and fractions required for the purpose are not readily available in the producing regions.

Terpeneless Bay Oil.—Terpeneless bay oil is prepared by removing the greater part of the terpenes from the regular bay oil, usually by fractional distillation. The removal of myrcene which so easily polymerizes in the regular oils renders these terpeneless oils not only more soluble but also prevents the oils from becoming insoluble with age. They are, therefore, very valuable for the manufacture of bay rum and toilet waters of similar type where good solubility is essential.

Terpeneless bay oils prepared by Fritzsche Brothers, Inc., New York, had properties ranging within these limits:

Specific Gravity at 15°/15°	1.029 to 1.050
Optical Rotation	$-0° 10'$ to $-1° 20'$.
Refractive Index at 20°	1.5271 to 1.5360.
Phenol Content	82 to 95.5%
Solubility at 20°	Soluble in 2 to 2.5 vol. of 60% alcohol, sometimes even in 6 to 6.5 vol of 50% alcohol

Chemical Composition

The chemistry of the volatile oil derived from the leaves of true *Pimenta acris* Wight [11] was investigated by several workers during the latter part of the past century, particularly by Power and Kleber [12] who discovered in this oil myrcene, the first terpene of the olefinic series observed in nature. In a more recent investigation Palkin and Wells [13] arrived at the conclusion (contrary to earlier belief), that the oil contains at least four optically active substances, instead of only one (viz., α-phellandrene), and that three of these four substances are dextrorotatory and one laevorotatory, the latter sufficiently predominant to give a negative rotation to the oil.

The following substances, listed approximately in order of their boiling points, have been identified as constituents of bay leaf oil:

α-Pinene. In accordance with the earlier findings of Mittmann,[14] and contrary to those of Power and Kleber,[15] Palkin and Wells [16] proved the occurrence (in small quantities only) of this terpene in bay oil by preparation of the nitrosochloride m. 104°–105°.

Myrcene. The presence of this olefinic terpene in the fraction b_{20} 67°–68° was first reported by Power and Kleber,[17] and later confirmed by Palkin and Wells [18] who prepared the tetrabromide of dihydromyrcene, m. 88° (recrystallized from absolute alcohol).

α-Phellandrene. Characterized by Power and Kleber [19] through the nitrite reaction. Palkin and Wells [20] prepared the nitrosite m. 104°–105° from the fraction b_{20} 66°–66.2°.

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[11] Now classified as *P. racemosa* (Mill.) J. W. Moore—see the section on "Botany," above.

[12] *Pharm. Rundsch., New York,* **13** (1895), 60.

[13] *J. Am. Chem. Soc.* **55** (1933), 1549, 1556.

[14] *Arch. Pharm.* **227** (1889), 529.

[15] *Pharm. Rundsch., New York,* **13** (1895), 60.

[16] *J. Am. Chem. Soc.* **55** (1933), 1549.

[17] *Pharm. Rundsch., New York,* **13** (1895), 60.

[18] *J. Am. Chem. Soc* **55** (1933), 1553.

[19] *Pharm. Rundsch., New York,* **13** (1895), 60.

[20] *J. Am. Chem. Soc.* **55** (1933), 1554.

Power and Kleber were of the opinion that the phellandrene which occurs in bay oil is responsible for its laevorotation, but Palkin and Wells found phellandrene only in dextrorotatory fractions following the myrcene.

Limonene and Dipentene. These authors also established the presence of limonene and dipentene in oil of bay through their derivatives, viz., limonene nitrosyl chloride m. 103°–104°, and dipentene tetrabromide m. 123°–124°, respectively

Cineole (Eucalyptol). In the course of their work on the chemical composition of true bay leaf oil, Palkin and Wells [21] also isolated cineole and identified this terpenic anhydride through its hydrobromide m. 56°–57°, and its resorcinol compound m. 79°–80°

Methyl Chavicol(?). Investigating the portions of the oil from which the terpenes and phenols had been removed, Power and Kleber [22] observed the methyl ether of chavicol, characterizing it by oxidation to anisic acid, and by conversion into anethole on treatment with alcoholic potassium.

Studying the chemical composition of an oil distilled from the leaves of true *Pimenta acris*, Palkin and Wells [23] did not encounter any anise scented fractions and arrived at the conclusion that this oil contains but little, if any, methyl chavicol (and methyl eugenol—see below). According to Warneford,[24] however, about 15 per cent of methyl chavicol occurs in the anise scented variety of *Pimenta acris.* In the usual harvesting of bay leaves by the natives, an admixture of leaves from the anise scented and lemoncillo varieties is almost unavoidable unless collected under the careful supervision of an expert botanist.[25] In the opinion of Palkin and Wells,[26] it is barely possible that the bay leaves used by Power and Kleber contained appreciable quantities of the anise scented variety, which may account for their findings with regard to these methyl ethers.

Citral. Treating the oil (from which the phenols had been removed) in the usual way with freshly prepared cold concentrated sodium bisulfite solution, these authors isolated citral which was identified through the preparation of the β-naphthylcinchoninic acid compound m. 195° (recrystallized from alcohol).

Chavicol. Treating the phenols (extracted from the oil with alkali solution) with methyl iodide, Power and Kleber [27] obtained a mixture of methyl eugenol and methyl chavicol which indicates that their oil aside from eugenol also contained chavicol. Palkin and Wells [28] later demonstrated that chavicol actually occurs in the oil derived from the leaves of true *Pimenta acris* by isolating the chavicol in the form of a crystalline mass from the fraction b_7 105.4°–114° of the phenol portion of the oil. The chavicol amounted to 10.7 per cent of the phenol fraction.

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[21] *Ibid.*

[22] *Pharm. Rundsch., New York,* **13** (1895), 60.

[23] *J. Am. Chem. Soc.* **55** (1933), 1555.

[24] *Trop. Agr. Trinidad* **4** (1927), 128. *Chem. Abstracts* **22** (1928), 2238.

[25] Compare the section on "Botany," above.

[26] *J. Am. Chem. Soc.* **55** (1933), 1555.

[27] *Pharm. Rundsch., New York,* **13** (1895), 60.

[28] *J. Am. Chem. Soc.* **55** (1933), 1556.

Methyl Eugenol(?). The presence of the methyl ether of eugenol in bay oil was first reported by Mittmann,[29] and confirmed by Power and Kleber.[30] Later, however, when investigating an oil derived from the leaves of true *Pimenta acris*, Palkin and Wells [31] concluded that the oil contained but little, if any, methyl eugenol (see above—methyl chavicol).

Eugenol. This aromatic phenol was first reported as the main constituent of bay oil by Markoe,[32] and later identified by Mittmann,[33] and by Power and Kleber.[34] Using repeated fractional distillation and fractional crystallization, Palkin and Wells [35] isolated eugenol from the phenol portion of true bay leaf oil in a high state of purity. These authors found that the proportion of eugenol in the total phenols of bay oil amounted to 89.3 per cent.

An Alcohol(?). The same workers also noted in the oil a very small quantity of an alcohol with a pleasant geraniol- or nerol-like odor. However, no crystalline phenylurethane or diphenylurethane could be obtained.

According to Schimmel & Co.,[36] the distillation waters of bay leaves contain *methyl alcohol, furfural* and *diacetyl*.

Investigating an oil distilled from the leaves of the anise-scented variety of the bay tree growing in Dominica, B W I. ("Bois d'Inde Anise"—see "Botany," above), the Imperial Institute [37] obtained an oil which had these properties:

Specific Gravity at 15°	0.9968
Optical Rotation	Too dark
Refractive Index at 20°	1.527
Phenol Content	10%
Methoxy Content	17.9%

The oil had a pronounced anise-like odor which masked a by-odor of clove.

The oil was composed chiefly of myrcene, about 15 per cent of methyl chavicol (estragol), about 13 per cent of methyleugenol, and a small quantity of eugenol.

USE OF BAY OIL AND PREPARATION OF BAY RUM

Use.—Owing to its pleasant and spicy odor, oil of bay is used widely in the perfume industry, particularly in bay rum and similar types of toilet waters. Limited quantities of bay oil serve for the flavoring of culinary preparations, chiefly table sauces.

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[29] *Arch. Pharm.* **227** (1889), 529.

[30] *Pharm. Rundsch., New York,* **13** (1895), 60.

[31] *J. Am. Chem. Soc.* **55** (1933), 1549, 1555.

[32] *Proc. Am. Pharm. Assocn.* **25** (1877), 438. *Pharm. J.* [3], **8** (1878), 1005.

[33] *Arch. Pharm.* **227** (1889), 529.

[34] *Pharm. Rundsch., New York,* **13** (1895), 60.

[35] *J. Am. Chem. Soc.* **55** (1933), 1556.

[36] *Ber. Schimmel & Co.,* April (1901), 12.

[37] *Bull. Imp. Inst.* **28** (1930), 8.

Preparation of Bay Rum.—Bay rum is prepared in two ways: (1) by distillation and (2) by mixing bay oil with white rum or alcohol; the former is considered the best. It is prepared by the following method: white rum and bay leaves are placed in a still in the proportion of 1.5 lb. of rum to each pound of green leaves or each ½ lb of dry leaves and enough water is added to cover the leaves. The whole of the distillate is collected, which forms the genuine distilled bay rum of commerce.

The second method of preparing bay rum is as follows: mix 2 gal. of bay oil with about 100 gal. of rum. The bay oil may be blended by the addition of varying quantities of citrus oils (bergamot, lemon, orange, for example) in order to lend refreshing and distinct tonalities to the composition.

A little magnesium is finally added to aid filtration of the solution.

OIL OF CLOVE

Essence de Girofle *Aceite Esencial Clavos* *Nelkenöl*
Oleum Caryophyllorum

Introduction.—The clove of commerce is the hand-picked, unopened, air- or sun-dried flower bud of the clove tree, *Eugenia caryophyllata* Thunb. (= *Caryophyllus aromaticus* L.).

The exact geographical origin of the clove tree is unknown. It is probable, however, that the tree originated in the warm and humid climate of tropical Asia, perhaps in the Moluccas. Here early Portuguese explorers encountered it on the island of Amboyna. Carrying cargoes of precious spices in the holds of bulging galleons, those adventurous navigators and traders unwittingly initiated that fabulous spice trade which caused many a bloody and lengthy sea war from the sixteenth to the beginning of the nineteenth century. The sea battles between Portuguese, Spanish, Hollandish, French, and English men-of-war, the capturing of merchantmen by privateers and pirates, the raiding and burning of plantations on tropical islands held by the enemy, and the stealing of seed form a most fascinating and romantic story.

The Portuguese held the Moluccas for about one hundred years. In 1605, the islands were conquered by the Hollanders, who soon monopolized the spice trade. They destroyed competitive plantations on neighboring islands, sparing only those on Amboyna, whose coasts could be easily guarded against enemy raiders intent on stealing plants and seeds. The Hollanders maintained their monopoly until, in 1769, the great French navigator, Poivre, overcoming innumerable difficulties—including intrigue at the court of France, resistance from his own superiors, and battles on the high seas—finally succeeded in transporting clove plants from the Moluccas to the island of Bourbon (the present Réunion Island) and to Île de France (the present island of Mauritius) where he was governor. Here the plants were greatly multiplied. Shortly afterward, the enterprising British East India Company, in its turn, procured some young clove trees from Mauritius. These were planted on the island of Penang, off the coast of Malacca. In 1818 the Arabs succeeded in introducing some clove seeds into the islands of Zanzibar and Pemba, off the east coast of Africa. The industry became firmly established on the two islands under the rule of the progressive Sultan Seyid Said (1804–1856). Today the British protectorate of Zanzibar (Zanzibar and Pemba Islands) produces and supplies the bulk of commercial cloves; the French island of Madagascar follows in importance.

Commercial clove bud oil is produced almost exclusively from Zanzibar (or Pemba) and Madagascar cloves.

Other, but much less important, clove producing areas are located on the islands of Ceylon and Penang, and in Indonesia (the former Netherlands East Indies), particularly on the Molucca Islands. The cloves grown here, however, are of such excellent quality that they command a high price as spice, and hence are never distilled.

Botany.—The clove tree, *Eugenia caryophyllata* Thunb., is a somewhat columnar-shaped evergreen tree, 30 to 70 ft. high. In general, the trees are somewhat smaller in Zanzibar than in Pemba, where conditions are even more favorable. They grow best in clearings, or on open slopes, and do not thrive well in the shade of other trees.

The buds grow on a main stem, forming clusters comprising 10 to 50 buds (or even more). Appearing first as tiny, pea-green shoots, these ultimately attain a length of three-quarters of an inch. The long calyx then exhibits a delicate pink color, indicating that the buds are ready for harvesting. If left on the tree, the buds change their color to a bright, deep red, and open, whereupon the flowers are pollinated and seed is produced. If left still longer on the tree, the flowers develop into fruit, known locally as "mother of clove." Immature dried buds, which have been picked at too early a stage, or regular clove buds, which have been rained upon during the process of drying, are known as "kokher cloves," a term heard frequently in the industry.

ZANZIBAR AND PEMBA CLOVE OIL

Geography.—Zanzibar is located in the Indian Ocean, six degrees south of the equator, and approximately 25 miles from the east coast of the African continent. The island is about 54 miles long and has an area of 640 square miles. The adjacent island of Pemba, 25 miles to the northeast of Zanzibar, is about 42 miles long and covers 380 square miles. Both islands are favored by a moist and warm tropical climate Rain, however, is somewhat more abundant in hilly Pemba.

The total population of the two islands in 1948 was 264,000, consisting of about 16 per cent Arabs, 6 per cent East Indians, and 76 per cent Africans. There are also about 300 Europeans and 300 Goans living on the two islands. Africans, Arabs, and some Indians cultivate the land; trade and finance is largely in the hands of Indians and a few European firms.

Development.—The seed of the clove tree was first introduced into Zanzibar in 1818. However, systematic plantings were not attempted until about 1830, when Seyid Said, the energetic and enterprising Sultan of Zanzibar, encouraged large-scale expansion of the infant industry. The wide use of cheap slave labor greatly aided the rapid development of Zanzibar's new clove industry, and the island, together with Pemba, became the world's leading producer of the precious spice. Large sections, previously devoted to the growing of coconut and rice, were, in the course of twenty or thirty years, planted with clove trees; finally Zanzibar and Pemba came to supply 80 per cent of the world's clove demand.

In 1872 a devastating cyclone destroyed most of the clove plantings on Zanzibar; those on Pemba, fortunately, were less affected. Within a few years the damage on Zanzibar was repaired, and the "shambas" (clove plantations) were expanded. Since the end of the last century the clove trees in Zanzibar have been known to suffer from a mysterious disease, known locally as "sudden death." It is estimated that on Zanzibar about 70 per cent of the trees have been lost by this disease. Other factors, such as drought, have contributed to the loss of trees—for example, three such periods have been responsible for very heavy losses. During the last drought (in 1946) about 70,000 trees perished. "Sudden death" usually affects the older trees. Steps are being taken to replant in order to keep pace with the losses. The disease occurs also in Pemba, and at the present time (1949) quite a number of small sporadic outbreaks are reported.

Producing Regions.—On Zanzibar, there are wide stretches of unproductive "wanda" land, where shallow soil overlies hard limestone rock; the cultivable land of Zanzibar, therefore, is restricted in large part to the western part of the island. In Pemba, on the other hand, the "wanda" land is confined to the eastern fringe and to the extreme northwest. Although there is much swampland in Pemba, the total area adapted to clove cultivation greatly exceeds that of Zanzibar.

Soil and Climate.—The clove tree grows vigorously in Zanzibar and Pemba, even at the highest elevations (which, however, are only 440 and

310 ft. respectively). The best soil for clove plantations is a well-drained, sandy, or red loam with the proper moisture-retaining capacity. Light loams are better than the stiffer red loams, which harden in dry weather. Poorly drained, marshy, or waterlogged clay soils are quite unsuitable for clove. On good, porous, alluvial land the clove tree grows superbly and produces an abundance of blossoms. (The quality of the spice, however, depends upon a number of other factors, rather than upon the soil.)

The clove tree cannot resist long spells of dry weather and requires a warm, moist, equable climate, with fairly well distributed rainfalls. In general, the tree prefers low altitudes. These fundamental requirements seem to restrict the cultivation of cloves to relatively few localities in the world. The plantings should not be too far from the sea. The fact that the tree generally grows more vigorously in Pemba than in Zanzibar is due in part to the greater abundance of rain in Pemba, and in part to the superior soil and topographic conditions, the numerous hills of Pemba affording well-drained slopes on which the tree flourishes.

Planting and Cultivating.—The plants produced in government nurseries are derived from seed, and the use of self-sown seedlings (a practice recommended formerly) has been discontinued. It has been found that plants raised from seed are hardier than transferred seedlings. A recent government pamphlet[1] recommends the so-called underplanting technique as the best and cheapest way of planting and rearing small clove trees—i.e., planting out the new seedlings under the shade of the old trees when it becomes obvious that the latter are soon to die. The mature trees are not removed even when they die, but left standing for several years, until the seedlings have become well established. The seedlings are planted out between the rows of the old trees. When these die and dry up, the seedlings grow quickly and strongly because of the shade of the old trees, which diminishes each year. The new generation will have come into bearing by the time the above-mentioned "sudden death" has run its course, and the old trees have ceased to be profitable. Old dead trees should never be cut down, because white ants will be attracted to the fragments of wood which remain, and because certain light-loving weeds will flourish abundantly.

The seedlings should be planted on a wet day, cultivated periodically, and the ring cultivation should be covered with dry clove leaves. Extreme care has to be exercised in transplanting, to prevent drying of the roots. The seedlings can survive in the shade for some time, but they are very sensitive to drought. After about one year in the nursery, the young plants are sufficiently strong to be planted out. Resetting in the regular plantations takes place during the coolest and rainiest period of the year. The soil around the

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[1] "Regeneration of Clove Plantations," *Dept. Agr., Zanzibar* (1946).

young trees requires ventilation and abundant moisture, and irrigation must be employed. This is expensive, and accounts for much of the total cost of cultivation.

The planting of thousands of young clove trees involves a great deal of labor. In the old slave days, when a new clove plantation was being started, cassava was used as a shade crop, its root serving as a staple food for the Negro slaves. Today, cassava is still being employed for shading.

When given proper care, the young trees reach the bearing stage five years after transplanting; if they are neglected, however, they may take eight to ten years to produce a worth-while crop. On prosperous plantations the soil is regularly hoed and aerated.

The yield of cloves per tree depends largely upon the shape of the tree itself, which for maximum efficiency should have a round, bushy crown of medium height, and a luxuriant foliage reaching down as low as possible. The large surface of such a tree greatly facilitates the harvest. If too crowded, the trees are apt to develop long ascending branches with a relatively sparse foliage. The inaccessibility of the crown of such trees makes harvesting difficult, and many of the clove buds may be lost. In Zanzibar the trees are usually planted in areas 21 ft. by 21 ft., which means that there are about 103 trees per acre. However, this amount of space is too generous in the early stages of the trees' growth (unless catch crops are grown), and is insufficient when the trees have passed the age of thirty. Troup[2] has suggested a spacing of 15 ft. by 15 ft., or 194 trees per acre. When this scheme is employed the weaker trees should be cut down as soon as the side branches meet, so that, in the thinned plantation, the remaining trees occupy sections of 30 ft. by 30 ft. (48 trees per acre).

After the eighth year, the clove tree begins to yield appreciable revenue; productivity increases with the development of the tree. It is difficult to determine the age at which a tree reaches its maximum yield. Some clove trees are known to be of great age, but in the absence of early records in Zanzibar and Pemba exact data are not readily available. The average span of productivity seems to be about sixty years, but trees one hundred years old are found whose productivity has remained undiminished. Such cases are more frequent among isolated trees than among trees on plantations.

A few words should be said about the practice of tree topping. Picking of the buds is easy up to a height of about 10 ft., and topping of the taller trees would seem to facilitate the harvest. Such harsh treatment, however, is apt to unbalance the tree in its normal development and to induce an abundant growth of leaves, to the detriment of the floral organs.

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[2] "Report on Clove Cultivation in the Zanzibar Protectorate," published by the Government of Zanzibar (1932).

Diseases.—The clove tree is affected by two major diseases, one the so-called "die-back," the cause of which has not yet been discovered. It takes the form of a gradual desiccation of the whole upper part of the tree. "Die-back" often occurs in trees planted on marginal soils or in places heavily interplanted with coconuts. The origin of the other disease—the so-called "sudden death"—is still a mystery which engages the full attention of the government. A Clove Research Department, financed chiefly by the British Government, and to a lesser extent by the Clove Growers Association in Zanzibar, has been organized to determine the nature of this blight. Such research is of major importance, owing to the spread of the disease, particularly on Zanzibar Island. Whole plantations have perished, and with them the income of the owners has vanished. To combat the disease, regeneration of trees is carried out steadily from year to year, as the disease does not normally appear to affect young trees. It seems that the trouble is caused by a virus, but no positive proof has yet been offered. There is hope that in Pemba the centers of infection (which are much smaller than in Zanzibar) may be controlled by strict isolation.

Economic Situation.—In the early days of Zanzibar's clove industry, plantations were relatively few in number, but large in extent. They were owned by wealthy Arabs, who operated their shambas with the help of abundant and low-priced slave labor, Zanzibar then being a great slave trading center. This condition, so favorable to the owners, prevailed until slavery was abolished shortly before the turn of the century. Abolition of slavery produced fundamental changes in Zanzibar's clove industry. Today most of Zanzibar's and Pemba's larger clove shambas are still owned by Arabs, but numerous smaller ones are owned by Africans (the latter term comprising Negro immigrants from Africa, descendants of Negro slaves, etc.). The African, and even the average Arab, is fundamentally a tiller of the soil, and illiterate. His education consists mainly in memorizing passages of the Koran; of the rudiments of accountancy and commerce he has little knowledge. Attracted by the splendid opportunities which the trade in cloves offered during the last century, a considerable number of East Indians arrived in Zanzibar and settled on the island as dealers and exporters. It is not at all surprising that these Indians, with generations of experience in spice trading behind them, and with their keen business instinct, soon dominated Zanzibar's clove industry. Fortunes were made, often at the cost of the Arabian shamba owners. From Zanzibar the power of the new Indian financiers spread all over the east coast of Africa. Arabian and African landowners finally became so heavily obligated to the Indian money lenders that the government was forced to adopt measures to protect the native growers.

In 1940–1941 the government, with the intention of relieving the Arab and

African owners of the weight of accumulated debt upon their properties, instituted a Debt Settlement Scheme, by the terms of which their indebtedness to Indians and others was paid by the government in cases where security value, measured in accordance with a decree, sufficed to cover the debts. The government then assumed the position of mortgagee, and collected the debts at a reasonable and fixed rate of interest over a period of years. This scheme, so far as collection of the indebtedness is concerned, has not yet been completed. Some complication may be introduced by the loss in value of many plantations in Zanzibar due to "sudden death." Along with the legislation enacted to cover this Relief of Agricultural Indebtedness, other legislation was enacted under which the alienation of land by an Arab or African was prohibited, except by permit of a Land Alienation Board. Furthermore, the attachment of land for payment of debt was prohibited, except under certain circumstances.

Prior to the enactment of this legislation many of the large plantations were broken up by the Islamitic laws of succession which require that the land of a deceased person must be divided among his sons or heirs.[3] The practice of selling and dividing bankrupt properties into smaller ones, too, brought about much subdivision of estates, especially because the Indian money lenders in general have no liking for actually operating the plantations. As a result of this development, there exist now more than 30,000 clove plantings of all sizes, from a dozen to several thousand trees. It is estimated that at least 50 per cent of all clove trees are in the hands of small owners. There remain, however, a few large and prosperous shambas owned and operated by Arabs, which fact proves that large plantations are still remunerative, provided of course that they are properly managed and worked according to modern principles of tropical agriculture. The government is anxious to extend every possible assistance to those proprietors who are willing to cooperate and take advantage of the government's advice in regard to proper methods of growing, cultivating and harvesting.

The small shambas will probably continue to play an important role in Zanzibar's clove industry, even if other, less specialized, crops are grown along with cloves. The small planter is not forced to spend part of his income for the amortization of capital investment, nor (unless he is in debt) for the payment of interest. He is not troubled with labor problems, as he and his family do all the work. Since he does not count his and his family's labor, his crop means an almost clear profit. He can devote to his small planting much more care than a large operator, and from time to time he plants a few new trees to keep up his shamba. For these reasons, the smaller plantings generally appear less neglected than many of the larger ones.

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[3] This system still prevails.

Since the buds on the trees do not all reach the harvesting stage at the same time, they must be picked at intervals. The irregular maturation of the buds makes harvesting on the large estates difficult and, since there is a shortage of labor, much of the crop remains on the trees. Moreover, the buds on very tall trees can hardly be reached. The small owner, on the other hand, can go through his shamba every day and, with the help of his family, gather practically his entire crop. It is possible, therefore, that the small shamba may be the solution to Zanzibar's and Pemba's pressing labor shortage.

Aside from the numerous privately owned properties, there exist in Zanzibar and Pemba a few government-owned plantings, all in excellent shape, and serving as models to the native growers. Here, the trees are planted in areas of 21 ft. by 21 ft., and not topped. In recent years the number of the government plantations has been reduced considerably, but the number of nurseries for seedlings—in many cases issued free, in others at a nominal charge—has been increased. The Clove Growers Association has provided funds for some of these nurseries, which help in the regeneration of shambas owned by individuals. In addition, extensive research work is being carried out at the Government Agricultural Experiment Station in Zanzibar.

The clove plantations in Zanzibar comprise a total area of about 16,000 acres, or 4 per cent of the total surface of the island. In Pemba they cover about 32,000 acres or 15 per cent of the island. Prior to the onslaught of "sudden death," the total number of clove trees on both islands amounted to approximately 4,000,000.

Harvest.—The flower buds, which are borne in small bunches on the tips of the twigs, begin to appear in January/February; in July they turn from green to reddish, an indication that they are ready to be harvested. During August new buds appear on the branches. These can be harvested in December and January. There are thus two yearly crops: one, the so-called "Mwaka" crop (July through October), and the other (less important), the so-called "Mvuli" crop, which is harvested after an interval of several weeks. Under favorable conditions the annual period of harvest lasts from six to seven months, with a short interruption in October/November. It should be pointed out, however, that in general the clove tree produces crops quite irregularly. In the course of three years there is usually a bumper crop, a half crop, and a very small crop.

It is very important to pick the buds at the right stage, i.e., when their heads develop a pinkish color. If gathered too early, the cloves will be wrinkled and will contain less eugenol; if collected a few days too late, the flowers will turn deep red and will bloom out. If picked a day after the stamens appear, the buds on drying will lose their corolla and male parts and yield cloves without heads. Five or six days after blooming the fecundated ovary grows in size, the calyx swells, and the clove becomes worthless. Hence the total crop cannot be gathered all at once without losing a considerable part of it.

Every single bud has to be hand-picked. The worker must know just which clusters are ready for picking, and which must be left on the tree for further development. Premature collection of the buds, carelessness in plucking the clusters at the base, and excessive breakage of twigs may heavily damage the following crop. Women and children gather buds mainly from the lower branches; the men climb into the trees and, pulling the higher and farther twigs toward them with the help of hooked staffs, collect the less accessible clusters. On tall trees the harvest is always incomplete because the upper branches are too frail to permit the men to stand on them. Strange as it may seem, in Zanzibar ladders are not used for the harvesting of clove buds. Large ants ("maji ya moto"), ferocious and hard-biting, sometimes prevent the pickers from staying in the trees for any length of time.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 29. Clove production in Zanzibar. Native separating clove buds and clove stems prior to drying.

When the day's crop has been collected, the natives, squatting around mats made of coconut fiber, remove the buds from the stems by holding a cluster in one hand and brushing it against the palm of the other hand. The buds are heaped on one side, the stems on the other side. This task completed, each worker carries his crop to the shed of his foreman, who measures the day's output in a "pishi," a brass vessel holding 4 lb. A good worker can collect daily up to twenty pishis of clove buds, his remuneration ranging from 0.2 to 0.25 shillings per pishi. The wage rates vary and depend upon the abundance of the crop, the labor available during the season, and other factors. The shamba owner permits his workers to erect simple huts on his property and furnishes them with food. Seasonal workers and their families usually stay for the entire harvest unless higher wages lure them to other plantations.

Labor Situation.—In Zanzibar and Pemba labor has become a serious problem. Prior to World War II it was customary to bring thousands of natives from the adjacent African coast, to gather the crop as rapidly as possible. This is no longer possible, because the labor shortage in Tanganyika itself has become very serious as a result of increased agricultural and mining activities in that territory. Some laborers still come from Tanganyika to do weeding work in the shambas, but few can be induced to do the harvesting.

The availability of labor greatly influences the size of the harvest and the cost of production. Under present conditions, a considerable amount of the crop remains on the trees. In an unfavorable market, cost of labor may result in actual loss. The demand for labor for harvesting is occasionally so great that the owners of large shambas compete with each other in offering wages, or resort to labor piracy, even when the prospective market for their products does not look favorable.

The Clove Growers Association grants advances to growers at harvesting time, to enable them to hire pickers and to start work. The Association also advances funds for the work of weeding shambas. Loans for both purposes are secured upon the future crop.

Average Yield of Cloves per Tree.—The yield of (dried) cloves per tree depends upon the age, size, form, and condition of the tree, and it is difficult to establish even an approximate figure. In 1928–1929 the yield was less than 1 lb. of (dried) cloves per tree, whereas in the bumper year of 1923 the yield was 6 lb. in Zanzibar and 7 lb. in Pemba. It is probably safe to estimate the yearly average yield as 6 lb. per tree.

Size and Quality of the Crop.—The size and quality of the clove crop show cyclic variation. According to government statistics, a bumper crop can be expected once every 2⅓ years, a poor crop once every 2⅝ years, and a medium crop once every 5¼ years. The record crop was obtained in 1937–1938 with 1,355,916 frasilas (1 frasila = 35 lb.).

Drying.—After separation from their stems, the buds must be dried, for which purpose well-equipped plantations employ concrete platforms ("sakafus"), whereas the small shambas employ mats made of grass or palm leaves. The buds are spread in thin layers upon these platforms or mats and are turned over at intervals. In good weather, they dry within four or five days. The stems change in color to a deep brown, the heads to a light brown. The abundant rainfall in Zanzibar and Pemba often interferes with drying in the open air, and attempts have been made to use furnaces (such as serve for the drying of copra) for artificial drying of cloves. The heat circulating in the furnace shortens the drying time to two days, but a substantial part of the essential (volatile) oil is lost. This method of drying has thus proved impractical.

Drying in the open air should be as short as possible, but sufficiently long to assure preservation of the spice. If rain interferes with sun-drying, the operation must be continued under a shed which, of course, requires more time. If rained upon, the cloves will be darker and of inferior quality, and a good deal of essential oil will be lost. Such cloves are called "kokher" cloves. High-quality cloves should be smooth, shiny, and of reddish-brown color, with a slightly lighter head.

On drying, the freshly picked buds lose 67 per cent of weight; in other words, the weight of dry cloves is only about one-third that of the fresh buds. To be more exact: 3.1 to 3.5 kg. of freshly picked buds yield 1 kg. of dry cloves. Twenty-eight pishis of fresh buds on the average yield 35 lb. of dried cloves.

The stems lose about the same percentage of moisture on drying. Whereas the buds are dried immediately after separation from the stems, the latter are usually left in heaps and dried toward the end of the harvest by spreading on concrete floors or mats. The stems do not require the same meticulous care in handling as the buds, which are much more valuable. It should be noted, however, that in recent years the quality of the dried stems has been improved considerably, and their value has risen.

Middlemen and Marketing.—Drying completed, the cloves are packed in 200 lb. bags and sold at auction—one of the most picturesque functions a visitor to the islands could possibly attend. After the auction the local buyers, largely Indian dealers, grade the cloves and repack them in the well-known "gonjes" (mats) for export all over the world. This sort of packing protects the spice against infiltration of moisture. The matting used in Zanzibar and Pemba comes chiefly from Lamu, on the neighboring African coast. (Exporters in Madagascar use jute bags.)

At one time the market of Malindi, near the port of Zanzibar, offered all the different qualities of clove demanded by various importing countries, each of which insisted upon certain specifications. Bombay, for instance, has always demanded a very high quality (for use in religious ceremonies). Egypt and certain Mediterranean countries have accepted shipments containing considerable waste, because the merchandise is often reshipped to Indonesia for the flavoring of cigarettes.

Today all cloves must pass through local public markets established at three centers in Pemba and one in Zanzibar. All cloves passing through these local markets are required to meet the standards established by law. Moisture must not exceed 16 per cent, extraneous matters 5 per cent. The percentage of khoker cloves varies according to grade. Cloves may be sold or stored only after they have been "passed"; otherwise they must be removed for further drying or conditioning. "Passing" upon the spice does not constitute grading it; it means only that it meets basic legal standards. If the Clove Growers Association buys the cloves, they are graded and go to buying depots of the Association, where they are purchased by grade and at prices established in advance for the ensuing twelve months. On the public market the cloves are bought by local dealers at the prevailing market price (if it is above the Association's price). They are then graded for export by the licensed dealer concerned, who to export must hold an exporter's license. The export grades (see below) are defined by law; and the spice must be examined by a government inspector at the time of export. The cloves are handled locally in branded bags provided by the Clove Growers Association from funds derived from an export levy.

Clove Markets.—Listed according to importance, the buying markets of cloves (in normal times) are: Indonesia,[4] India, the United States,[5] the United Kingdom and continental Europe. Indonesia (formerly the Netherlands East Indies) which uses the spice principally for the flavoring of cigarettes, imports its supply either directly from Zanzibar or via Bombay and Singapore. Bombay and Calcutta are the centers of the clove trade in India. The United States, third largest consumer of cloves, employs them chiefly as a spice; a small percentage is distilled. Europe imports cloves either for use as spice or for distillation of the oil. A small quantity, particularly waste matter in the form of distilled cloves, is re-exported to India.

Thus, the bulk of the total clove production is consumed as spice, the balance being used (in Indonesia) for the flavoring of cigarettes, and (in Europe and in the United States) for the distillation of clove oil—of which a part, in turn, is converted into vanillin.

Although the clove tree flourishes on almost all of the Indonesian Islands, only insignificant quantities of the spice have so far been produced there, because other crops are more remunerative.

Total Clove Production.—In order of importance, the principal clove producing regions are: the British Protectorate of Pemba and Zanzibar; Madagascar; the island of Amboyna in the Moluccas; and the island of Penang in Malaya (this last produces a very fine quality of cloves). Of these regions, Pemba and Zanzibar are the most important producers, with the

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[4] Prior to World War II, Java alone consumed from 4,000 to 4,500 tons of cloves yearly.

[5] At the time of this writing (1949) the United States is importing the cloves chiefly from Madagascar.

French island of Madagascar following closely and gaining in importance. Amboyna and Penang supply small quantities only.

Prior to World War II, the production of cloves in the British Protectorate of Zanzibar and Pemba was on the average 9,500 tons per year, Zanzibar supplying about one-third and Pemba two-thirds. As a result of the tree disease discussed previously, Zanzibar's clove plantations have been seriously damaged and the island now produces only about one-fifth of the Protectorate's clove output. The world's total annual consumption (in normal times) is estimated at about 12,000 tons, which means that Zanzibar and Pemba, in normal times, supply about 80 per cent of the world's demand. However, should the Zanzibar plant disease spread to the neighboring island of Pemba, the seat of clove production may well change once more. As Bartlett[6] has pointed out, the effect of reduced and lost clove production in Zanzibar cannot as yet be accurately assessed. Fortunately, because of the large-scale planting of young trees the overall position of both islands does not show any marked reduction in cropping on a cyclic consideration. In fact, as late as 1946–1947 almost 1,100,000 frasilas were produced (Williams[7]).

The Zanzibar Clove Growers Association.—Space does not permit delving into the history and the statutes of the Clove Growers Association in Zanzibar and Pemba which has benefited the Protectorate immensely. An industry which, although very speculative, has brought wealth to the islands and upon which so much of its prosperity depends, must be protected by the government so that it may continue to function for the benefit of the entire population.

As far back as 1896 the government of Zanzibar recognized the advisability of establishing a clove monopoly, but it was not until 1927 that the first Clove Growers Association was created as a subdivision of the Department of Agriculture. It did not function successfully, however, until June 1934 when the present Clove Growers Association was founded. The objects of the Clove Growers Association are to foster the production and marketing of the agricultural products of the Protectorate, and to encourage the spirit and practice of thrift, cooperation, and self-help among the producers.

A most important function of the Clove Growers Association is the establishment of guaranteed minimum purchasing prices, which the Association offers for cloves of various grades on the local market. The substantial stocks of cloves that the Association has held for many years have undoubtedly had a most beneficial stabilizing effect in home and overseas markets.

During the first years of its existence, the Association aimed clearly at

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[6] *Flavours* **10**, No. 3 (1947), 17.

[7] Private communication of Mr. R. O. Williams, General Manager, Clove Growers Association, Zanzibar (March 1949).

obtaining complete control of the industry through purchasing and selling until it could ultimately acquire the entire crop directly from the producers and sell directly to the merchants or consumers abroad. The Association claims that actually there exists no excess production over the world's requirements for a period of years and, therefore, the real problem is the elimination of violent fluctuations in annual production and prices, by carrying over the surplus of one year until in ensuing years supplies adjust themselves by short crops; in other words prices should be stabilized by regular supplies. In its efforts toward this end, the Association was publicly supported by the government of Zanzibar, and by 1938 it had practically attained its long desired goal. The Association thereby became the trustee of Zanzibar's and Pemba's clove industry, acting and operating solely in this capacity.

It has been the practice for many years to maintain a margin of s. 7/- per hundred pounds of cloves, between buying and selling prices, to cover costs of administration, handling, storage, shrinkage, etc. The clove crop passes directly to the Association, and is sold to local exporting houses for export abroad. This system of centralized buying and selling minimizes price fluctuations and limits speculative manipulations. The Association sees to it that growers find just remuneration not through speculation but through regularity of prices. Also a more direct commercial relationship between producers and consumers has been brought about by the elimination of a number of middlemen whose services were uneconomical and unnecessary.

Indian Middlemen.—Desirable as the activities of the Clove Growers Association may be to producers and consumers alike, it was widely criticized and attacked at that time, particularly by the Indian financiers, exporters, and middlemen in Zanzibar, and through their influence, by the Indian National Assembly in Calcutta. The Indian speculators operating in Zanzibar were variously affected by the monopoly of the Clove Growers Association whose real aim was the elimination of these speculators from this industry. The Indian traders objected chiefly to the decree of 1934, according to which, first, cloves could not be exported except by licensed (reliable) exporters who had to pay a considerable yearly fee, and, second, the licensing authority should be the Association which, incidentally, was at that time a competing licensed exporter. As a result, the Indian dealers in Bombay and Calcutta declared a boycott on Zanzibar cloves and purchased the Madagascar spice. At the same time, the Indian National Assembly protested through the Indian Office in London and, since India has always been a very important buyer of the highest and most expensive grades of Zanzibar and Pemba cloves, the situation became rather critical for the Protectorate.

The present statutory position of the Association is as follows:

By law, each year on July 1st the Association must publish the prices (stated according to grade of the spice) at which it is bound to buy cloves during the ensuing season. There are certain provisions allowing for amendments during the course of the year, but they all aim at seasonal stability. No producer is bound to sell to the Association but may sell on the open market, and obviously would do so if that price were higher than the price offered by the Association. At the same time, the law specifies that each licensed exporter must buy, from the Association, a certain proportion of each export he wishes to make. This proportion was originally fixed at 50 per cent. Here again the law aims at a fair and stable return to the growers, and at steady prices on the buying markets overseas. This object has been achieved over a period of years, and throughout World War II Zanzibar continued to supply cloves to all markets in a position to buy, and did so without the violent fluctuations and rising prices which generally prevailed in the spice markets. (As far as the United States is concerned, imports of cloves rose during the war, but, since the end of hostilities, United States importers have chosen to buy from Madagascar at cut rates and have bought nothing from Zanzibar for many months.) At present (1949) the law of Zanzibar obliges the exporters to purchase 15 lb. of cloves from the Association for every 100 lb. exported.

Future Outlook.—Although the ravages caused by "sudden death," particularly on the island of Zanzibar, cannot be ignored, there is no reason for an unduly gloomy outlook, taking the Protectorate as a whole. The bright features of the situation are:

1. A large number of young trees have been planted during the past twenty years. This practice resulted in the maintenance of yields at a high level.
2. Energetic action has been taken by the British and Zanzibar Governments in the field of research to determine the cause of the disease and any remedy or control which may be applied.
3. At present only part of the crop borne on the trees is harvested. The total annual crop can be increased appreciably by improving methods of harvesting.
4. A network of excellent motor roads constructed by the government permits rapid movement of labor during the harvest, and lowers cost of transport of the picked cloves to port.
5. The Protectorate's population has been increasing, as a result of sanitary measures, and more agricultural labor is becoming available.

Grading of the Cloves.—According to the Agricultural Produce Export Decree of July 6, 1934, and the Clove Export Rules of 1939, Zanzibar and Pemba cloves are graded and shipped as follows:

Special Grade: Good, sound cloves which are whole, bright, bold, uniform, regular, free from mustiness, and which contain not more than—

3% of stems, "mother of cloves" and foreign superfluous or inferior matter,
2% of Kokher cloves,
16% of moisture.

Each clove is hand selected. The quantity of this grade, however, is small and usually sold with No. 1 Grade. India uses this quality mainly for religious ceremonies.

No. 1 Grade: Good, sound cloves which are bold, reasonably regular, free from mustiness, and which contain not more than—

5% of stems, "mother of cloves" and foreign superfluous or inferior matter,
3% of Kokher cloves,
16% of moisture.

Here, too, the entire production goes to India; this is a quality which has hardly, if ever, been sold in the United States.

No. 2 Grade: Cloves which are free from mustiness, and which contain not more than—

5% of stems, "mother of cloves" and foreign superfluous or inferior matter,
7% of Kokher cloves,
16% of moisture.

This quality is the one sold in the United States as spice and for grinding purposes.

No. 3 Grade: Cloves which contain not more than—

5% of stems, "mother of cloves" and foreign superfluous or inferior matter,
20% of Kokher cloves,
16% of moisture.

There is very little difference between Grade No. 2 and No. 3. So far as distillation is concerned, however, the No. 3 Grade seems preferable because the cloves of this quality are very much harder and drier, producing no gumming and packing in the stills. During the drying process, the material has sometimes been rained upon, and the gummy and resinous matter has been bleached out. For this reason, No. 1 and No. 2 Grades are not very well suited for distilling purposes. The No. 3 quality is now well standardized by careful selection and blending.

Rain-damaged, discolored, or withered and shriveled cloves fallen from trees are known as kokher cloves. "Mother of cloves" is the ovary containing the seed which is formed after the bud has fully blossomed, and the stamen and style have fallen off. "Mother cloves" contain considerable starch and are of inferior flavor.

Clove stems may not be exported from the Protectorate; they are used in Zanzibar for the distillation of clove stem oil (see below).

Assay of the Oil Content.—The content of volatile oil in the spice can be determined by several methods, among them the well-known Clevenger method; or by trial distillation in a pilot still, details of which will be found in Vol. I, pp. 157 and 317. Raymond[8] suggested a simple apparatus for the estimation of essential oil in cloves and other spices. His apparatus permits experimental distillation with boiling water or with low-pressure steam, with or without cohobation. It holds 500 to 1,000 g. of spice or ground leaves and thus yields a quantity of oil sufficient for routine analysis. Figures for the yield of oil obtained with the use of Raymond's apparatus agree well with those for oils produced with large-scale industrial apparatus.

In modern stills and with proper precautions, distillation of Zanzibar or Pemba cloves yields, on the average, 17 per cent of oil. This, incidentally, is the basis on which Zanzibar and Pemba cloves are sold for distillation purposes. In the usual commercial production, however, the yield of dried oil from buds is not higher than 15.5 per cent.[9]

Assay of the Moisture Content.—Cloves should not contain more than 16 per cent of moisture. Several methods have been suggested for the determination of the water content of the spice.

In the method of Brown-Duvel,[10] a weighed quantity of cloves together with lubricating oil (flash point not lower than 200° C.) is placed into a still and heated to 190° C. The water, which gradually distills over, is collected and measured in a graduated cylinder. The method is exact, but requires several hours.

Another method, equally exact, but requiring only 45 min., has been suggested by May.[11] Fifty grams of cloves and 100 g. of kerosene (b. 165°–195°, d 0.8135) are placed in a still of the type described in Vol. I of this work, p. 325. The water and kerosene vapors are condensed in the reflux condenser. The condensed water accumulates, and is measured, in the graduated part of the still head, while the excess kerosene flows back into the distilling flask.

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[8] *Perfumery Essential Oil Record* **27** (1936), 393.

[9] Private communication of Mr. R. O. Williams, General Manager, Clove Growers Association, Zanzibar (1949).

[10] *Perfumery Essential Oil Record* **17** (1926), 7.

[11] Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 281.

Zanzibar Oil of Clove Stems.—As was explained in the section describing the harvest and drying of the clove buds, the stems removed from the buds are also dried, but not exported from Zanzibar. They serve for the distillation of the so-called clove stem oil which has an odor less pleasant than that of the bud oil, and therefore is not suitable in flavor or perfume compositions. The stem oil, however, contains a high percentage of (free) eugenol and, therefore, represents an excellent starting material for the isolation of eugenol which, in turn, can be converted into isoeugenol and vanillin.

There exists only one clove distillery in Zanzibar (in Malindi); it is owned and operated by the Clove Growers Association for the special purpose of utilizing a valuable product and preventing the export of clove stems, which could be used abroad to adulterate the ground spice (dried buds). The stems are occasionally distilled together with dried buds to produce a high grade of so-called "Vanillin" clove oil. The operation of the Association in connection with the distillery in Malindi has thus raised the position of the stems to a standard product of good quality. Like the dried buds, it is bought in the Protectorate under strict grading rules. At the same time, this distillery has been conducted entirely by African labor under European supervision, and wage rates as well as the standard of living of the Africans employed have risen. Full medical services are provided, a provident fund operates, and all labor is adequately nourished. The Zanzibar clove stem oil is now certified by the government chemist, and has achieved a world-wide reputation as a good, well-packed standard product. Zanzibar has exported the following quantities of this type of clove oil in the course of the past years, the seasonal year ending on June 30th:

	Pounds[12]
1941	429,546
1942	427,732
1943	292,287
1944	362,955
1945	438,605
1946	565,046
1947	433,538
1948	260,925

All oil was distilled in Zanzibar and exported under exclusive license held by the Clove Growers Association.

In commercial distillation (in Malindi) the yield of oil from the stems does not exceed 5.5 per cent.

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[12] Figures by courtesy of Mr. R. O. Williams, General Manager, Clove Growers Association, Zanzibar (1949).

Madagascar Clove Oil

During the first part of the last century, the clove tree was introduced, from Réunion Island, to Sainte-Marie, a small island located close to the northeast coast of Madagascar. The first clove plantings on the east coast of Madagascar proper were started about 1900.

Botany.—In Madagascar (including Sainte-Marie) the clove tree occurs as only one species, *Eugenia caryophyllata* Thunb. (*Caryophyllus aromaticus* L.). Several planters have observed that at each harvest certain trees give a much greater yield, or grow larger cloves than the other trees, which might be interpreted as indicating the existence of several clove varieties. However, when seed was taken from these heavy bearing trees and planted out, the seedlings developed into regular clove trees, which had none of the high yielding qualities of the parent trees, nor did they bear cloves larger than the average size.

Soil Conditions.—In Madagascar the clove tree grows in various soils—slightly sandy, clayey, laterite, and alluvial, provided none is wet. The region of Saonierana Ivongo, however, offers the most suitable soil, its lower slopes consisting of loose laterite. The subsoil there contains decomposed basalts, into which the roots of the clove tree penetrate. On hillsides of compact laterite, clove trees grow slowly and never attain full development. Sandy soils, as well as black, young volcanic soils, are not very suitable.

The clove tree is fragile and easily damaged by cyclones, for which reason it should be planted in protected localities. Since Madagascar's east coast is very hilly, the clove plantations are laid out on hillsides which are less exposed to cyclones.

Conditions differ somewhat on the adjacent island of Sainte-Marie. The soil there is generally rather poor as a result of abusive deforestation, which laid bare the laterite. The clove plantations extend mainly along the western slopes, which are protected from strong winds. On the laterite slopes descending to the sea, the dark red clay soil is quite compact, but the water drains off sufficiently. However, it is really the very favorable climate of this section which enables the clove trees to flourish.

Climatic Conditions.—Since the clove tree requires an atmosphere of tropical humidity, it cannot be cultivated profitably on Madagascar's western coast, where, at certain times of the year, the climate is too dry. Nor are the regions of Diego Suarez in the north, or those of Fort-Dauphin in the south, suitable for growing the tree, because these sections are too exposed to strong winds. The warm and moist sea breezes prevailing on Madagascar's east coast and on Sainte-Marie favor development of the tree and ample growth of the flowers.

The small island of Sainte-Marie is only about 25 miles away from the Saonierana Ivongo region of Madagascar proper. Nevertheless, the rainfall, temperature, and humidity of Sainte-Marie are decidedly more favorable for the clove tree, with the result that the harvest there begins about four weeks earlier than it does in Saonierana Ivongo.

Producing Regions.—Madagascar's clove industry had its beginning on the western coast of the island of Sainte-Marie, which faces Madagascar. Clove trees literally cover the lower slopes and valleys of this small island. On Madagascar proper, the main clove producing region extends from Mahanoro in the south to Maroantsetra in the north. The center of the industry is the district of Saonierana Ivongo, where climatic and soil conditions are excellent.

The clove producing areas of Madagascar are rather small in relation to the size of the island, yet quite extensive when compared with the total areas planted on the islands of Zanzibar and Pemba. It is estimated that there are about 5,000,000 clove trees in Madagascar, of which 4,000,000 grow in the Saonierana Ivongo region.

Altitude.—In Madagascar one encounters plantations at altitudes varying from sea level up to 600 m., but since the clove tree prefers the neighborhood of the sea or the lower hillsides, the most suitable altitudes are those below 200 m. At elevations above 500 m. the tree is apt to become stunted.

Diseases.—"Sudden death," or "apoplexy" as it is called locally, appears less frequently in Madagascar than in Zanzibar, but "die-back" is becoming more common, especially in regions where the soil is being depleted by leaf sweeping and neglect of cultivation.

Planting.—The clove tree of Madagascar is one of extraordinary virility, and, in contrast to Zanzibar and Pemba (where clove trees are carefully cultivated), it grows there under semiwild conditions. The planting is done in a rather primitive way. Lines are cleared through the bush and holes dug for the planting of clove seedlings. In some cases these seedlings may have been raised in a nursery bed, but usually they are self-sown seedlings, carefully removed from beneath the old trees. At the time of transplanting they are usually eighteen months or two years old. The distance between the holes ranges from 4 to 8 m., but 8 m. distance triangularly would be advisable; otherwise, on reaching the age of twenty years, the branches of neighboring trees may meet and interlace.

The fruit or "mother clove" is surrounded by a pulpy mass, which when fully mature has a deep red color. It is advisable to use very ripe fruit, which has recently fallen to the ground, and whose pulp is fresh and not yet wrinkled, because the germinating faculty diminishes after one month. When collecting fruit from trees, the pickers often gather premature fruit, which has not yet developed full germinating power. One kilogram contains about 350 to 370 "mother cloves."

The seed is sown in nursery beds, on plots 1.20 m. wide, in which little furrows, 1 to 2 cm. deep and 25 cm. (or, better, 30 cm.) apart, have been made. The seed is then covered with a light layer of earth or sand, if the nursery soil is clayey. Sometimes it is also covered with straw, especially if the soil is heavy. A shade is erected about 70 cm. above the ground. Germination is slow; it starts only about the fifth week after sowing, and requires from one to two months. Some planters prefer to sow in baskets of wire netting imbedded into the nursery soil. At the time of final transplanting, these baskets can be lifted out without damaging the young plants.

The planting out is usually done during the height of the rainy season, when the plants are from eighteen months to two years old, and about 50 to 70 cm. high. Wide spacing is advisable, because it affords the trees ample air and light and permits the lower branches to develop—all of which increase productivity. Moreover, the harvesters can handle the ladders more easily. Planting holes are covered two or three weeks before planting, to prevent waterlogging. The young plants should be protected by light shades.

Cultivation.—After the plants have taken root there is usually little more to be done. The clove tree possesses a hairy root system which nourishes the plant, so that neither surface nor deep plowing is advisable, as either might damage the fine root net. Only simple weeding is necessary. The young trees in native plantings usually receive very little cultivation; they are simply left to compete with the undergrowth, which they seem to overcome quite easily. In the larger plantations owned by white planters, the ground is more thoroughly cleared and the undergrowth cut back occasionally. Weeding beneath the trees during March seems to favor formation of ample buds. Clearing the ground around the trees also facilitates picking. Few planters apply fertilizers, although with proper manuring the clove tree develops superb buds, as can be seen in Penang. Toward the eighth year the trees reach full productivity.

Plantations.—Ninety-five per cent of Madagascar's clove crop is produced by natives, the rest by white colonists. Most plantings consist of small patches with ten to fifty trees, but there are also a few large ones with several hundred to several thousand trees. The natives of Madagascar frequently raise the clove tree and the coffee tree together. Most plantings have an appearance of neglect; planted too closely together, the semiwild trees are surrounded by thick underbrush, not nearly as well cleaned out as in Zanzibar.

Harvesting.—There is only one clove harvest per year in Madagascar. The abundant sunshine of the dry months contributes greatly to the quality of the cloves because it facilitates drying. In this respect, the regions of

Sainte-Marie and Saonierana Ivongo have an advantage over the islands of Zanzibar and Pemba, where frequent rainfall may damage the cloves during the drying process.

In Sainte-Marie the clove harvest begins the middle of October and ends toward the last days of December, whereas in Saonierana Ivongo it rarely commences before the middle of November. As in Zanzibar, all harvesting is done by hand; stems and buds are separated in the evening when the workers return from the fields to their huts. A good picker can collect daily from 15 to 25 kg. of unstemmed green cloves. He is paid daily wages, the piece work system of Zanzibar being unknown in Madagascar.

Courtesy of Fritzsche Brothers, Inc., New York.

Fig. 30. Clove production in Madagascar. Harvesting.

On taller trees harvesting necessitates the use of ladders, and on numerous trees only part of the crop can be collected. The production of cloves in Madagascar cannot, therefore, be very considerably increased, even should prices be much more remunerative. For the same reason, many planters top the trees at a height of 4 to 5 m. This practice has, naturally, a damaging effect upon the trees, as such sudden mutilation greatly hinders their metabolic functions and the development of flowers. But the topped clove tree develops in width, which facilitates harvesting and permits the employment of women and children, a type of labor becoming more and more important in Sainte-Marie and along the east coast of Madagascar. The practice of topping the trees has become quite a menace to the existence of the clove plantations in Madagascar, particularly since the natives cut the branches and leaves in a very crude way, even when the branches are in bloom. As a result, the trees frequently die. The cut-off branches and leaves are left to dry, and are then carried in bundles to nearby primitive field stills for distillation, which we shall discuss later.

As a rule, the natives of Madagascar pick the clove buds only when prices are sufficiently attractive and if, incidentally, the trees show an ample growth of buds. When clove prices are low, or the growth on the trees is only meager, the natives prefer to cut branchlets, leaves, stems, and buds together, because this involves much less work than hand picking the sparse clove buds.

Labor.—The labor problem in Madagascar, as it affects the clove industry, is a serious matter indeed. The very small native grower can collect his harvest with the help of his family, but the larger plantations are so badly handicapped by shortage of labor that very often a considerable part of the crop remains on the trees and is lost. Even for the harvesting of the staple crops which Madagascar produces (such as coffee, rice, cassava, sweet potatoes, and vanilla beans), labor is scarce. Some years ago, state prisoners were pressed into the gathering of cloves; of course this form of labor offers no solution. In the Saonierana Ivongo and Sainte-Marie clove producing regions, the local population is only about 30,000 as compared with 264,000 in Zanzibar and Pemba. Besides, the natives are rather indolent; they do not even crop their own clove trees, not to speak of hiring themselves out as laborers on estates. It is necessary, therefore, to rely upon help from certain tribes in the southeast, who migrate over long distances and return to their own villages, after having saved enough money to purchase a few cattle. However, these people are quite independent and if they do not like a job, they simply disappear in the jungle.

Prior to the outbreak of World War II, the government of Madagascar seriously considered the advisability of importing skilled farm laborers from over-populated Java for field work, and of unskilled laborers from Siam for house work, as a means of alleviating Madagascar's labor shortage. This policy seemed preferable to the unrestricted immigration of Chinese who, instead of settling down to manual work in the fields, usually became shop owners, traders, and intermediaries, invading every phase of Madagascar's economic life. The native uprisings, which took place after World War II and led to a bloody guerilla war, have rendered Madagascar's labor problem even more difficult.

Yield per Tree.—In Sainte-Marie there are a number of very old trees which have produced as much as 50 kg. of (dried) cloves per year. This yield, however, is exceptional. Generally, a fifteen-year-old plantation gives about 3 kg. of dried cloves per tree during good years. Another estimate is an average of 2 kg. per tree.

Since the clove harvest in Madagascar takes place in the driest period of the year, natural drying of the cloves may be effected in as short a period as two days. The result is a uniform, bright quality of cloves.

Every afternoon men, women, and children work at separating the buds from the stems. The buds are then spread on mats and exposed to the sun. Rapid sun drying is ideal. When the sky is overcast, drying may require three or four days. Cloves dried this slowly are sold at lower prices, because they contain less essential oil, and are of inferior appearance, frequently being wrinkled.

On the average, 3.35 kg. of fresh cloves yield 1 kg. of dried cloves. At the Agricultural Station of Ivoloina, the following figures were obtained:

Ten kilograms of unstemmed green cloves gave: 7.96 kg. of green cloves, 2.04 kg. of green stems; 2.36 kg. of dried cloves, and 0.75 kg. of dried stems—i.e., 3.37 kg. of green cloves gave 1 kg. of dried cloves. The loss of weight in drying was, therefore, 70.32 per cent, as compared with an average of 67 per cent in Zanzibar.

In Madagascar there are no local clove auctions, like those held in Zanzibar. The European exporters in Tamatave buy from the growers through Chinese middlemen, and often consign their stocks to home offices in France.

Moisture Content.—The moisture content of the various grades of Zanzibar cloves is standardized and controlled by the Clove Growers Association according to the Brown-Duvel test. Madagascar, however, has no such government regulations, with the result that every exporter follows his own standards and specifications, according to which he offers and ships his cloves. There is wide variation on this point, some exporters specifying not more than 16 per cent of moisture, others permitting up to 25 per cent.

Of course the latter moisture content is abnormal, especially in view of the fact that drying of the cloves is easier in Madagascar than in Zanzibar. The Department of Agriculture in Tamatave has been advocating adoption of the same standards as the Zanzibar Government has enacted through the Clove Growers Association, but so far the Madagascar exporters do not seem able to agree on this point, desirable as such agreement would be.

The unnaturally high moisture content occasionally found in exported Madagascar cloves is often a result of fraudulent manipulation. The growers in the clove regions sell their dried cloves largely to Chinese middlemen who, in turn, resell to European exporters in Tamatave. Sometimes the cloves pass through several hands before reaching the port of Tamatave.

The entire middleman trade is in the hands of Chinese who, during the last years, have succeeded in penetrating the economic life of Madagascar to an astonishing extent.

Middlemen.—Not all of these Chinese are honest in their business dealings. The illiterate native of Madagascar is easily deceived by figures, which he can check only by counting pebbles, and which in decimals become absolutely unintelligible to him. Chinese intermediaries may buy cloves from the natives in the interior at, let us say, Fr. 7.50 per kg. (prewar figures!) and resell them at Fr. 7 in Fénérive to the white agent of some French export house in Tamatave.

How at such prices the middlemen can make a profit remains a mystery. The explanation is probably that they moisten the dried cloves in order to increase the weight. This may be done by injecting water into the center of the filled sacks—for example, with a bicycle pump—so that on the surface the merchandise appears normal. The practice of moistening the spice has been a deep concern to the exporters in Tamatave because of the effect abroad upon the reputation of Madagascar cloves. The French Administration, aware of the danger, has even considered steps that would eliminate the Chinese entirely from the clove trade, just as the Zanzibar Government had to protect the Zanzibar growers from the Indian middlemen and speculators.

On occasions, buyers of Madagascar cloves abroad have complained about a too high moisture content, which seems to be the sole basis for criticism of an otherwise excellent product. If the Madagascar clove industry could be organized, and the quality strictly controlled (for instance, along the lines followed by the Zanzibar Clove Growers Association), Madagascar could certainly become a formidable competitor of Zanzibar.

Total Clove Production.—Madagascar's clove industry has expanded so rapidly that in 1939 the total acreage under cultivation was estimated at about 40,000 acres, which then was only about 8,000 acres less than the total clove acreage of Zanzibar and Pemba combined. However, in Madagascar considerably less cloves are harvested than the plantings actually produce because of labor shortage, the condition of the trees, and the dearth of good roads. Moreover, the clove plantings of Madagascar are frequently ravaged by cyclones.

It has been said that Madagascar will never be able to produce more than 3,000 tons of cloves a year and therefore could not possibly menace Zanzibar's monopoly; but according to Ledreux[13] Madagascar produced 4,612 metric tons of cloves in 1936. Many young trees have been planted during the last years, and total production is on the increase. In order to raise

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[13] Personal information during a meeting of the author with Mr. A. Ledreux in Tamatave, Madagascar.

figures of production, it was considered necessary to construct good roads for the faster transport of labor. As a matter of fact, much progress has been made in this respect during the past ten years.

Findlay [14] estimates that Madagascar could produce about 8,000 tons of cloves annually, if the crop were fully harvested. The same author states that about 50 per cent of the crop remains on the trees each year. He bases his estimate upon a yield of 2 kg. of dried cloves per tree. Obviously, if the total Madagascar clove crop were to be harvested and exported, it would be a serious threat to Zanzibar's industry.

In 1946 (from September through December) Madagascar produced 3,307 short tons of cloves.[15] However, in 1947 the crop amounted to only about 660 short tons, a result of the civil strife then plaguing the east coast, which hindered picking and bagging of cloves.

Prior to World War II the principal buyer of Madagascar cloves was France, but since the end of the war the United States, too, has become a very large user of the Madagascar spice.

Organization of Madagascar's Clove Industry.—While Zanzibar's clove industry has a powerful protector in the Clove Growers Association, Madagascar's clove industry is absolutely unorganized and uncontrolled. The occasional fraudulent activities of the Chinese intermediaries would soon be stopped by strict government control. An initial step toward such control was taken with the foundation of the Société Cooperative Agricole de Fénérive. Founded on December 1, 1936, it comprised 428 planters, most of them natives. The aim of the organization is to pass the cloves from the native growers directly to the exporters, thus eliminating the Asiatic intermediaries. Undoubtedly, the cooperative could develop into a broad organization, with proper government action. The director of the cooperative, who is also the acting official of the Department of Agriculture in Fénérive, the center of the clove region, is the only link between the cooperative and the Madagascar Government.

Comparison of Zanzibar and Madagascar Clove Industries.—The difference between Madagascar's and Zanzibar's clove industries may be summarized as follows:

1. In Zanzibar and Pemba the clove industry is very well organized and controlled by the Clove Growers Association and by the Department of Agriculture, whereas in Madagascar there is practically no control over production and the quality of outgoing shipments.
2. Labor is more abundant in densely populated Zanzibar and Pemba. In relation to its population, Madagascar is overplanted with clove trees.

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[14] "The Clove Industry of Madagascar," Zanzibar (1934).

[15] *Spice Mill* 70, No. 12 (1947), 73.

3. A network of good roads facilitates the transport of workers through the compact clove regions of Zanzibar and Pemba, whereas the rough jungle paths of Madagascar become practically impassable during the rainy season. However, many new roads have lately been constructed in Madagascar.

4. Cyclones are frequent in Madagascar, whereas Zanzibar and Pemba lie outside their regular path.

5. Madagascar's dry climate permits quicker and better drying of the cloves, although this advantage is somewhat offset by the occasional unethical practice of moistening the cloves (by Asiatic middlemen).

Madagascar Oil of Clove Buds.—As a result of the widely practiced topping of the clove tree, there has developed in Madagascar a rather unique industry, viz., the production of clove leaf oil. It was initiated about 1911 in the south of Sainte-Marie. Madagascar, including the island of Sainte-Marie, is the only country in the world that produces this oil on a large scale. In fact, the clove oil distilled in Madagascar is derived mainly from the leaves, only a small proportion being distilled from clove stems and insignificant quantities from the buds.

There is only one distillery in Sainte-Marie that produces small quantities of clove bud oil, and this chiefly from damaged, unexportable clove buds grown nearby. Lack of roads in these sections makes it almost impossible to transport large amounts of cloves to the distillery. It may seem rather surprising that Madagascar distillers do not produce clove bud oil in larger quantities, because it would appear more economical to distill the oil on the spot and so avoid the long transport of the cloves from Madagascar to Europe. The reason is that the small field stills of clove leaf oil operating in the clove regions are too primitive to produce a good yield and quality of bud oil. Most growers, therefore, sell the buds as such, and content themselves with distilling leaf oil and small quantities of stem oil. Distillation of clove bud oil is much more difficult than the distillation of leaf oil, and feasible only in modern apparatus. When distilled in crude, open-fire stills, the cloves form a sticky mass and give a poor yield of oil. While the yield of clove bud oil in modern steam distilleries is 16 to 18 per cent (in the usual stills not higher than 16.5 per cent), the crude stills employed in Madagascar give only about 15 per cent.

Madagascar Oil of Clove Stems.—In order to secure ready cash, the growers in Madagascar sell the dried cloves as soon as possible to Chinese middlemen; usually, however, they keep the separated stems. The material on hand is not sufficient to fill the stills daily, and distillation of the stems is postponed until sufficient material has accumulated after the harvest. Distillation is thus postponed and takes place in February and March. Aside from the numerous native distillers, there are also a number of Chinese and a few white producers. The native still owners rarely purchase stem material from other growers, because they usually have no money. Therefore, they distill stems of their own harvest only.

The difference between stem oil and leaf oil cannot always be clearly drawn and depends upon the method of harvesting. The author observed in Madagascar that the natives usually collect small branchlets with adhering bunches of stems and buds and two or more leaves. The harvested material therefore consists of clove buds, clove stems, and clove leaves. If the distillation material is cut off the trees with knives, it contains mostly leaves, and only few stems and buds; if picked by hand, it contains mostly buds and stems, and only a few leaves. (The buds are separated, dried and sold.) Frequently the remaining stems and leaves are distilled together, while still fresh. Therefore, the line between stem oil and leaf oil cannot be drawn sharply. Approximately 80 per cent of the clove oil produced in Madagascar is leaf oil, and only 15 to 20 per cent is stem oil.

A few white colonists, however, actually do distill pure stem oil. They purchase the stem material from neighboring native growers, who obtain it as by-product in the drying of clove buds. Since these distillers would not accept any adhering leaves, their output can really be classified as genuine stem oil, unless, of course, their lots are afterward purposely cut with leaf oil, a practice frequently resorted to. The stills are the same as those used for the distillation of clove leaf oil. The stem oil, like the leaf oil, is generally sold through Chinese middlemen.

In the crude open fire stills of Madagascar, the yield of stem oil on the average amounts to 5.5 per cent. It could probably be increased in modern stills. The eugenol content of genuine stem oils is about 88 per cent. Oils of very good quality contain more than 90 per cent. It is interesting to note that in the course of distillation the eugenol content of the oil falls off; it is higher in the first fractions and lower in the last fractions. (Cf. Vol. I of this work, p. 116.)

Madagascar Oil of Clove Leaves.—As was said, the clove trees are usually topped in Madagascar. The result is a large supply of leaf material for distillation, which enables the growers to obtain cash throughout the year. The distillers are in large part natives, but some Chinese and a very few white planters are also engaged in this work. These producers may be classified:

1. Native proprietors of small plantings *and* stills.
2. Native owners of stills, who purchase the leaves from other growers.
3. Native still owners who distill for other growers. In this case the still owner rents his still against payment either in cash or in oil, according to

arrangement. If, for instance, the yield of oil per charge of still should be 8 lb., 4 lb. go to the still owner and 4 lb. to the grower.

Production goes on during practically the entire year, with only short intermissions. A large, healthy tree gives as much as 100 kg. of twigs and leaves per year; but, on the average, only 50 kg. from trees older than twenty years, and 25 kg. from trees below that age, are obtained. Younger trees, of course, yield less plant material. Sometimes, in addition to the tops, the side branches, bearing buds, are cut off. This crude treatment of the trees has had a very damaging effect upon Madagascar's clove trees and can be excused only by the fact that it offers the planters a certain remuneration throughout the year, particularly in periods when the trees do not flower. In Sainte-Marie not only the hacked-off branches, but also the leaves fallen from the trees, are gathered from the ground and used for distillation—a practice which has resulted in serious soil depletion. Frequently the branches and leaves are bunched and allowed to dry under the trees for several days.

It has been estimated that there are in Madagascar about 170 clove leaf stills, 100 of them operating in the Saonierana Ivongo district, and 70 on the island of Sainte-Marie. They are scattered throughout the clove areas, and situated at central places which offer a good water supply and wood for fuel. The distillation posts are usually located on hillsides, where cool spring water can be conducted easily through bamboo pipes to the condensers. Some of the stills are very primitive, being made of sheet iron (which gives dark colored oils); those of the more advanced Deroy type are constructed of copper. The still capacity, usually 1,000 liters, permits a charge of 280 to 300 kg. of leaves. Other stills hold 1,500 liters and are charged with 450 kg. The bottom of the still is imbedded into a stone or mud hearth where a wood fire supplies the heat. The condenser is placed high to permit the distillation water to run back into the still—in other words, to provide for cohobation. After 6 hr. of heating, the water comes to a boil, and the oil starts to distill over. Distillation is then continued for 18 hr.; one charge thus requires altogether 24 hr. Sometimes, through carelessness, the water in the still evaporates during the course of distillation; in this case the operator must quickly add water (although the oil may already have been damaged). The oil is separated in ordinary kerosene cans. In the smaller stills the yield per charge ranges from 5 to 5½ liters or is about 2 per cent, and in the larger stills about 1.5 per cent. The yield varies with the season; in the dry period it is higher than in the rainy season.

Local Trading in Oil.—Here, again, the shrewd Chinese middlemen frequently take advantage of the illiterate native. They often pay the native producers according to liter, claiming that one liter is equal to one kilogram; but since the middlemen resell the oil, which is heavier than water, per kilogram, they gain the balance of about 65 g. The small oil lots are finally purchased by the exporting houses in Tamatave, where they are bulked and shipped abroad, according to certain standards of a minimum eugenol content. These standards vary with practically every exporter, but the most common is 85 per cent of eugenol.

Most of the leaf oil goes from Madagascar to Marseilles, and from there to other parts of Europe or to the United States.

The stem oil, as well as the leaf oil, is used mainly for the isolation of eugenol, and conversion into isoeugenol and vanillin, but exact figures as to the quantities employed for this purpose are not available.

Clove Production in Ceylon, Malaya, and Indonesia

A. Ceylon.—The clove tree was introduced into Ceylon about a hundred years ago, when a small grove was established in the Royal Botanical Garden. Since then, however, clove trees have not been planted systematically in large groves, but rather indiscriminately in scattered groups. There are also a few small holdings of 100 to 200 clove trees grown from seedlings, which were planted among other trees such as coconut, rubber, cocoa, and mangosteen. These well tended, healthy trees produce cloves of very high quality.

It is interesting to note that in the Kandy district the clove tree thrives at an altitude of about 1,600 ft., and about 50 miles from the sea, although it has always been claimed that proximity to the sea is of fundamental importance for the successful cultivation of cloves. However, these trees are rather slow in reaching the bearing stage, twelve to fifteen years being required, which probably is due to the high altitude and distance from the sea.

B. British Malaya.—The producing regions in British Malaya lie on the island of Penang and in the province of Wellesley. The clove tree was introduced from the Moluccas in 1800 by the botanist Smith, who held a commission with the East India Company. He brought about 15,000 young clove plants to Penang. From the first spice garden containing clove and nutmeg trees, quite a number of plantings were later established; in 1850 about thirty were in existence in Penang and Wellesley Province. However, the cultivation of spices suffered a serious setback with the introduction of the rubber tree, and today most of these early spice plantings are either entirely replaced by, or interplanted with, rubber trees.

The clove tree seems to flourish in the yellow, loamy and clayey hillsides of Penang. Since these slopes are very steep, terraces are constructed with small walls of granite boulders, and subsequently filled with earth (to prevent soil erosion). The clove plantings are found from 200 to 2,000 ft. above sea level, on slopes facing the sea. In Wellesley Province the tree does not seem to grow at altitudes above 1,000 ft.

The trees are planted by means of seedlings raised from seed in shaded beds and are transplanted when about 6 in. high. Fish refuse and prawn dust are preferred as fertilizers, and applied once a year in trenches dug around the trees. The trees reach the bearing stage at the age of six to seven years. The cloves are picked by hand; on the taller trees light bamboo ladders are used. The harvesting takes place when the flower buds show a reddish color, but before the buds break, and before the small white petals have expanded. Great care is exercised in handling the cloves, especially when they become dry, because at that stage the heads fall off easily. A very good quality of cloves should not contain more than 5 per cent of headless cloves. As in the case of Zanzibar and Madagascar cloves, too rapid drying causes them to become shriveled and brittle.

C. Indonesia.[16]—The producing regions in Indonesia (formerly Netherlands East Indies) are located around Padang, Benkoelen, and Lampong (on the island of Sumatra), near Minahasa (on the island of Celebes), and on Tenate, Tidore, Makian, Amboyna, Nussa Laut, Saparoea, Amadina, Ceram, and Banda (islands of the Moluccas group). The Moluccas, those storied islands of the early spice trade, are still the most important clove producers in Indonesia. In regard to output, the Moluccas rank first, with Sumatra and Celebes following; Java is of no commercial importance. The agriculture of Indonesia, in general, has shifted during the last century toward the development of bulk crops, and the production of spices, such as cinnamon and cloves, has been relegated to scattered cultivations that are largely owned by native growers. Nevertheless, there exists a good potentiality for increased clove production throughout the archipelago.

Today the growing of cloves in these regions is allied with that of nutmegs, clove groves being interplanted with nutmeg trees, as well as with other crops. For this reason the plantings receive very little attention and show the characteristics of forest crops. The vigorous growth, healthy condition, and unusual height of the clove trees on the island of Amboyna are due largely to the more plentiful and scattered rains, and not so much to the soil (which is similar to that of Zanzibar). In Amboyna the trees reach the bearing stage after six to ten years and continue to flourish at an age well above one hundred years. However, harvesting of these trees is very difficult because of the absence of lower branches. Moreover, flowering is irregular, probably due to lack of cultivation. These factors are not very encouraging to the native growers, many of whom have abandoned clove cultivation for the raising of nutmegs, coconut, and other more regular crops. Here again,

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[16] At the time of this writing (1949) the United States of Indonesia are being created.

it must be remembered that there is always the possibility of expanding the clove production if, for some reason or other, the production of major crops should have to be restricted. It is simply a question of which crop brings higher returns.

One interesting feature in connection with the *wild*-growing clove trees of the Moluccas should be mentioned. A few years ago Smith[17] wrote: "To obtain an authentic sample of *wild* cloves from their original home in the Moluccas would be no easy matter now, but, if such a sample could be obtained, a comparison of the essential oil distilled from it with that from *cultivated* Zanzibar cloves might prove of great interest." At the time of his writing, Smith had not learned yet that, shortly before the invasion of the Netherlands East Indies by Japanese forces, the Experiment Station of Buitenzorg (Java) had organized a botanical expedition into the interior of the Moluccas in order to investigate the clove trees which grow wild there. After the end of the hostilities, Dr. Th. M. Meijer,[18] who had spent years in Japanese captivity, but had been permitted to continue his scientific research in the laboratories of Buitenzorg, came to New York on a visit. Dr. Meijer showed the author a sample of *wild* cloves (*Eugenia caryophyllata* Thunb.) collected in the Moluccas and explained that they contained no eugenol whatsoever, but *eugenone* $C_{13}H_{16}O_5$, m. 97°–98°, i.e., 2,4,6-trimethoxybenzoyl acetone,[19] and *eugenine* $C_{11}H_{10}O_4$, m. 119°–120°, which was later shown to be 2-methyl-5-hydroxy-7-methoxychromone.[20] Other chromone derivatives identified in the ether extract of *wild* growing cloves are *eugenitine* $C_{12}H_{12}O_4$, m. 162°, i.e., 2,6-dimethyl-5-hydroxy-7-methoxychromone,[21] and *isoeugenitol* $C_{11}H_{10}O_4$, m. 229°–230°, i.e., 2,8-dimethyl-5,7-dihydroxychromone.[22] All these crystalline substances are practically odorless.

In the course of many generations, during which it has been intensively cultivated, the clove tree (*Eugenia caryophyllata* Thunb.) has thus undergone profound physiological changes.

METHODS OF DISTILLATION AND YIELD OF OIL

The distillation of cloves is by no means so simple a problem as it may appear. The yield, as well as the physicochemical properties, of the oil depend upon the origin and quality of the cloves, their condition prior to distillation (whole or crushed), and the type of distillation employed (water distillation, water *and* steam distillation, or direct steam distillation). For

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[17] *Perfumery Essential Oil Record* **37** (1946), 143.

[18] *Rec. trav. chim.* **65** (1946), 843.

[19] See Vol. II of this work, p. 544.

[20] *Ibid.*, p. 669. Meijer and Schmid, *Helv. Chim. Acta* **31** (1948), 1603.

[21] Schmid, *Helv. Chim. Acta* **32** (1949), 813.

[22] Schmid and Bolleter, *ibid.*, p. 1358.

details, particularly regarding hydrodiffusion, the reader is referred to Vol. I of this work, pp. 117, 144, and 159. If whole (uncomminuted) cloves are distilled, the forces of hydrodiffusion play a considerable role, and the first fractions of oil distilling over consist chiefly of eugenol.

According to Gildemeister and Hoffmann,[23] whole cloves on distillation yield oils with a high eugenol content and a specific gravity above 1.06, whereas comminuted cloves give oils with a slightly lower eugenol content and a specific gravity below 1.06. If comminuted, the material must be distilled immediately, to prevent loss of oil by evaporation.

According to Smith,[24] water distillation, still carried out today on a small scale, yields the finest oils for perfumery and flavor purposes, containing 85 to 89 per cent of eugenol by volume. Dry steam distillation, on the other hand, yields the so-called "strong oils" which are rich in eugenol (91 to 95 per cent by volume) and are used chiefly wherever a high eugenol content is the principal consideration.

In the United States today practically all of the clove bud oil is obtained by direct steam distillation of imported cloves. Eugenol, isoeugenol, and vanillin are now prepared from the lower priced clove stem oil or from clove leaf oil.

Distillation of one batch of cloves in a good still requires from 8 to 24 hours, depending upon the size and insulation of the still, the nature and volume of the steam, the condition of the cloves, etc. Quite a number of distillers, it seems, use whole (uncomminuted) cloves for distillation. In fact, prior to World War II there existed a demand, on the part of the Near East and India, for very low-priced cloves, for use in incenses. At that time substantial quantities of exhausted, residual (whole) cloves were shipped from Europe to the East.

As it distills over and runs off the condenser, the clove oil is collected, in the receiver, in two fractions, one lighter, the other heavier, than water. The two fractions must be mixed to obtain the complete oil. (Re "Oil Separator," see Vol. I of this work, p. 138.) The distillation waters should be redistilled (cohobated) to recover all the oil extracted from the spice by distillation (see Vol. I of this work, p. 154).

The yield of oil derived from clove buds is usually about 17, occasionally even 18, per cent; that from clove stems 6 per cent; and that from the leaves 2 to 3 per cent.

PHYSICOCHEMICAL PROPERTIES

A. Clove Bud Oil.—The quality of a clove oil is evaluated by its content of phenols, chiefly eugenol. Since clove oil contains some aceteugenol

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[23] "Die Ätherischen Öle," 3d Ed., Vol. III, 284.

[24] *Perfumery Essential Oil Record* **37** (1946), 144.

(eugenol acetate), in addition to free eugenol, and since both constituents contribute to the value of the oil, it is customary to saponify the former and to report the total phenol content as eugenol. Details of procedure will be found in Vol. I of this work, pp. 292 and 293.

As was pointed out above, the phenol content of a clove oil depends upon the condition of the cloves (whole or crushed) and the method of distillation. Smith[25] reported the following figures for clove bud oils distilled in England from imported cloves:

	Oils Obtained by Water Distillation	*Oils Obtained by Steam Distillation*
Specific Gravity at 15°	1.048 to 1.055	1.059 to 1.065
Eugenol Content (by Volume)	85 to 89%	91 to 95%

Raymond[26] carried out an experiment, distilling Zanzibar cloves with boiling water (I), and with low-pressure steam (II), in both cases with cohobation, and reported these figures:

	I	*II*
Yield of Oil	17.3%	17.35%
Specific Gravity at 15.5°/15.5°	1.0652	1.0691
Refractive Index at 20°	1.5315	1.5319
Eugenol Content	91.5%	92.5%
Solubility	Soluble in 1.1 vol. of 70% alcohol	

Oils with a high phenol content exhibit a high specific gravity.

Distilling imported Zanzibar and Madagascar cloves in the same stills and by the same method, the author of the present work obtained oils which had very similar properties and odor characteristics:

	Oil from Zanzibar Clove Buds	*Oil from Madagascar Clove Buds*
Yield of Oil	17.46%	17.4%
Specific Gravity at 25°	1.051	1.054
Optical Rotation	−0° 32′	−0° 25′
Refractive Index at 20°	1.5318	1.5321
Total Phenol Content	91%	93%
Solubility	Soluble in 1 vol. and more of 70% alcohol	

Gildemeister and Hoffmann,[27] recorded these properties for clove bud oil:

Specific Gravity at 15°	1.043 to 1.068
Optical Rotation	Up to −1° 35′
Refractive Index at 20°	1.529 to 1.537

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[25] *Ibid.* **37** (1946), 144.

[26] *Ibid.* **27** (1936), 395.

[27] "Die Ätherischen Öle," 3d Ed., Vol. III, 285

Total Eugenol Content (Including Eugenol Acetate, Determined by Heating with a 3% Sodium Hydroxide Solution)	78 to 95%, very seldom up to 98%
Solubility at 20°	Soluble, sometimes with slight turbidity, in 1 to 2 vol. and more of 70% alcohol. Only freshly distilled oils are soluble in 2.5 to 3 vol. of 60% alcohol; the addition of more alcohol causes cloudiness, except in the case of oils with a very high percentage of eugenol

Freshly distilled clove oil is an almost colorless to yellowish, strongly refractory liquid, which darkens on aging. Its odor and flavor is typical of the spice, highly aromatic, strong, and lasting.

B. Clove Stem Oil.—As in the case of clove bud oil, the physicochemical properties, particularly the phenol content and specific gravity, of the clove stem oil are influenced by the condition of the stem material (whole or comminuted), and by the method of distillation (see above).

Raymond [28] examined a clove stem oil bulked from some scores of distillation tests carried out in Zanzibar. The oil had the following properties:

Specific Gravity at 15.5°/15.5°	1.0699
Refractive Index at 20°	1.5393
Eugenol Content	95.0%

Smith [29] recorded these properties for clove stem oils, distilled in England (I), and in Zanzibar (II):

	I	*II*
Specific Gravity at 15°	1.060 to 1.063	1.055 to 1.063
Eugenol Content (by Volume)	92–94%	90–95%

Gildemeister and Hoffmann [30] noted the following limits:

Specific Gravity at 15°	1.040 to 1.067
Optical Rotation	Up to −1° 30′
Refractive Index at 20°	1.531 to 1.538
Eugenol Content (Determined with 3% Sodium Hydroxide Solution)	83 to 95%, in exceptional cases higher
Solubility	Soluble in 1 to 2 vol. and more of 70% alcohol. Often soluble in 2.5 to 3 vol. of 60% alcohol, but then in many cases opalescent to turbid on further dilution, especially with older oils

Two samples of clove stem oils distilled in Madagascar [Sainte-Marie (I), and Ivoloina (II)] under the author's supervision had these properties:

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[28] *Perfumery Essential Oil Record* **27** (1936), 396.

[29] *Ibid.* **37** (1946), 144.

[30] "Die Ätherischen Öle," 3d Ed., Vol. III, 289.

	I	*II*
Specific Gravity at 25°	1.050	1.055
Optical Rotation	−0° 36′	−0° 32′
Refractive Index at 20°	1.5352	1.5357
Total Phenol Content	91.0%	93.5%
Solubility	Soluble in 1 vol. and more of 70% alcohol	Soluble in 2 vol. and more of 60% alcohol

Oil (I) represented a commercial production; oil (II) was distilled in a modern experimental still, at the Government Experiment Station in Ivoloina.

While surveying the clove oil producing regions of Madagascar, the author also had occasion to attend the distillation of plant material, consisting of leaves, twiglets, and attached stems, after the buds had been removed (see above). Oil (I) was distilled in a primitive still operated by natives; oil (II) was produced in a more advanced still owned by white settlers. The two oils exhibited the following properties:

	I	*II*
Specific Gravity at 25°	1.046	1.051
Optical Rotation	−0° 54′	−0° 50′
Refractive Index at 20°	1.5341	1.5353
Total Phenol Content	88.5%	91.5%
Solubility	Soluble in 1 vol. of 70% alcohol, and more	

C. Clove Leaf Oil.—Three samples of genuine clove leaf oils distilled in Madagascar under the author's supervision—(I) was produced commercially on the island of Sainte-Marie, (II) and (III) experimentally in the Government Experiment Station at Ivoloina (Tamatave)—had the properties recorded in the table below. The same table includes the properties of commercial shipments (IV) examined by Fritzsche Brothers, Inc., New York:

	I	*II*	*III*	*IV*
Specific Gravity at 25°/25°	1.041	1.040	1.054	1.036 to 1.044
Optical Rotation	−1° 14′	−1° 40′	−1° 20′	−0° 40′ to −1° 36′
Refractive Index at 20°	1.5329	1.5321	1.5379	1.5312 to 1.5339
Total Phenol Content	85.5%	84.0%	88.5%	82 to 87%
Solubility	Soluble in 1 vol. and more of 70% alcohol			Clearly soluble in 1 vol. and more of 70% alcohol. Some oils were slightly hazy in 1 vol. of 70% alcohol, and turbid on addition of more alcohol

When tested for the presence of heavy metals (cf. Vol. I of this work, p. 309), most lots gave a positive reaction.

Smith[31] recorded for Madagascar clove leaf oil:

Specific Gravity at 15°	1.043 to 1.055
Eugenol Content (by Volume)	80 to 88%

Six clove leaf oils from the Seychelles Islands (I), three oils from Mauritius (II), and two oils from Madagascar (III) and (IV), examined by Schimmel & Co.,[32] had these properties:

	I	*II*	*III*	*IV*
Specific Gravity at 15°	1.0324 to 1.0493	1.061 to 1.067	1.0535	1.0462
Optical Rotation	−1° 40′ to −1° 53′	−0° 50′ to −1° 0′	−0° 49′	−1° 20′
Refractive Index at 20°	1.53329 (one determination)	1.5363 to 1.5391	1.53513	1.53244
Eugenol Content	78 to 87%	92 to 93%	90%	86%
Solubility in 70% Alcohol	Soluble in 1.5 vol. and more; usually turbid in 2.5 vol. and more	Clearly soluble in 1 vol. and more	Soluble in 1 vol. and more	Soluble in 0.9 vol. and more

ADULTERATION

Obviously, the adulterants most difficult to identify in clove bud oil are clove stem oil, and particularly the low-priced clove leaf oil, the addition of which changes the properties of the bud oil only slightly. To prove sophistication with these oils by routine analysis is not easy and, therefore, one must rely also upon organoleptic tests. A real expert will, in most cases, have no difficulty in detecting the presence of leaf oil by its somewhat harsh note.

Another form of adulteration consists in the addition of clove terpenes, obtained as by-products in the extraction of eugenol from clove oil. It is difficult to prove the addition of small quantities, but the addition of larger amounts increases the optical rotation, and lowers the eugenol content, the specific gravity, and the refractive index of the oil.

Adulteration with terpineol, dibenzyl, or dibenzyl ether is best detected by the odor on a blotting paper after standing for a few days or, even better, by the odor of the nonphenolic portions of the oil. Acetins, too, are occasionally encountered in commercial clove oils and can be detected by washing the oil with a saturated salt solution. A high saponification number of the water soluble material is indicative of acetins (see Vol. I of this work, p. 338).

Gross adulteration with constituents foreign to clove oil is seldom encountered. A careful study of the odor of the nonphenolic portions of the oil

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[31] *Perfumery Essential Oil Record* **37** (1946), 144.

[32] *Ber. Schimmel & Co.*, April (1914), 70; (1937), 54. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 291.

should always be made; if purity is doubtful, a large sample should be freed from eugenol and the remaining nonphenolic portions fractionated *in vacuo* with a careful examination of each fraction.

The detection of water soluble adulterants can be effected by determining any change in properties before and after washing the oil with saturated salt solutions.

The most important test in the analysis of clove oil is the determination of the total phenols (chiefly eugenol)—see above, section on "Physicochemical Properties."

Chemical Composition

A. Clove Bud Oil.—The volatile oil derived from dried clove buds by distillation contains, as its main constituents, free eugenol (70 to 90 per cent), eugenol acetate, and caryophyllene. Although these substances amount to some 99 per cent of the oil, they are not, as Smith[33] has pointed out, responsible for the characteristic fresh and almost fruity note of a pure clove bud oil. The proof of this lies in the fact that it is only necessary to prepare a mixture of pure clove eugenol, eugenol acetate, and caryophyllene in correct proportions, and to compare it with a sample of natural clove bud oil. This is one of the many examples of the importance of those substances which are found only in traces in natural essential oils. Clove bud oil contains several of these substances, the most important one being methyl-*n*-amyl ketone. As a characteristic feature it should also be mentioned here that clove bud oil contains a substantial percentage of eugenol acetate, whereas clove stem oil and clove leaf oil contain only traces of it.

The following compounds[34] have been identified in clove bud oil:

Eugenol. The chief constituent of clove bud oil, constituting from 70 per cent to more than 90 per cent in free form.

Eugenol Acetate (Aceteugenol, Acetyl Eugenol). See above. Erdmann[35] reported 2 to 3 per cent, Spurge[36] 7 to 17 per cent, Smith[37] 10 to 15 per cent of eugenol acetate in clove bud oil.

Caryophyllene. This sesquiterpene was first noted in clove oil by Church;[38] later it was named caryophyllene by Wallach.[39] According to Gildemeister and Hoffmann,[40] it occurs in clove oil chiefly as lower boiling, laevorotatory β-caryophyllene

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[33] *Perfumery Essential Oil Record* **37** (1946), 144.

[34] Details regarding these substances will be found in Vol. II of this work.

[35] *J. prakt. Chem.* [2], **56** (1897), 143.

[36] *Pharm. J.* **70** (1903), 701, 757. According to Spurge, the method of assay used by Erdmann is faulty.

[37] *Perfumery Essential Oil Record* **37** (1946), 144.

[38] *J. Chem. Soc.* **28** (1875), 113.

[39] *Liebigs Ann.* **271** (1892), 287.

[40] "Die Ätherischen Öle," 3d Ed., Vol. III, 286.

(blue nitrosite m. 164°-165°) and, in smaller proportion, as higher boiling, optically inactive α-caryophyllene (nitrosochloride m. 177°). According to Naves,[41] the volatile oil derived from cloves by steam distillation contains from 5 to 12 per cent of α- and β-caryophyllene, whereas the oil extracted from the spice with volatile solvents contains almost none.

Caryophyllene Oxide (Caryophyllene Epoxide). As far back as 1912, Vielitz[42] had noted a strongly laevorotatory hydrocarbon in the highest boiling fractions of clove oil, but it was only recently that Treibs[43] actually isolated caryophyllene oxide from clove oil. The biological parent substance of this oxide is undoubtedly caryophyllene. Treibs[44] reported these properties for caryophyllene oxide:

m.	64°
d_4^{20}	0.9658
α_D^{20}	−68° 0′
n_D^{20}	1.4958

According to a more recent publication of Naves,[45] the (benzene) extract of clove buds does not contain caryophyllene, but epoxy-dihydrocaryophyllene $C_{15}H_{24}O$ (the caryophyllene oxide of Treibs). However, the extracted mass of clove buds, under the influence of boiling water yields an essential oil composed chiefly of caryophyllene. The latter, therefore, is not a natural, biological constituent of the clove buds.

The epoxy-dihydrocaryophyllene observed by Naves in the (benzene) extract of clove buds had these properties:

m.	63°-64°
$b_{1.8}$	114°-117°
d_4^{20}	0.966
$[\alpha]_D$	−70° 2′
n_D^{20}	1.49564

As concerns those important substances that occur only in traces in clove bud oil, the following have been reported:

Methyl Salicylate. By Masson.[46]

Methyl-*n*-amyl Ketone. This compound, which is particularly responsible for the peculiar, almost fruity by-odor of the clove bud oil, was identified in the laboratories of Schimmel & Co.[47] through its semicarbazone m. 122°-123°, and through oxidation into valeric and acetic acids.

Methyl Alcohol, Furfural, β-Pinene(?), and Methyl Benzoate. In the course of their investigations the Schimmel chemists[48] isolated traces of still other substances from clove bud oil: methyl alcohol, furfural, β-pinene(?), and methyl benzoate.

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[41] *Helv. Chim. Acta* **31** (1948), 378. Cf. Naves and Perrottet, *ibid.* **24** (1941), 790. Deussen, *Liebigs Ann.* **356** (1907), 1.

[42] *Inaugural Dissertation, Leipzig* (1912).

[43] *Chem. Ber.* **80**, No. 1 (1947), 56.

[44] *Ibid.*

[45] *Helv. Chim. Acta* **31** (1948), 380.

[46] *Compt. rend.* **149** (1909), 795.

[47] *Ber. Schimmel & Co.*, April (1897), 50; April (1902), 44.

[48] *Ibid.*, October (1896), 57; April (1903), 51, 52.

Methyl-*n*-heptyl Ketone. Identified through its semicarbazone m. 118°–119°.

Valeraldehyde(?). According to Schimmel & Co. the oil contains probably valeraldehyde.

Further work on the minor constituents of clove bud oil was carried out by Masson [49] who noted the presence of these compounds:

Methyl-*n*-amyl Carbinol (2-Heptanol). B. 157°–158°, d_0 0.8344. Isolated from the fraction b_{15} 50°–75° by treatment with phthalic anhydride. Oxidation of the carbinol gave methyl-*n*-amyl ketone b. 151°–152°.

Furfuryl Alcohol. The treatment of the fraction b_{15} 50°–75° with phthalic anhydride yielded also furfuryl alcohol b. 170°–171°, d_0 1.1615, which was identified through its diphenylurethane m. 97.5°.

α-Methyl Furfural. The fraction b_{15} 65°–95° contains (aside from methyl-*n*-heptyl ketone—see above) α-methyl furfural b. 184°–186°, b_{20} 75°, d_0 1.1365, which Masson identified through its semicarbazone m. 210°–211°, its phenylhydrazone m. 147°–148°, and through oxidation to α-methyl-pyromucic acid m. 107°–108°.

Methyl-*n*-heptyl Carbinol (2-Nonanol) and Benzyl Alcohol. In the fraction b_{15} 75°–100° Masson observed methyl-*n*-heptyl carbinol b. 195°–196°, d_0 0.8399, which was characterized by oxidation to methyl-*n*-heptyl ketone, and benzyl alcohol b. 206°, d_0 1.0627, which was oxidized to benzoic acid.

Methyl Furfuryl Alcohol(?). The same fraction of the oil probably also contains methyl furfuryl alcohol.

A Dimethyl Furfural(?). In the fraction b_{15} 105°–120° Masson reported a dimethyl furfural b. 206°–208°, which on oxidation yielded a pyromucic acid m. 129°–130°. It was not possible, however, to determine the position of the methyl groups in the molecule.

Vanillin. This aromatic aldehyde is most probably present in clove bud oil, at least in traces, and undoubtedly originates by air-oxidation of eugenol. According to Gildemeister and Hoffmann,[50] dried clove buds contain vanillin. Jorissen and Hairs [51] observed vanillin in clove oil. Shaking clove oil with (1/5 of its volume) sodium hydroxide solution, van Urk [52] extracted crystals m. 90°–92° which had a vanillin-like odor and which, on treatment with phloroglucinol and hydrochloric acid, developed a red color.

B. Clove Stem Oil.—The chemical composition of the oil derived from clove stems has not been investigated as thoroughly as that of the commercially much more important clove bud oil, which is used widely in food products and in pharmaceuticals. Literature on the subject agrees that in general the chief constituents present in clove bud oil occur also in the stem oil, but in somewhat different proportions. The percentage of *free eugenol* present in the stem oil, for example, is usually somewhat higher than that present in the bud oil. The stem oil, on the contrary, contains only a small

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[49] *Compt. rend.* **149** (1909), 630, 795.

[50] "Die Ätherischen Öle," 3d Ed., Vol. III, 288.

[51] *Chem. Zentr.* (1890), II, 828.

[52] *Pharm. Weekblad* **65** (1928), 345.

amount of *eugenol acetate,* whereas the bud oil has been reported to contain up to 17 per cent of this ester. Among the other constituents present in clove stem oil, α- and *β-caryophyllene, furfural,* and *methyl alcohol* have been identified by the same workers who concerned themselves chiefly with the bud oil (see "Chemical Composition of Clove Bud Oil").

Substances, occurring only in traces, which impart the characteristic, almost fruity odor to the bud oil, seem to occur in the stem oil in still more minute quantities, or to be lacking entirely, which explains the coarser and "flatter" odor of the stem oil. Judging from the odor, *methyl-n-amyl ketone* appears to be present in clove stem oil but in a smaller proportion than in the bud oil.

On the other hand, clove stem oil contains a few constituents which have not yet been observed in clove bud oil. Von Soden and Rojahn[53] isolated traces of *naphthalene* from clove stem oil. Semmler and Mayer[54] observed an apparently bicyclic *sesquiterpene alcohol,* $C_{15}H_{26}O$, containing one double bond, which had these properties: b_8 138°–148°, d_{20} 0.9681, α_D −17°, n_D 1.5010, Mol. Refr. found 68.18, calculated for $C_{15}H_{26}O |^{\overline{}}$=68.07. When treated with alcoholic potassium hydroxide, the hydrochloride b_{12} 147°–155°, d_{20} 0.990 of this sesquiterpene alcohol yielded a hydrocarbon b_{10} 123°–126°, d_{20} 0.9273, α_D^{20} −23°, n_D^{20} 1.5024.

Fractionating the sesquiterpene portions of clove stem oil *in vacuo* (after removal of eugenol), Deussen[55] isolated from the distillation residue about 0.1 per cent of an amorphous, alcohol-insoluble substance m. 146° (not sharp), to which he assigned the empirical molecular formula $(C_{21}H_{30}O)_5$.

C. Clove Leaf Oil.—What has already been said about the chief constituents and the trace substances present in clove stem oil applies equally well to the oil derived from clove leaves. The chemical composition of clove leaf oil, like that of the stem oil, has not yet been as thoroughly investigated as that of the bud oil. Clove leaf oil usually contains a somewhat lower percentage of total eugenol than is present in clove bud oil; eugenol acetate occurs in the leaf oil, as in the stem oil, only in very small quantities. The trace substances, methyl-*n*-amyl ketone for example, which impart the characteristic, almost fruity odor to the bud oil, occur in the leaf oil probably in even more minute quantities than in the stem oil; hence the much coarser and "flatter" odor of the leaf oil.

As far as the substances which occur in the stem oil (but not in the bud oil) are concerned, viz., a sesquiterpene alcohol $C_{15}H_{26}O$, and naphthalene, only the latter (traces) has been observed in clove leaf oil.[56]

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[53] *Pharm. Ztg.* **47** (1902), 779.

[54] *Ber.* **45** (1912), 1392.

[55] *Ibid.* **42** (1909), 380, 680.

[56] *Ber. Schimmel & Co.* (1939), 57.

Use

Oil of clove (derived from the dried buds) represents one of the most important essential oils, indispensable for the flavoring of all kinds of food products (meats, sausages, baked goods, confectioneries, candies, table sauces, pickles, etc.). It is used also for the flavoring of oral preparations (dentrifrices, gargles) and chewing gums.

Because of its antiseptic and bactericidal properties, numerous pharmaceutical preparations contain oil of clove.

The use of clove oil in perfumes, toilet waters, and soaps of oriental and spicy odor is well known.

The lower-priced oil derived from clove stems, and particularly that from the leaves, offer an excellent starting material for the isolation of eugenol, which can be converted into isoeugenol and a very high grade of vanillin.

THE EUCALYPTUS OILS

Australian Eucalyptus Oils

by
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and
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The genus was named *Eucalyptus* by L'Héritier in 1788 (*Sert. Angl.*, 18, T.20), the word being derived from the Greek *eu* "well," and *kalypto* "I cover," in allusion to the operculum or lid which covers the stamens until they are fully developed. (Operculum = calyx, at least in some species.)

Introduction.—Eucalyptus trees, which are evergreen, form about three-quarters of the flora of Australia. They are often, but erroneously, called "Gum Trees," since the exudation from the bark is not a gum, but a tannin-

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[*] The authors are greatly indebted to Mr. H. H. G. McKern, Assistant Chemist, and Mr. J. L. Willis, Botanical Research Officer, Museum of Technology and Applied Science, Sydney, Australia, for their assistance in the preparation of this chapter, particularly of the tables describing the eucalyptus oils.

like substance known as a "kino." The kinos were formerly much used medicinally on account of their astringent properties (see British Pharmacopoeia 1914), but only small quantities averaging about 2,000 lb. per annum derived from *E. rostrata* are exported today.

The genus is typically Australian, although some species have been recorded from New Guinea, Timor, and the Philippine Islands. The extensive plantations in Algeria and other parts of Africa, California, India, New Zealand, Spain, South America, Belgian Congo and many other parts of the world were planted with seed obtained originally from Australia.

Courtesy of the Museum of Technology and Applied Science, Sydney, Australia.

FIG. 31. Production of eucalyptus oil in Australia. A forest of eucalyptus trees.

The eucalypts are found widely distributed over the whole of the Australian continent. They range from the dwarfed and stunted forms called "Mallees," which occur in the areas of low rainfall, to the tall and luxuriant trees which grow in the coastal and mountainous regions. Some species are at home at sea level; others thrive on the snowline of the Australian Alps. Eucalyptus trees form a very valuable asset to Australia, for apart from the essential oils distilled from the leaves and terminal branchlets, rutin and kinos, used respectively in medicine and as a source of tanning materials, are well known commercial products.

Botany.—Since *Eucalyptus globulus* was discovered in Tasmania in 1792 by Labillardière, the genus has been severely handled by systematic botanists. Results have been most confusing to research workers and to commercial distillers; nevertheless competition among rival botanists has stimulated intensive investigation of the genus. Consequently, an extensive literature has accumulated, which has tended rather to discourage than to attract the interest of systematic botanists in the study of the eucalypts. We are confronted today not only with a voluminous and conflicting literature on the subject, but a multiplicity of species which present almost insuperable difficulties to all workers, except the experienced eucalyptologist.

In the early days of the eucalyptus oil industry, it was customary to use the vernacular names of the principal species, such as "Blue Gum," "Peppermint," "White Gum," "Messmate," etc., but more than one species would often be found under one common name. Attempts were made, therefore, to adopt the botanical names with some degree of success. Unfortunately, a certain botanical name would be accepted for quite a long time, only to be replaced with a new name by some overzealous botanist, with consequent endless confusion. For example, the name of *Eucalyptus polybractea* was changed to *E. fruticetorum;* that of *E. numerosa*, var. "A," to *E. lindleyana* var. *stenophylla.* Although the change in name from *Eucalyptus polybractea* to *E. fruticetorum* was strictly in accord with the International Rules of Botanical Nomenclature in relation to priority, the fact remains that the former name had gained general acceptance in commerce. Any attempt to introduce a new name for the well-established one of *E. polybractea* would have seriously disturbed the eucalyptus oil industry.

In 1930 we had occasion to discuss the botanical nomenclature of a then recently named species, *Eucalyptus bicostata,* which in our opinion was established on very slender morphological evidence. The following statement[1] summarizes our views on the irresponsible changing of botanical names of well-established species:

> "In reality, *Eucalyptus bicostata* is a form of *Eucalyptus globulus* common to the mainland of Australia. Botanists apparently are agreed that the true *Eucalyptus globulus* is confined mainly to Tasmania, although growing sparsely in parts of Victoria. In our opinion it is most unfortunate that this form was not described as *Eucalyptus globulus*, var. *bicostata*, so that botantists, chemists, timber cutters, merchants and others interested in the technology of the eucalypts would be able to trace the relationship without the necessity of consulting the extensive bibliography on the subject. We are very reluctant to criticize workers in any branch of science, but feel it incumbent upon us to direct attention to the naming of new species of plants, more particularly essential oil-yielding ones, such as occur so abundantly in the families *Myrtaceae* and *Rutaceae.* We venture to suggest that it would add greatly to the general interest of botanical science, and its requirements be fully met, if names which furnished some idea of the relationship of new species to well established ones, were adopted. It would also be as well to view the matter from a practical and common-sense point of view, and to consider the influence of a new name upon the layman and technologist, more particularly when the plant or tree which is to receive the new name is a well-known one in commerce. The name *bicostata,* which refers in this case to the two-

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[1] Penfold and Morrison, *J. Proc. Roy. Soc. N. S. Wales* **64** (1930), 218.

ribbed fruits, gives no indication of the relationship of the tree to *Eucalyptus globulus*, one of the most famous of all *Eucalyptus* species. A much greater appreciation of the service of botany to mankind would be manifested if more careful consideration were given to this aspect of the science. These remarks apply more particularly to those species where the morphological characters which differentiate them from one another are ill-defined, or the evidence upon which their separation was effected somewhat slender."

It is not practicable, nor desirable, in a treatise of this nature to deal at length with the controversial issues involved in these botanical studies, but readers who wish to pursue the subject further are referred to the following publications:

J. H. Maiden, "Critical Revision of the Genus Eucalyptus," Government Printer, Sydney, 1909–1928.
R. T. Baker and H. G. Smith, "A Research on the Eucalypts and Their Essential Oils," 2d Ed., Government Printer, Sydney, 1920.
W. F. Blakely, "A Key to the Eucalypts," The Worker Trustees, Sydney, 1934.

It was the confused state of the botanical nomenclature that induced the earlier botanists to seek additional aids for the differentiation of the species. This led to the classic collaboration of Baker and Smith who, in 1896, commenced a series of botanico-chemical investigations on the Australian flora.[2] They were the first to use chemistry as a means of differentiating species which showed very slight botanical differences. In other words, they made the chemical composition of the oil a decisive factor in the identification of species, with the result that many eucalypts were raised to specific rank on these grounds. From their joint and classical investigation, which lasted until 1921, Baker and Smith concluded that the oil from any *Eucalyptus* species, growing under natural conditions, maintains a comparatively constant composition; that each chemical constituent increases in amount through a sequence of species, until it reaches a maximum in one or more of them. This important observation proved of great value in stimulating research into the botanico-chemical characteristics of the Australian flora, although it is untenable today owing to evidence which has become available since 1924. However, even recent writers[3] on the subject persist in maintaining the infallibility of Baker and Smith's original contention.

The first exception to the generalization of the constancy of species was noticed with *Eucalyptus dives*, a fact of considerable significance in view of the commercial importance of that species.[4]

[2] "A Research on the Eucalypts and Their Essential Oils," 1st Ed. (1902), and 2d Ed. (1920).

[3] John Read, "Chemistry of the Australian Bush," *Endeavour* **3**, No. 10, April (1944), 47; and editorial entitled "Present Imperfect," *Chemistry Industry* **1** (January 1948), 2.

[4] "The Occurrence of a Number of Varieties of *Eucalyptus dives*, as Determined by Chemical Analyses of the Essential Oils," Pt. 1, A. R. Penfold and F. R. Morrison, *J. Proc. Roy. Soc. N. S. Wales* **61** (1927), 54.

In the examination of a group of *Eucalyptus dives* trees (five in all) growing but a few feet apart, it was possible to identify three trees which contained an essential oil comparatively rich in cineole, whereas the other two trees contained oils rich in piperitone. Cineole and piperitone are two totally distinct compounds, the former possessing a very strong camphoraceous odor, and the latter a pronounced peppermint odor. Moreover, the five trees could not be distinguished by any differences in leaves, buds, fruit and bark, or by any other morphological characteristics. Soon afterward a large stand of *Eucalyptus dives* was found, the oil of which was quite free from piperitone; it contained 75 per cent of cineole, and provided an entirely new source of medicinal eucalyptus oil. These areas had formerly been neglected, in the belief that the oil present in the foliage would be similar to that of the normal *Eucalyptus dives,* i.e., it would contain piperitone and phellandrene.

Later, another variant was observed, the oil of which consisted almost entirely of *l*-α-phellandrene and other terpenes, less than 10 per cent of piperitone being present. The chemical composition of this oil thus differed considerably from that of the normal *Eucalyptus dives,* which contains not less than 45 to 50 per cent of piperitone. It is evident, therefore, that four different oils may be obtained from trees identical in every botanical respect. The question naturally arose: how were these four groups of botanically identical trees to be designated? We could, of course, with considerable justification, have followed the lead of our predecessors and regarded them as different species. If this had been done, a student studying the eucalypts for the first time would inquire about the relationship such species bear to *Eucalyptus dives,* an established species which would, no doubt, be known to him. From the economic point of view, a bushman seeking a stand of eucalypts from which to distill a pharmaceutical oil would experience considerable difficulty if the names bore no relation to that of the well-known *Eucalyptus dives.*

After consultation with some of the world's leading botanists who had studied the subject from many angles, we came to the conclusion that these variants would be best termed "physiological forms" of the type species, for it was believed that the variations had probably developed as the result of hybridization. The fact that differences in soil and climate were in no way responsible for the variations furnished additional evidence for our decision.

Physiological Forms.—In view of the evidence, we are of the opinion that one of the most important results of the investigations into the chemistry of the eucalypts during the past twenty-five years has been the discovery of these physiological forms. These are best defined as forms or varieties of well-known species indistinguishable from one another on botanical grounds, but which yield essential oils of diverse chemical composition. As indicated above, these investigations have not only been the means of opening up new areas of country for exploitation which had previously been rejected, but have created very important problems in genetics.

Experimental plantations have already been established by the Museum of Technology and Applied Science, Sydney, for the express purpose of prosecuting research on these problems. Although we directed attention to the importance of our discovery as far back as 1927, the far-reaching effects of our observations on botanico-chemical investigations of essential oil-yielding plants have not yet, after almost a quarter of a century, been fully realized.

Researches at the Museum of Technology and Applied Science, Sydney, continue to bring to light numerous examples of physiological forms, not only in the vast group of the eucalypts, but in other essential oil-yielding plants of the Australian flora. An indication of the wide occurrence of these forms in the eucalypts alone is afforded by the following examples:

Eucalyptus dives (Type and three forms), *Eucalyptus australiana* (Type and three forms), *Eucalyptus numerosa* (Type and two forms), *Eucalyptus piperita* (Type and one form), *Eucalyptus micrantha* (Type and two forms), *Eucalyptus citriodora* (Type and one form).

Only a small number of the 638 species and varieties described by botanists [5] are at present exploited for essential oils, for the eucalypts are Australia's principal source of hardwood timbers, being used for both fuel and structural purposes. It should be mentioned that, as a general rule, those eucalypts which are exploited for timber contain very little oil in the foliage, whereas those which are utilized for essential oils are of little use as timber. The wood of these oil-yielding trees is used principally for fuel. A notable exception to the rule is *Eucalyptus citriodora,* which in addition to yielding a volatile oil, is exploited for its timber.

Over two hundred species of eucalypts have been examined for their essential oils, but only a relatively small number are distilled commercially today.

Early Exploitation.—One of the first natural products exported from Australia in 1788 was eucalyptus oil derived from the "Sydney Peppermint," *Eucalyptus piperita* Sm., which was found growing on the shores of Port Jackson, where Sydney now stands.[6] The historical development of the eucalyptus oil industry in Australia since the establishment of the first still in Victoria by J. Bosisto in 1854, was fully dealt with by one of the authors in 1935.[7] The species distilled by Bosisto was *Eucalyptus amygdalina.*

It is interesting to note that the oil distilled by Surgeon-General White

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[5] W. F. Blakely, "A Key to the Eucalypts," The Worker Trustees, Sydney (1934).

[6] Journal of a voyage to New South Wales by Surgeon-General White, Surgeon General to the Settlement, published in 1790.

[7] A. R. Penfold, "The Development of our Knowledge Concerning the Essential Oils of the Eucalypts," *Australasian J. Pharm.* [N.S.] **16** (1935), 29.

from *Eucalyptus piperita* was sent to England for test, where it was found to be "much more efficacious in removing all cholicky complaints than that of the oil obtained from the well-known English peppermint, being less pungent and more aromatic." [8] The tree was thus aptly named the "Sydney Peppermint."

The oil of this species (*E. piperita*) was not marketed before 1930, when stills for its commercial production on a limited scale were established at Brookvale, a few miles to the north of Sydney, New South Wales. The oil could not be distinguished in respect to chemical composition from that of *Eucalyptus dives*, Type, but the lower yield restricts commercial production.

The next authentic record shows that Baron von Mueller, the Government Botanist in Victoria, in 1852, suggested to J. Bosisto the investigation of the essential oils of the eucalypts on a commercial basis. Bosisto took his advice and established the industry in 1854. His first operations were conducted in a small, rudely constructed still at Dandenong Creek, two miles out of Dandenong, Victoria. The species *Eucalyptus amygdalina* grew profusely in that district.

It is difficult to decide which was the next species to be exploited, as *Eucalyptus globulus, E. oleosa,* and *E. cneorifolia* were distilled for commercial purposes in the early 1880's. Many farmers in Tasmania were distilling *Eucalyptus globulus* at about the same time. *Eucalyptus cinerea* was distilled in the Goulburn district of New South Wales between 1880 and 1900. There is no doubt that considerable interest was evinced in the exploitation of *Eucalyptus globulus,* which ranked only second to *Eucalyptus amygdalina* as a commercial oil-producing species. Indeed, no species of *Eucalyptus* has received so much attention from both botanists and chemists as *Eucalyptus globulus.*

Practically all of these species, with the exception of *Eucalyptus cneorifolia,* have been superseded by those giving larger yields of oil. The pioneer investigations of Baker and Smith showed that other species, such as *Eucalyptus polybractea, E. australiana, E. dives, E. phellandra,* etc., gave higher yields of oil of equal or better quality. It is from these latter species that the present-day eucalyptus oils of commerce are won.

Production.—The principal producing areas are located in New South Wales and Victoria, where the best commercial, high yielding species, such as *Eucalyptus australiana, E. dives, E. polybractea,* etc., abound. Limited quantities of *Eucalyptus citriodora,* the "citron-scented gum," are distilled in Queensland; the same applies to *Eucalyptus cneorifolia* in South Australia. In Western Australia the exploitation of several "Mallees" (dwarfed eucalypts) for medicinal oils has been commenced.

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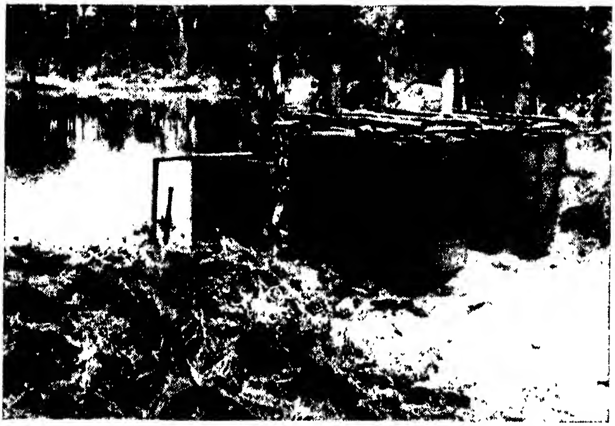
[8] Journal of a voyage to New South Wales by Surgeon-General White, Surgeon General to the Settlement, published in 1790.

As a general rule, distillation is carried out in 400-gal. ships' tanks, coupled together and directly fired. Notwithstanding their primitive character, they are very suitable for the purpose, as many of the species grow in rough and mountainous country. There are several hundreds of these stills operating in the Braidwood district of New South Wales alone. Such stills are flexible units which can be moved readily from place to place. We have seen many of these plants working efficiently in the hands of intelligent distillers who have displayed considerable originality and ingenuity.[9]



Courtesy of the Museum of Technology and Applied Science, Sydney, Australia.

FIG. 32. Production of eucalyptus oil in Australia. A typical distillation post consisting of movable field stills.

There is a tendency to replace these 400-gal. ships' tanks, which are normally operated in pairs, with large welded tanks of greater capacity. Some of these tanks hold about 1 ton of leaves and terminal branchlets, compared with 800 to 1,000 lb. weight packed into the smaller tanks.

The process of distillation, briefly, is as follows:

When an area of country (which may vary from a few hundred to three or four thousand acres, according to the species to be worked) has finally been selected, and certain formalities, such as obtaining a license from the Forestry Department and permission to use a still from the Commonwealth Department of Trade and Customs, have been complied with, one may proceed to collect the leaves and distill the oil therefrom. Trees of the selected species are cut down to within 1 or 2 ft. of the ground (although some prefer to cut to ground level under certain conditions), and the leaves and terminal branchlets are removed either with a hand axe or a cane-cutter's

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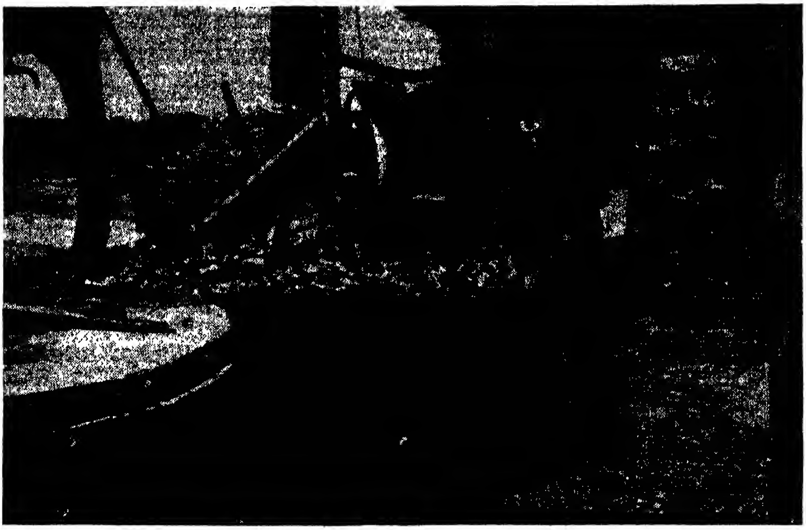
[9] "Guide to the Extraction of Eucalyptus Oil in the Field," *Sydney Technological Museum, Bull.* No. 4, 4th and Rev. Ed. (1945).

knife, an operation which usually requires the services of two men. The leaves are then carted to the still. The method of working is to place about 80 gallons of water in each tank, and to pack the leaves very tightly upon a grid supported about 12 in. from the bottom. Before the lid is placed in position a thick mixture of mud, clay, or "ant-heap" is placed along the flange. On top of this is placed a strip of hessian or similar packing material, and a second layer of clay, etc., applied. The lid is then carefully lowered onto the flange and fastened down by means of iron "stirrups" attached to the tanks. Four squared timbers 3 in. by 3 in. are required. Two of these are laid on opposite sides of the lid, and two along the remaining sides with the ends resting on the first timbers. The ends of the upper two are placed in the "stirrups," and wooden wedges are driven between the lid and the upper timbers. The pressure thus exerted brings the lid and flange together, and a steam-tight joint is made. The still is built upon a support of bricks or stones, and a wood fire is placed beneath. When the water boils, the steam passing up through the leaves separates the oil from the plant cells, and carries it over in the vaporous state into the iron pipe, which acts as a condenser. This piping is attached to the still near the top, and conducted under water in a small creek or running stream. The oil and water condense in the pipe and flow out into a suitable receptacle, where the oil floats upon the surface of the water and is ultimately separated. The period of distillation



Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 33. Production of eucalyptus oil in Australia. A stationary distillation post in the field. Placing a layer of mud paste on top of the still walls in order to tighten the still head to the vat.

varies from 3 to 18 hr., according to the species. The necessity for an ample water supply is evident from the procedure of distillation, especially as the pipes must be kept cool by running water. The yields of oil obtained per tank vary according to the species distilled, from 1.6 lb. in the case of *E. macarthuri* to 40 lb. per tank with *E. dives,* and *E. australiana* var. "B" (*E. phellandra*).

Where large areas are exploited, particularly in the "Mallee" country (nonmountainous, flat land) around Wyalong in New South Wales, and Bendigo in Victoria, large stills operated by pressure boilers have been installed. This modern method of distillation is now gradually being extended to all areas, particularly those where the eucalypts are conserved for oil production. A typical steam distillation unit operating in the Tumbarumba district of New South Wales consists of a Cornish boiler having great steam capacity, operating at 40 lb. pressure. The actual pressure on the digesters does not exceed 5 lb. per sq. in. The stills or digesters comprise two brick pits, each 11 ft. 6 in. deep by 6 ft. 6 in. wide. The unit is equipped with overhead gear for loading and discharging the leaves. A "grab" charges and discharges 2½ tons of leaves in five loads. A total of 2 to 2½ tons, and not infrequently 3 tons of leaves, according to the cut, are packed into the two digesters. The yield of oil varies from 130 lb. to 230 lb., according to the species.

Statistics.—The total annual production of eucalyptus oil in Australia is difficult to estimate, but information collected from distillers during the past ten years points to an average of 200,000 gal. (Imp.).

On the other hand, reliable figures are available for exports. These data, supplied by the Statistician of the Australian Commonwealth Government, are of interest, for they afford some indication of the fluctuations which occur from time to time with this primary product. The figures for the last ten years follow:

Year	*Gallons*	*Value £A.*
1938–1939	134,207	86,714
1939–1940	164,971	130,422
1940–1941	184,175	206,082
1941–1942	190,192	208,282
1942–1943	51,945	94,050
1943–1944	62,823	124,148
1944–1945	67,730	136,297
1945–1946	92,000	201,948
1946–1947	186,000	408,451
1947–1948	164,602	323,894

These exports are made up of 65 to 70 per cent of medicinal oil, and 30 to 35 per cent of industrial oil. The medicinal oils are derived chiefly from the following species:

Species	*Approximate Percentage*
Eucalyptus polybractea	33
Eucalyptus sideroxylon	20
Eucalyptus leucoxylon	20
Eucalyptus australiana and *E. dives* var. "C"	20
Remaining varieties	7

The consumption of eucalyptus oil in Australia is approximately 50,000 gal. per annum, made up of 40,000 gal. of industrial oils and 10,000 gal. of medicinal oils.

Yields of Oil.—Yields vary according to species. The yields obtained from the distillation of the principal commercial species are given in the following table:

Species Distilled and Location	*Yield of Oil per 1,000 Lb. Foliage*	*Prices per Lb.*	*Uses*
E. polybractea, Wyalong, N. S. W., and Bendigo, Victoria	20 lb.	3/6 d.	Medicinal
E. australiana, southern district, N. S. W., Bathurst district, N. S. W., Alexandra, Victoria	30 lb.	3/-	Medicinal
E. phellandra, Braidwood and south coast, N. S. W., and mountain ranges extending into Victoria	30–50 lb.	2/1 d.	Disinfectants and mineral flotation
E. dives, coastal ranges N. S. W., and Victoria, especially Braidwood, N. S. W., and northeast Victoria	30–45 lb.	2/2 d.	Source of piperitone for synthetic thymol and menthol
E. dives, var. "C," Batlow-Tumut-Tumbarumba district, N. S. W.	30–33 lb.	3/-	Medicinal
E. dives, var. "A," Braidwood, N. S. W., Trentham, Victoria	40 lb.	2/1 d.	Mineral flotation
E. macarthuri, Moss Vale and Wingello districts, N. S. W.	2 lb.	25/-	Perfumery
E. citriodora, North Coast district of Queensland around Mount Morgan, Gladstone and Maryborough	8–10 lb.	6/6 d.	Source of citronellal
E. cneorifolia, Kangaroo Is., S. A.	20 lb.	1/9 d.	Medicinal
E. elaeophora, principally Bendigo district, Victoria	20–25 lb.	2/8 d.	Medicinal
E. sideroxylon, principally Bendigo district, Victoria	20–25 lb.	2/8 d.	Medicinal
E. leucoxylon, principally Bendigo, Victoria	20–25 lb.	2/8 d.	Medicinal
E. numerosa (*E. radiata*), southern districts of N. S. W.	30–35 lb.	2/1 d.	Disinfectants and mineral flotation
E. numerosa (*E. radiata*) var. "A," N. S. W.	45 lb.	2/2 d.	Same as *E. dives* (Type)
E. viridis, Bendigo district, Victoria	15–20 lb.	2/10 d.	Medicinal
E. dumosa, Wyalong, N. S. W., and Bendigo district of Victoria	15–20 lb.	1/10 d.	Medicinal

For reference purposes, we have included other data, such as location of the species, fixed prices at point of production, and uses. The prices at point of production as fixed by the Australian Commonwealth Prices Commissioner as of July 1st, 1943, are those obtaining in Australia at the time of this writing (1948). More recently, government control has been discontinued, and prices, for various reasons, have risen considerably.

Use.—Until about 1910 eucalyptus oil was used principally for medicinal purposes. Large quantities of eucalyptus oil, rich in cineole and free from phellandrene, are still sold in the stores for domestic purposes. The oil is used for embrocation, inhalation (especially with the addition of a few crystals of menthol), as a vermifuge, clothes-cleaner, spot and stain remover, etc.

Notwithstanding the requirements of the British Pharmacopoeia and other pharmacopoeias that the oil contain not less than 70 per cent of cineole and be free of phellandrene (nitrosite test), there still exists a difference of opinion on the relative pharmacological values of cineole and phellandrene. The literature on this controversial subject was reviewed by McKern and Morrison.[10] The authors conclude that in view of very recent work, both these substances possess similar pharmacological effects, and the order of toxicity is the same. They raise the question of excluding the phellandrene test entirely from the British Pharmacopoeia. The stipulated cineole content of 70 per cent, together with physical characters—more particularly the solubility in alcohol—constitutes an ample safeguard against the presence of more than a small quantity of phellandrene. Apparently there is scope for a great deal of further work on the pharmacology of these two substances, as well as other essential oil constituents.

Considerable quantities of eucalyptus oil containing phellandrene were formerly used for mineral flotation, especially in the separation of zinc and associated sulfides. However, consumption of eucalyptus oil for this purpose has declined steadily of recent years through competition with xanthates and other new mineral flotation agents. Small quantities continue to be employed as frothing agents in these processes. At one time, the Broken Hill mines used over 10 tons of eucalyptus oil per month, employing less than ½ lb. of oil per ton of ore.

Since 1920 there has been a steadily increasing demand for eucalyptus oils for industrial purposes. One oil in particular—*Eucalyptus phellandra* (*E. australiana*, var. "B")—containing much phellandrene with 20 to 50 per cent of cineole, has found favor for the manufacture of inexpensive germicides and deodorants for use in theatres and other public places. These products are comparatively cheap to prepare by emulsification of the oil with soap

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[10] *Australasian J. Pharm.* [N.S.], **28** (1947), 858.

solutions. They are preferred by users to the coal tar preparations.[11] Incidentally, the addition of a small quantity of *Eucalyptus citriodora* oil greatly improves the odor of the above preparations.

The oil of *Eucalyptus dives,* Type, containing 50 per cent of piperitone came into prominence in 1920, when the chemists of the Sydney Technological Museum [12] showed that laevorotatory piperitone, isolated from the oil of this species, could be easily converted to thymol by oxidation with ferric chloride, and to menthol on reduction with hydrogen. The manufacture of synthetic menthol was timely, for it assisted in breaking the Japanese Government's monopoly of the natural product. Commercial production by leading manufacturers of the United Kingdom, Europe, and the United States of America quickly followed, with the result that synthetic thymol and menthol are produced on an extensive scale today. Considerable quantities are also made in Australia. *Eucalyptus dives* oil is now a recognized source of the important ketone, *l*-piperitone.

Practically all eucalyptus oils for medicinal purposes are refined by redistillation before sale. The first runnings, consisting of volatile aldehydes, and some terpenes, as well as the residues of sesquiterpenes, aromatic aldehydes and alcohols, phenols, etc., find important industrial applications.[13] Some of the uses of the principal constituents are:

1. *Volatile aldehydes* (principally isovaleric) are used in various proprietary preparations, including disinfectants, sheep dips, etc.
2. *Pinene* and other terpenes are used in the manufacture of certain blended turpentines.
3. *Cineole,* the principal constituent of medicinal eucalyptus oils, has a very restricted use. Production rarely exceeds a few tons per annum. It is employed in pharmacy and confectionery and, to a limited extent, as a spot and stain remover.
4. *Phellandrene* is obtained as a by-product in the separation of piperitone from *Eucalyptus dives,* Type, oil and the oils of allied species and is in demand as a general solvent. In combination with piperitone and other constituents it is sold as a blended eucalyptus oil for mineral flotation purposes. Purified phellandrene is manufactured both in Australia and the United Kingdom for perfumery purposes.
5. *Terpineol*—the well-known perfumery constituent of lilac odor—may be separated from the high boiling fractions of *Eucalyptus australiana, E. dives* var. "C," etc.

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[11] "Uses of Commercial Eucalyptus Oils," *Sydney Technological Museum, Bull.* No. 17, Rev. Ed. (1938).

[12] Smith and Penfold, *J. Proc. Roy. Soc. N. S. Wales* **54** (1920), 40.

[13] "Uses of Commercial Eucalyptus Oils," *Sydney Technological Museum, Bull.* No. 17, Rev. Ed. (1938).

6. *Citronellal.* The oil of *Eucalytus citriodora* is an excellent source of citronellal for the preparation of citronellol.

7. *Geranyl acetate* is obtained from the oil of *Eucalyptus macarthuri.* The rectified oil of *Eucalyptus macarthuri* is used not only for perfumery purposes, but as a denaturant of the alcohol required in the manufacture of Australian perfumes. The residue left in the still is a good source of eudesmol.

8. *Eudesmol,* the principal sesquiterpene alcohol of eucalyptus oils, is a very satisfactory fixative for certain perfumes.

9. *Eudesmyl acetate.* This ester is prepared by the acetylation of eudesmol. It was used as a wartime substitute for oil of bergamot and its constituents. It blends fairly well with lavender oil.

10. *Piperitone* (technical), assaying 90 to 95 per cent ketone, is the raw material for the manufacture of synthetic thymol and menthol.

11. *Still residues from the rectification of pharmaceutical oils.*

The principal constituents are the aromatic aldehydes cuminal and phellandral, and the ketone cryptone, together with some of the corresponding alcohols, sesquiterpenes, and the phenol australol (*p*-isopropylphenol). Cuminal, phellandral, cryptone, and australol all possess marked germicidal properties; consequently the still residues rich in these constituents are much sought after for the manufacture of disinfectants and germicides.

Commercial Eucalyptus Oils

The eucalyptus oils usually met with in commerce today are the following, which are grouped, for convenience, under three main headings—medicinal, industrial, and perfumery oils.

Medicinal Oils

Name	*Principal Constituents*
Eucalyptus globulus	Cineole 70 to 80%
Eucalyptus polybractea	Cineole 80 to 88%
Eucalyptus australiana	Cineole 70 to 75%
Eucalyptus dives, var. "C"	Cineole 70 to 75%
Eucalyptus elaeophora *	Cineole 70 to 75%
Eucalyptus sideroxylon *	
Eucalyptus leucoxylon *	
Eucalyptus cneorifolia	Cineole 70%
Eucalyptus viridis	Cineole 70 to 80%
Eucalyptus dumosa	Cineole 70%
Eucalyptus smithii	Cineole 75 to 80%

*** In admixture known as "Apple Jack" and "Ironbark."**

(The principal pharmacopoeias require eucalyptus oils for medicinal purposes to contain a minimum of 70 per cent of cineole. It is customary to supply oils of this quality by the distillation of selected species like the aforementioned.)

INDUSTRIAL OILS

Name	*Principal Constituents*
Eucalyptus dives, Type	Piperitone and phellandrene
Eucalyptus australiana, var. "B" (*Eucalyptus phellandra*)	Phellandrene and cineole
Eucalyptus dives, var. "A"	Phellandrene
Eucalyptus numerosa	Phellandrene and piperitol
Eucalyptus numerosa, var. "A"	Piperitone and phellandrene

PERFUMERY OILS

Name	*Principal Constituents*
Eucalyptus macarthuri	Geranyl acetate, geraniol and eudesmol
Eucalyptus citriodora	Citronellal

Until recently it was practicable to supply commercial eucalyptus oils according to species, but the insistent demand for a minimum of 70 per cent of cineole has resulted in merchants blending oils of several species, and exporting the refined product as eucalyptus oil containing 70 per cent of cineole, without specifying any particular species.

In this connection, we have selected the species *Eucalyptus globulus* for special discussion, although it is not produced in Australia today. Overseas merchants continue to ask specifically for *Eucalyptus globulus* oil, and, although oil is often supplied under this name, it is not distilled from that species in Australia; the term is interpreted as referring to quality. So far as we are aware, any true *Eucalyptus globulus* oil marketed in Europe must be derived from sources outside of Australia, i.e., Spain, Brazil, and the Belgian Congo. There is no doubt *Eucalyptus globulus* was one of the earliest species to be distilled in Australia, for, as mentioned under the heading "Early Exploitation," farmers were distilling it in Tasmania in the year 1880. Newer species, richer in cineole and higher in oil content, were subsequently exploited, gradually supplanting the production of *Eucalyptus globulus* oil. These newer species yield over 2 per cent of oil in comparison with 0.75 per cent from *Eucalyptus globulus*. As *Eucalyptus globulus* is well-known in the essential oil markets of the world, it is considered necessary to open this chapter with an account of that species.

Oil of *Eucalyptus Globulus* Labillardière

Botany and Occurrence.—This species was described by Labillardière[14] in 1799. It is a tall tree with a smooth whitish-blue bark. A conspicuous feature of the normal adult leaves is their length, which varies from 9 in. to 18 in. The fruit, too, is easily distinguished from that of most other species of the genus.

No eucalypt has received so much attention from botanists and chemists as this particular species. Its systematic botany has been discussed by Baker and Smith,[15] and by Maiden.[16] The tree, known in Australia by the common name of "Blue Gum," has been cultivated in all parts of the globe, particularly in California, where it is planted as a windbreak in orchards, in southern Spain, Brazil, and Africa, where it is used both as fuel and as a structural timber in mines. According to Singh,[17] much experimental work has been done with this species in the Nilgiri Hills of India. Closely allied species, such as *Eucalyptus maideni* and *E. bicostata,* are often confused with *E. globulus*, for the morphological differences are not very pronounced.[18]

As a general rule botanists are agreed that in Australia the true *Eucalyptus globulus* is confined principally to Tasmania, although growing sparsely in parts of Victoria. The New South Wales tree is generally referred to as *Eucalyptus bicostata.*

Producing Regions.—The principal producing regions are in Spain, Portugal, Brazil, and the Belgian Congo. No oil is distilled commercially in Australia.

Yield of Oil.—The leaves and terminal branchlets yield from 0.75 to 1.25 per cent of oil.

Physicochemical Properties.—The crude oil is a mobile liquid, usually light yellow in color, with a pronounced odor of the volatile aldehydes, principally isovaleraldehyde. The latter manifests itself by an irritating action which causes coughing. The oil, after rectification, is usually free from this disagreeable constituent.

Although not produced commercially in Australia today, as the oil of the species has been replaced by others, the following properties have been recorded for the oil:

Specific Gravity at 15°/15°	0.910 to 0.930
Optical Rotation	+0° 18′ to +15° 0′

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[14] "Relation du Voyage à la Recherche de La Perouse," Vol. I, Paris (1799–1800), 153.

[15] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 165.

[16] "Critical Revision of the Genus Eucalyptus," Pt. 18 (1913), 249.

[17] *Indian Forest Records* **5**, Pt. 8 (1917), 1–26. *Perfumery Essential Oil Record* **8** (1917), 326.

[18] Penfold and Morrison, "Notes on the Essential Oils from Some Cultivated Eucalypts," *J. Proc. Roy. Soc. N. S. Wales* **64** (1930), 218.

Refractive Index at 20°	1.4600 to 1.4700
Cineole Content	70 to 75%
Solubility in 70% Alcohol (W/W)	Soluble in 1.5 to 3 vol.

Chemical Composition.—The chemical composition of this type of oil will be described in the monograph on Spanish Oil of *Eucalyptus globulus*, p. 482.

Oil of *Eucalyptus Polybractea* R. T. Baker

(Syn. *E. fruticetorum* F.v.M.)

Botany and Occurrence.—This species, the so-called "Blue Mallee," was described by Baker[19] in 1900, and later by Baker in association with his colleague Smith.[20] It is a typical "Mallee"—a dwarfed eucalypt having several stems growing up from the main root stock. The term "Blue" refers to the glaucous appearance of the leaves which is most marked when observed over large areas.

The tree occurs in extensive stands in the low rainfall areas of New South Wales and Victoria. The principal districts from which commercial supplies are drawn are Wyalong in New South Wales, and Bendigo in Victoria.

The oil was formerly distilled in very large quantities, but much of the area of production has been converted into wheatland. On the other hand, several owners, realizing the urgent need for preservation of this species for oil production, have taken steps to stimulate the production of younger and more vigorous growth. The following excerpt from Baker and Smith's publication entitled "A Research on the Eucalypts and Their Essential Oils" (1920), page 434, describes one of the methods:

> "In the Wyalong district a considerable area of country is covered with 'Mallee,' and in some portions *Eucalyptus polybractea* is present to the extent of from 40 to 50 per cent, of the total eucalyptus growth. The material from the older trees of the 'Blue Mallee' is not so useful for oil production as the younger growth, one reason being that the yield of oil is not so great, and in order to secure an abundance of new leaf various devices have been adopted. One method is to employ a heavy roller, and with this crush down the whole of the natural growth of the 'Mallee Scrub.' When the broken-down material becomes dry enough it is burnt off, all vegetation upon the ground being destroyed in the fire, but in a few weeks the young growth commences to appear in abundance, springing from the buried nodular root masses of the 'Mallee,' and in twelve to eighteen months is ready to be cut for oil distillation."

Yield of Oil.—The yield of oil from the leaves and terminal branchlets varies from 1.5 to 2.5 per cent by weight at the time of cutting in the field. The season of harvest and age of the plants influence the yield; the young material is richer in oil.

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[19] *Proc. Linnean Soc. N. S. Wales* **25** (1900), 692.

[20] Baker and Smith, "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 189.

Physicochemical Properties.—From many distillations of leaves made by the authors, the following average results were obtained:

Specific Gravity at 15°/15°	0.922 to 0.930
Optical Rotation	+0° 30′ to +2° 0′
Refractive Index at 20°	1.4594 to 1.4616
Cineole Content	77 to 84%
Congealing Point	−7° to −10° C.
Flash Point (closed cup)	60° C. (140° F.)
Solubility in 70% Alcohol (W/W)	Soluble in 1 to 1.2 vol.
Solubility in 70% Alcohol (V/V)	Soluble in 1.8 to 2 vol.

The examination of hundreds of commercial samples has given the following range of properties:

Specific Gravity at 15°/15°	0.9225 to 0.9267
Optical Rotation	+0° 30′ to +1° 51′
Refractive Index at 20°	1.4584 to 1.4613
Cineole Content	80 to 90%
Congealing Point	−4° to −9° C.
Solubility in 70% Alcohol (V/V)	Soluble in 1.8 to 2 vol.

Chemical Composition.—Oil of *Eucalyptus polybractea* contains 75 to 90 per cent of cineole and a number of other constituents, among them several aldehydes (cuminal and *l*-phellandral), and a ketone (*l*-cryptone) which impart a characteristic odor to the oil. Years ago Baker and Smith [21] used the term "aromadendral" to denote a mixture of high-boiling carbonyl constituents occurring together in certain eucalyptus oils, usually in association with *p*-cymene. Penfold [22] showed that "aromadendral" consisted of three aldehydes, viz., cuminal, *l*-phellandral and cryptal. Penfold's specimen of cryptal, prepared from the oil of *E. hemiphloia* F.v.M., was investigated by Penfold and Simonsen [23] who concluded that it had the structure 4-isopropyl-2-cyclohexen-1-al. The same authors, in a re-examination of this compound, isolated from the oil of *E. cneorifolia,* showed it to be the nine carbon atom ketone, *l*-4-isopropyl-2-cyclohexen-1-one. These observations were confirmed by Berry, Macbeth and Swanson [24] who proved the presence of this ketone, now termed "cryptone," in the oils of *E. polybractea, E. hemiphloia,* and *E. cneorifolia.* No evidence for the existence of cryptal was found by these workers [25] in these oils.

Earl and Trikojus [26] showed that the constituent of the oil of *Eucalyptus*

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[21] *Ibid.,* 61 (footnote), 383–8.

[22] *J. Chem. Soc.* **121** (1922), 266.

[23] *Ibid.* **132** (1930), 403.

[24] *Ibid.* **139** (1937), 986.

[25] *Ibid.,* 1443.

[26] *J. Proc. Roy. Soc. N. S. Wales* **59** (1925), 301. Cf. Robinson and Smith, *ibid.* **48** (1914), 518.

polybractea, formerly known as "Australol," was in reality *p*-isopropylphenol.

Baker and Smith,[27] Earl and Trikojus,[28] Berry, Macbeth and Swanson,[29] Reuter,[30] and Berry and Swanson [31] identified the following compounds in oil of *Eucalyptus polybractea:*

Cineole. The oil contains from 75 to 90 per cent of cineole (Baker and Smith).

p-Cymene. Characterized by oxidation to *p*-hydroxyisopropylbenzoic acid m. 156°–157° (Berry and Swanson).

A Terpene(?). The same authors observed in the oil a dextrorotatory terpene which, however, was not identified.

Cuminal, *l*-Phellandral, and *l*-Cryptone (4-Isopropyl-2-cyclohexen-1-one). The two aldehydes cuminal and *l*-phellandral, and the ketone *l*-cryptone, impart to the oil its characteristic odor (see above and Vol. II of this work, pp. 352, 344, and 388, respectively).

p-Isopropylphenol ("Australol"). The phenol formerly called "Australol" is in reality *p*-isopropylphenol (see above, and Vol. II of this work, p. 499).

A Ketophenol(?). Reuter reported the occurrence of an unidentified ketophenol in the oil.

Use.—Oil of *Eucalyptus polybractea* is used for the same purposes as all other cineole-containing (medicinal) eucalyptus oils (see above).

OIL OF *Eucalyptus Australiana* BAKER AND SMITH, TYPE
(Syn. *E. radiata* Sieber)

Botany.—This species, formerly classified as *Eucalyptus amygdalina,* was raised to specific rank by Baker and Smith [32, 33] in 1915. Their action was justified by reason of the exceptional demand for the oil for medicinal purposes. The classification has since been confirmed by the present authors who, after thirty years of experience in handling the oil, regard it, with the single exception of *Eucalyptus dives,* var. "C," as the finest medicinal eucalyptus oil produced in Australia today. The tree is known by the common name of "Black" or "Narrow-leaved Peppermint."

Habitat, Range, and Occurrence.—*Eucalyptus australiana* is a medium sized forest tree with fibrous bark, characteristic of that group of eucalypts

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[27] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 190.

[28] *J. Proc. Roy. Soc. N. S. Wales* **59** (1925), 301. Cf. Robinson and Smith, *ibid.* **48** (1914), 518.

[29] *J. Chem. Soc.* (1937), 989.

[30] *J. Proc. Australian Chem. Inst.* **5** (1938), 290.

[31] *J. Proc. Roy. Soc. N. S. Wales* **76** (1941), 65.

[32] *Ibid.* **49** (1915), 514.

[33] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 169.

called "Peppermints." It occurs in extensive belts in the main Dividing Range of New South Wales, west and south of Sydney (Isabella River, Barraga, and Black Springs, Nerrigundah, Yourie, Quaama, Cobargo, Batlow, Tumbarumba, and Tumut) and in the Marysville district of Victoria (Alexandra).

Yield of Oil.—The leaves and terminal branchlets yield, on an average, from 3 per cent to 3.5 per cent of oil, varying with the season, and lowest during the winter months (about 2.5 to 2.7 per cent).

Physicochemical Properties.—The crude oil usually exhibits a very pale lemon tint, but is colorless after rectification:

Specific Gravity at 15°/15°	0.9162 to 0.930
Optical Rotation	+1° 0′ to +5° 0′
Refractive Index at 20°	1.4632 to 1.4644
Cineole Content	65 to 72%
Phellandrene Content	Absent
Congealing Point	−15° C. to −18° C.
Solubility in 70% Alcohol (W/W)	Soluble in 1.2 to 1.5 vol.

Chemical Composition.—The oil of *Eucalyptus australiana,* Type, contains from 70 to 75 per cent of cineole, 5 per cent of citral, some α-terpineol, geraniol, pinene, sesquiterpenes, and a few other compounds (see below). Commercial oils occasionally show the presence of phellandrene by the nitrosite test. According to Penfold and Morrison,[34] however, the occurrence of phellandrene may be due to the admixture of "Type" oil with oils from botanical variants, which these authors have described as "Physiological Forms." An extensive investigation carried out by Penfold and Morrison in 1935 and 1937 brought to light various physiological forms of *Eucalyptus australiana.*

Baker and Smith,[35] and Ralph [36] identified the following substances in oil of *Eucalyptus australiana,* Type:

1,8-Cineole. According to Baker and Smith the oil contains about 70 per cent of cineole.

l-α-Terpineol. Identified by means of the nitrosochloride m. 113°, the nitrolpiperidine m. 159°–160°, and the phenylurethane m. 112° (Baker and Smith).

Geraniol. Characterized by oxidation to citral (Baker and Smith).

Citral. The oil contains about 5 per cent of citral, identified by means of the *p*-naphthocinchoninic acid m. 199°–200° (Baker and Smith).

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[34] "The Essential Oils of *Eucalyptus australiana* Baker and Smith and Its Physiological Forms," *J. Proc. Roy. Soc. N. S. Wales* **69** (1936), 111; **71** (1937), 357. Cf. Penfold, *ibid.,* **60** (1926), 55. *Perfumery Essential Oil Record* **13** (1922), 324.

[35] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 174, 336, 371.

[36] *J. Proc. Roy. Soc. N. S. Wales* **80** (1946), 208.

Pinene, and a Paraffin(?). According to the same authors.

Geranic Acid. The oil contains about 0.2 per cent of geranic acid, which Ralph identified by cyclization to α-geranic acid m. 104.5°, and by oxidation of the latter to dihydroxydihydro-α-cyclogeranic acid m. 200° (Ralph).

Methyl Cinnamate. According to Ralph the oil contains about 2 per cent of methyl cinnamate.

Cinnamic Acid (free), a Sesquiterpene(?), and a Sesquiterpene Alcohol(?). The same author also reported the presence of free cinnamic acid, of a sesquiterpene probably aromadendrene, and of a sesquiterpene alcohol.

Use.—Oil of *Eucalyptus australiana,* Type, has the same uses as other cineole-containing (medicinal) eucalyptus oils (see above).

Oil of *Eucalyptus Dives* Schauer,[37] Var. "C"

Introduction.—This plant represents one of the most robust eucalypts belonging to the "Broad-leaved Peppermint" group. A physiological form of the well-known *Eucalyptus dives,* Type, it is consequently identical with the latter from the botanical point of view. However, the oil, in both chemical and physical properties, is practically identical with that obtained from *E. australiana* and bears no resemblance whatsoever in chemical composition to that from *E. dives,* Type. The species grows in good stands in the Tumbarumba-Tumut-Batlow District of southern New South Wales. It is a very attractive tree. Considerable quantities of the oil are exported. No better oil for medicinal purposes has yet been marketed. There would be a greatly increased demand for eucalyptus oil in all parts of the world if the oil from this species could be marketed in greater quantity.

Yield of Oil.—The leaves and terminal branchlets yield from 2 to 4 per cent of a water white oil.

Physicochemical Properties.—

Specific Gravity at 15°/15°	0.917 to 0.922
Optical Rotation	Up to +4°
Refractive Index at 20°	1.4609 to 1.4640
Cineole Content	68 to 75%
Congealing Point	−12° to −16° C.
Solubility in 70% Alcohol (W/W)	Soluble in 1.1 to 1.5 vol.

Chemical Composition.—The chemical composition of oil of *Eucalyptus dives,* var. "C" resembles that of oil of *E. australiana,* Type. The oil contains a high percentage of cineole, and some α-terpineol, geraniol, and citral,

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[37] G. G. Walpers, "Repertorium Botanices Systematicae," Vol. 2, Leipzig (1843), 926.

the latter imparting a refreshing odor to the oil. Penfold and Morrison,[38] and Ralph [39] identified the following compounds in oil of *Eucalyptus dives,* var. "C":

Cineole. According to Penfold and Morrison, the oil contains from 60 to 70 per cent of cineole, which they identified by means of the resorcinol addition compound m. 83°.

α-Terpineol. Identified by preparation of the phenylurethane m. 113°, and the α-naphthylurethane m. 148° (Penfold and Morrison).

Piperitone, Geraniol, Sesquiterpene, l-α-Phellandrene, and Citral. The same authors found that the oil contains up to 6 per cent of piperitone, some geraniol, a sesquiterpene, l-α-phellandrene, esters, and citral.

Methyl Cinnamate and Geranic Acid. Ralph noted the presence of methyl cinnamate (4.4 per cent) and geranic acid (0.7 per cent).

Eudesmol. The same author identified eudesmol m. 79.5°, $[\alpha]_D$ +37° 42′. A mixed melting point determination with an authentic sample of eudesmol gave no depression.

Use.—Oil of *Eucalyptus dives,* var. "C" is used like all other cineole-containing (medicinal) eucalyptus oils (see above).

OILS OF *Eucalyptus Elaeophora* F. VON MUELLER, *E. Sideroxylon* WOOLLS. AND *E. Leucoxylon* F. VON MUELLER

Introduction.—These three trees are discussed together here, as they are invariably exploited as a group.

***Eucalyptus Elaeophora* F. von Mueller.**[40]—This is a rather low, stunted tree with fibrous bark, known vernacularly as "Apple Jack." It was described in detail by Baker and Smith [41] in 1920. The tree grows in Victoria and in the central districts of New South Wales.

***Eucalyptus Sideroxylon* Woolls.**[42]—This tree, commonly known as the "Red Flowering Ironbark," is a medium sized forest tree with a deeply furrowed black bark. Its botanical characteristics have also been described by Baker and Smith.[43] The tree occurs in the coastal area of Eastern Australia.

***Eucalyptus Leucoxylon* F. von Mueller.**—The tree known as "White Gum" was described by Baron von Mueller [44] who confused it with *E.*

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[38] *J. Proc. Roy. Soc. N. S. Wales* **61** (1927), 63; **62** (1928), 78.

[39] *Ibid.* **80** (1946), 208.

[40] "Fragmenta Phytographiae Australiae," Vol. 4, Melbourne (1863–4), 52.

[41] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 177.

[42] T. L. Mitchell, "Journal of an Expedition into the Interior of Tropical Australia," London (1848), 339. Cf. *Proc. Linnean Soc. N. S. Wales* [2], **1** (1886), 859.

[43] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 135.

[44] *Trans. Victorian Inst. Melbourne* **1** (1855), 33.

sideroxylon. It is a moderate sized tree with a smooth bark, found in Victoria and South Australia.

Range, Habitat, and Occurrence.—*Eucalyptus sideroxylon* and *E. leucoxylon* grow near Bendigo and Maryborough in Victoria. *Eucalyptus elaeophora* is found around St. Arnaud, Navarre, Avoca, and distilled in the same state.

Commercial production is restricted to Victoria.

Yield of Oil.—The leaves and terminal branchlets of all three species yield from 1.5 to 2.5 per cent of oil.

Physicochemical Properties.—

	E. sideroxylon	*E. elaeophora*	*E. leucoxylon*
Specific Gravity at 15°/15°	0.915 to 0.919	0.916 to 0.922	0.910 to 0.920
Optical Rotation	+0° 30′ to +2° 0′	+0° 30′ to +2° 0′	+0° 30′ to +2° 54′
Refractive Index at 20°	1.4612 to 1.4624	1.4612 to 1.4624	1.4612 to 1.4624
Cineole Content	65 to 75%	65 to 80%	65 to 75%
Congealing Point	−12° to −19°	−8° to −19°	−12° to −19°
Solubility in 70% Alcohol (V/V)	Soluble in 4 vol.	Soluble in 2 vol.	Soluble in 6 vol.

The cineole content and solubility of the three oils vary according to the age of the leaf. The adult foliage yields an oil richer in cineole and more soluble in dilute alcohol than that obtained from the "sucker" leaves.

The leaves of all three species are invariably distilled together, the "Ironbark" and "Apple Jack" predominating. The mixed commercial oil is known as "Apple Jack" and "Ironbark."

Chemical Composition.—The oils consist principally of cineole (70 to 75 per cent), pinene, sesquiterpenes, and small amounts of volatile aldehydes, chiefly isovaleraldehyde.

OIL OF *Eucalyptus Cneorifolia* DE CANDOLLE[45]

Botany.—This tree, a narrow-leaved "Mallee," is confined almost entirely to Kangaroo Island, South Australia. It is the principal tree on the island, and serves for the distillation of eucalyptus oil for pharmaceutical purposes. The botanical characteristics of this shrub have been described in detail by Baker and Smith.[46]

Yield of Oil.—The yield of oil obtained from the leaves and terminal branchlets by commercial distillers is about 2 per cent.

The oil derived from this species has recently been examined by a number

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[45] A. P. and A. L. P. P. de Candolle, "Prodromus Systematis Naturalis Regni Vegetabilis," Vol. 3, Paris (1828), 220.

[46] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 192.

of workers in South Australia.[47,48,49] Monthly distillations were made of (a) old leaf material and (b) young leaf material and growing tips. It was found that the yield of oil from young leaves increased during the period of active growth and, concomitantly, a fall in the density and a rise in the laevorotation of the oil were observed. The terpenes were found to contain considerable quantities of *l*-β-phellandrene during the flush period. Oil from the old leaves showed no marked change in the nature of the terpenes, nor in the terpene content throughout the year. On the other hand, wide fluctuations were found in the oil obtained from the young leaves and growing tips. The yield of oil increased gradually in the late spring and early summer months, which is the period of active growth; the oil had then an exceptionally high hydrocarbon content.

Physicochemical Properties.—The following results were obtained by an examination of a selection of authentic *E. cneorifolia* samples personally collected and furnished by Messrs. F. H. Faulding & Co. Ltd., Sydney:

Specific Gravity at 15°/15°	0.915 to 0.925
Optical Rotation	−1° 0′ to −5° 0′
Refractive Index at 20°	1.4654 to 1.4681
Cineole Content	70 to 73%
Congealing Point	−13.5° to −15°
Solubility in 70% Alcohol (V/V)	Soluble in 1.5 to 3 vol.

The crude oil is usually of a reddish-brown color, with a most pronounced odor of aromatic aldehydes (cuminal and phellandral). The crude oil, therefore, has to be rectified.

Chemical Composition.—Oil of *Eucalyptus cneorifolia* contains about 70 per cent of cineole, and a number of constituents of minor importance, among them aldehydes, ketones, and phenols (in this connection see the monograph on Oil of *Eucalyptus polybractea,* re "Aromadendral" and "Australol").

The following constituents have been identified in the oil of *Eucalyptus cneorifolia:*

Cineole. The oil contains about 70 per cent of cineole (Baker and Smith[50]).

Pinene. Berry, Macbeth and Swanson[51] observed a green color, indicating the presence of pinene, on treatment of the terpene fraction of the oil with nitrous acid; but in a later investigation Berry[52] found no pinene in this fraction of the oil distilled from young tips.

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[47] Berry, Macbeth and Swanson, *J. Chem. Soc.* (1937), 986, 1443.

[48] Berry, *J. Proc. Australian Chem. Inst.* **14** (1947), 173.

[49] Berry, *ibid.*, 383.

[50] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 193.

[51] *J. Chem. Soc.* (1937), 1447.

[52] *J. Proc. Australian Chem. Inst.* **14** (1947), 196.

α- and β-Phellandrene and Dipentene. The same author [53] identified α- and β-phellandrene by means of their α-nitrosites (m. 119°, and m. 102°–103°, respectively), and dipentene, by preparation of its tetrabromide m. 124°.

p-Cymene. Characterized by oxidation to *p*-hydroxyisopropylbenzoic acid m. 158° (Berry [54]).

Cuminal and Phellandral. Berry, Macbeth and Swanson [55] identified cuminal by means of its oxime m. 57.2° (Berry), and its semicarbazone m. 210°–211°, and phellandral by means of its semicarbazone m. 202°–203°. Oxidation yielded the carboxylic acid of phellandral m. 143.5°–144.5°.

Cryptone. Identified by Cahn, Penfold and Simonsen,[56] who prepared the semicarbazone m. 185°, and the *p*-nitrophenylhydrazone m. 168°–169°. Reduction yielded 4-isopropylcyclohexanone; subsequent oxidation gave β-isopropyladipic acid.

p-Isopropylphenol. This phenol, formerly called "Australol," was isolated by Penfold and Grant.[57] It melts at 62°–63°, and yields a benzoyl derivative m. 72°–73°.

Macropone and A Ketonic Substance(?). Reuter [58] observed in the oil of *Eucalyptus cneorifolia* a ketophenol which he named "macropone." It gave a semicarbazone m. 216°, and a semicarbazone of the benzoate m. 173°.

The other ketonic substance yielded a semicarbazone m. 188°, and a 2,4-dinitrophenylhydrazone m. 208°.

Use.—Oil of *Eucalyptus cneorifolia* serves for the same purposes as all other cineole-containing (medicinal) eucalyptus oils (see above).

OIL OF *Eucalyptus Viridis* R. T. BAKER [59]

Botany and Occurrence.—This shrub, known as the "Green," "Red," or "Brown Mallee," has been fully described by Baker and Smith.[60] It occurs in commercial stands in the "Mallee" country of New South Wales and Victoria. The shrub rarely attains tree size. The oil was not produced commercially until within comparatively recent years, for early investigations showed the leaves and terminal branchlets to yield only 1 per cent of oil, the latter containing less than 50 per cent of cineole.[61] The oil is now produced at Bendigo in Victoria, where good areas of *Eucalyptus viridis* are found in association with *E. sideroxylon.*

Yield of Oil.—Leaves and terminal branchlets yield 1.5 per cent of oil.

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[53] *Ibid.* 383.

[54] *Trans. Proc. Roy. Soc. South Australia* **46** (1922), 207.

[55] *J. Chem. Soc.* (1937), 988.

[56] *Ibid.* (1931), 1366. Cf. Berry, Macbeth and Swanson, *ibid.* (1937), 986, 1443.

[57] *J. Proc. Roy. Soc. N. S. Wales* **56** (1922), 220.

[58] *J. Proc. Australian Chem. Inst.* **5** (1938), 290.

[59] *Proc. Linnean Soc. N. S. Wales* **25** (1900), 316.

[60] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 231.

[61] *Ibid.*

Physicochemical Properties.—A typical specimen of the oil had these properties:

Color	Pale Lemon
Specific Gravity at 15°/15°	0.926
Optical Rotation	$+0° 53'$
Refractive Index at 20°	1.4632
Congealing Point	$-9°$ C.
Cineole Content	80%
Solubility in 70% Alcohol (V/V)	Soluble in 2 vol.

Chemical Composition.—The oil consists principally of cineole (70 to 80 per cent), pinene, cymene, sesquiterpene, and cuminal, phellandral, and *l*-cryptone.

Oil of *Eucalyptus Dumosa* Schauer[62]

Botany and Occurrence.—This "Mallee," sometimes called the "Bull Mallee," has been described by Baker and Smith.[63]

Leaves and terminal branchlets have been examined from areas in New South Wales, Victoria, and South Australia. Until recently the oil was rarely obtained commercially, for the low yield of oil (about 1 per cent), as well as a low cineole content (60 per cent), precluded its economic exploitation.

An increased demand for eucalyptus oil at higher prices brought about by World War II stimulated production, with the result that *dumosa* oil, either alone, or in admixture with other "Mallee" oils, is now obtainable in small quantities.

Eucalyptus dumosa occurs in the principal oil producing areas in New South Wales and Victoria, where *Eucalyptus polybractea* also abounds. The foliage is distilled either alone or in admixture with the latter species, especially where stands have been found to yield oil in greater quantity and of higher cineole-content than those formerly examined.

Yield of Oil.—The leaves and terminal branchlets yield 2 per cent of oil.

Physicochemical Properties.—A typical specimen of the oil had these properties:

Specific Gravity at 15°/15°	0.9187
Optical Rotation	$+5° 30'$
Refractive Index at 20°	1.4620
Congealing Point	$-18°$ C.
Cineole Content	66%
Solubility in 70% Alcohol (V/V)	Soluble in 5 vol.

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[62] Schauer, in G. G. Walpers, "Repertorium Botanices Systematicae," Vol. 2, Leipzig (1843), 925.

[63] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 187.

Chemical Composition.—The oil of *E. dumosa* consists principally of cineole (70 per cent) and pinene, with some cuminal, phellandral and *l*-cryptone. Small quantities of volatile aldehydes are also present.

OIL OF *Eucalyptus Smithii* R. T. BAKER[64]

Botany and Occurrence.—*Eucalyptus smithii* is a medium sized forest tree, but often attains a height of 150 ft., and a diameter of 2 to 5 ft. The bark in the lower portion of the main trunk is similar to that of the so-called "Peppermint" group of eucalypts, but the upper trunk and branches are smooth. The abnormal or juvenile leaves are difficult to distinguish from those of other oil-yielding eucalypts, such as *Eucalyptus australiana, E. phellandra, E. numerosa,* etc. In this connection the article by Baker and Smith[65] should be consulted.

The tree is known by various vernacular names, such as "White Top," "Gully Ash," or "White Ironbark." It grows sparingly in the southern districts of New South Wales, particularly around Hilltop, Monga, and Braidwood, extending into Victoria.

Yield of Oil.—The leaves and terminal branchlets yield 2 per cent of a good cineole-type of oil. Rectification is necessary to remove the volatile aldehydes.

Physicochemical Properties.—Commercial samples examined by the authors, together with those of their own distillation from cultivated trees, have given the following results:

Specific Gravity at 15°/15°	0.9160 to 0.9198
Optical Rotation	+4° 48′ to +5° 36′
Refractive Index at 20°	1.460 to 1.465
Cineole Content	75 to 80%
Solubility in 70% Alcohol (W/W)	Soluble in 1 vol.

Chemical Composition.—According to Baker and Smith,[66] the principal constituents of the oil are cineole (75 to 80 per cent), pinene, eudesmol, sesquiterpenes, volatile aldehydes (chiefly isovaleraldehyde), a phenol, small quantities of esters, and a paraffin m. 64°.

OIL OF *Eucalyptus Dives* SCHAUER,[67] TYPE

Botany.—*Eucalyptus dives,* commonly known as the "Broad-leaved Peppermint" is usually a moderate sized tree, although it often attains large

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[64] *Proc. Linnean Soc. N. S. Wales* **24** (1899), 292.

[65] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 138.

[66] *Ibid.*, 346.

[67] In G. G. Walpers, "Repertorium Botanices Systematicae," Vol. 2, Leipzig (1843), 926.

dimensions. It has a grayish-brown stringy bark, very similar in appearance to that of other species known as "Narrow-leaved Peppermints."

The leaves vary greatly in shape and size, being sometimes sessile, opposite and cordate, or ovate-lanceolate on the same tree. The tree bears flowers and fruit in a very early stage of its growth.[68]

The "sucker" or abnormal leaves are often of characteristic glaucous color. An area of these trees awaiting cutting presents a very pleasing appearance.

Habitat, Range, and Occurrence.—The tree is common throughout the whole of the coastal ranges of New South Wales and Victoria.

Yield of Oil.—The leaves and terminal branchlets yield from 2 to 4 per cent (general average 3 per cent) of a pale yellow oil, the yield varying within these limits, according to the district, season, etc.

Physicochemical Properties.—Oils obtained from material distilled by the authors exhibited the following values:

Specific Gravity at 15°/15°	0.8892 to 0.9063
Optical Rotation	−58° 0′ to −70° 0′
Refractive Index at 20°	1.4784 to 1.4812
Piperitone Content	45 to 53%
Flash Point (Closed Cup)	60° C. (140° F.)
Solubility in 70% Alcohol (W/W)	Soluble in 1.4 to 2 vol. for oil from old leaves, and up to 10 vol. for oil from young growth

Commercially distilled oils submitted for examination have given the following range of properties, viz.:

Specific Gravity at 15°/15°	0.889 to 0.910
Optical Rotation	−43° 48′ to −73° 30′
Refractive Index at 20°	1.4769 to 1.4814
Piperitone Content	40 to 50%
Solubility in 70% Alcohol (W/W)	Soluble in 4.5 to 10 vol.

Chemical Composition.—Oil of *Eucalyptus dives*, Type, contains from 40 to 50 per cent of piperitone, from 20 to 30 per cent of *l*-α-phellandrene, and small amounts of other terpenes, alcohols and *n*-valeraldehyde.

The following compounds have been identified by Baker and Smith,[69] Birch and Earl,[70] and Schimmel & Co.: [71]

n-Valeraldehyde. Identified by means of its semicarbazone m. 81° (Schimmel & Co.).

Camphene. Characterized by hydration to isoborneol m. 208° (Schimmel & Co.).

p-Cymene. Characterized by oxidation to isopropylbenzoic acid m. 161° (Schimmel & Co.).

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[68] Baker and Smith, "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 304.

[69] *Ibid.*, 305, 390, 412.

[70] *J. Proc. Roy. Soc. N. S. Wales* **72** (1938), 55.

[71] *Ber. Schimmel & Co.* (1928), 46; (1930), 41.

γ-Terpinene. Characterized by oxidation to tetrahydroxy-*p*-menthane m. 235°–236° (Schimmel & Co.).

Dipentene. Identified by means of the dihydrochloride m. 52°, and the tetrabromide m. 120°–121° (Schimmel & Co.).

α-Thujene. Identified by preparation of the nitrolamine m. 162°, and by oxidation to thujaketonic acid m. 75°–76° (Birch and Earl).

1-Terpinen-4-ol (Δ^1-Terpinenol-4). Schimmel & Co. found that the oil contains from 3 to 4 per cent of 1-terpinen-4-ol, which they identified by preparation of the α-naphthylurethane m. 105°, and by oxidation to trihydroxymenthane m. 113°–115°. Incidentally, oil of *Eucalyptus dives*, Type, is a very suitable raw material for the isolation of 1-terpinen-4-ol.

l-α-Phellandrene and Piperitone. The two principal constituents of the oil, *l*-α-phellandrene (20 to 30 per cent) and piperitone (40 to 50 per cent), were identified by Baker and Smith. *l*-α-Phellandrene yielded a nitrosite m. 110°–111°; piperitone gave two semicarbazones m. 219°–220°, and m. 175°–176°, respectively.

p-Menthane-1,2,3-triol(?). According to recent investigation carried out by Ralph,[72] this triol crystallizes from the higher boiling fractions of piperitone, after separation by means of the bisulfite compound. Oxidation gave α-isopropylglutaric acid. Dehydration yielded carvotanacetone and *p*-cymene. More recent work, however, indicates the empirical formula to be $C_{10}H_{18}O_2$, and not that of a triol.

Use.—Very large quantities of this oil are distilled for the manufacture of synthetic thymol and menthol from its principal constituent, piperitone. A considerable proportion of the oil is exported for the same purpose.

The oil is also used for the separation of metallic sulfides in the flotation process.

Physiological Forms.—The occurrence of physiological forms among the oil-yielding eucalypts was first observed with this species[73] (see above).

The following table gives the physicochemical properties of the oils obtained from *Eucalyptus dives*, Type, and varieties "A," "B" and "C" for comparison:

	Type	*Var. "A"*	*Var. "B"*	*Var. "C"*
Yield of Oil	2.5 to 4%	1.5 to 4%	3 to 4%	2 to 4%
Specific Gravity at 15°/15°	0.889 to 0.907	0.863 to 0.877	0.906 to 0.915	0.917 to 0.922
Optical Rotation	−58° 0′ to −70° 0′	−44° 0′ to −66° 0′	−13° 0′ to −28° 0′	Up to +4° 0′
Refractive Index at 20°	1.4788 to 1.4810	1.4750 to 1.4792	1.467 to 1.471	1.4635 to 1.4742
Piperitone Content	45 to 53%	5%	10 to 20%	Under 5%
Cineole Content	Nil	Nil	25 to 45%	68 to 75%
Phellandrene * Content	About 40%	60 to 80%	Present in quantity	Absent

* "Phellandrene" in Type and Var. "A" includes other terpenes.

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[72] *Soap, Perfumery & Cosmetics* **22** (1949), 38. *Australian J. Sci.* **11** (1948), 98.

[73] Penfold and Morrison, *J. Proc. Roy. Soc. N. S. Wales* **61** (1927), 54.

Oil of *Eucalyptus Australiana*, Var. "B"
(*Eucalyptus phellandra*, B. and S.[74])

Botany.—This species, one of the well-known "Narrow-leaved Peppermints," is botanically identical with *Eucalyptus australiana*, Type,[75] and is thus a physiological form. This species was formerly confused with the *Eucalyptus amygdalina* of Labillardière, a name now confined to the "Narrow-leaved Peppermint" of Tasmania.

For a detailed discussion on the controversial issues involved in the botanical differentiation of this species, the work of Baker and Smith and, particularly, our own paper should be consulted.

Habitat, Range, and Occurrence.—*Eucalyptus australiana*, var. "B" occurs extensively on the mountain ranges of New South Wales and Victoria, being especially abundant in the Braidwood and South Coast districts of New South Wales. Thousands of tons of the oil of this species have been marketed during the past fifty years.

No other species has been exploited so extensively for industrial purposes, for the oil is ideally suited for the manufacture of disinfectants and deodorants.[76]

Yield of Oil.—The leaves and terminal branchlets yield from 3 to 4.5 per cent of a colorless to pale yellow oil.

Physicochemical Properties.—Commercially distilled oils fall within the following range of values, viz.:

Specific Gravity at 15°/15°	0.902 to 0.905
Optical Rotation	−13° 24′ to −28° 18′
Refractive Index at 20°	1.4660 to 1.4695
Cineole Content	20 to 50%
Phellandrene and Other Terpenes	35 to 40%
Solubility in 70% Alcohol (W/W)	Soluble in 1.3 to 10 vol.

Chemical Composition.—The chemical composition of oil of *Eucalyptus australiana*, var. "B," was investigated by Baker and Smith,[77] and by Penfold and Morrison,[78] who identified the following constituents:

l-α-Phellandrene. The oil contains from 35 to 40 per cent of *l*-α-phellandrene (characterized by the nitrosite test), and other terpenes.

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[74] Baker and Smith, "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 280.

[75] Penfold and Morrison, *J. Proc. Roy. Soc. N. S. Wales* **69** (1935), 111.

[76] Penfold and Morrison, "Uses of Commercial Eucalyptus Oils," *Sydney Technological Museum, Bull.* No. 17, Rev. Ed. (1938).

[77] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 280, 344 and 372.

[78] *J. Proc. Roy. Soc. N. S. Wales* **69** (1935), 111.

1,8-Cineole. The oil contains from 20 to 50 per cent of 1,8-cineole.

α-Terpineol. The α-terpineol was identified by means of its phenylurethane m. 112°.

The oil also contains: pinene, piperitone, geraniol, eudesmol, esters, and sesquiterpenes.

Use.—The oil is used extensively for disinfectants, deodorants, and many other industrial purposes. It is an admirable solvent, and is also employed in the separation of useful minerals by the so-called flotation process.[79]

OIL OF *Eucalyptus Dives* SCHAUER, VAR. "A"

Introduction.—It has been known for many years that oil of *Eucalyptus dives* from many parts of Victoria contained only 5 to 15 per cent of piperitone and, consequently, was of no value for the manufacture of synthetic thymol and menthol. The tree is indistinguishable from *Eucalyptus dives*, Type, in the field. Careful investigations have shown that this physiological form of *E. dives* is identical botanically with *E. dives*, Type. The essential oil, of course, differs from that of the Type, for it contains a large quantity of *l*-α-phellandrene and less than 20 per cent of *l*-piperitone. The oil possesses an odor characteristic of piperitol, which readily distinguishes it from *E. dives*, Type.

Yield of Oil.—The yield of oil from the leaves and terminal branchlets varies from 2 to 4 per cent.

Physicochemical Properties.—The physicochemical properties fall within the following range:

Specific Gravity at 15°/15°	0.8630 to 0.8772
Optical Rotation	−44° 0′ to −66° 0′
Refractive Index at 20°	1.4759 to 1.4792
Solubility in 70% Alcohol (W/W)	Insoluble in 10 vol.

Chemical Composition.—According to Penfold and Morrison,[80] oil of *Eucalyptus dives*, var. "A" contains from 60 to 80 per cent of *l*-α-phellandrene and other terpenes, 5 to 15 per cent of *l*-piperitone, piperitol, and sesquiterpenes.

Use.—The oil is employed for numerous industrial purposes—such as mineral flotation, disinfectants, and as a solvent.

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[79] Penfold and Morrison, "Uses of Commercial Eucalyptus Oil," *Sydney Technological Museum, Bull.* No. 17, Rev. Ed. (1938).

[80] *J. Proc. Roy. Soc. N. S. Wales* **61** (1927), 60.

OIL OF *Eucalyptus Numerosa* MAIDEN, TYPE
(Syn. *E. lindleyana* De Candolle)

Botany.—This eucalypt has had a "battledore and shuttlecock" experience at the hands of systematic botanists.

Although accurately described by Maiden,[81] it was synonymized by Blakely [82] as *E. lindleyana* de Candolle.

Baker and Smith [83] refer to the same species as *Eucalyptus radiata* Sieber.

It is a fairly tall tree with narrow lanceolate leaves about 6 in. long. The abnormal leaves are thin, sessile and almost perfoliate, about 3 to 4 in. in length, and closely resemble the "Narrow-leaved Peppermint" (*Eucalyptus australiana*). A distinctive feature is the clean white upper limbs, free from bark. This very attractive and foliaceous tree grows quickly under favorable conditions.

Yield of Oil.—The leaves and terminal branchlets yield a yellow-colored oil, averaging from 2.3 to 3 per cent, with a pronounced odor characteristic of piperitol.

Physicochemical Properties.—A great number of distillations conducted by the authors have yielded oils whose properties fall within the following range:

Specific Gravity at 15°/15°	0.8904 to 0.8948
Optical Rotation	−25° 0′ to −35° 0′
Refractive Index at 20°	1.4775 to 1.4786
Cineole Content	Trace only
Phellandrene Content	Present in abundance
Ester Number (1½ Hr. Hot Sap.)	16 to 19
Ester Number after Acetylation	66 to 94
Solubility in 70% Alcohol (W/W)	Soluble in 10 vol.

Toward the end of the year (summer season) and in various localities, leaves have been distilled which yielded oils low in piperitol content and possessing the following characters:

Specific Gravity at 15°/15°	0.8643 to 0.8865
Optical Rotation	−50° 22′ to −59° 45′
Refractive Index at 20°	1.4762 to 1.4777
Solubility in 80% Alcohol (W/W)	Insoluble in 10 vol.

Chemical Composition.—Oil of *Eucalyptus numerosa,* Type, consists chiefly of *l*-α-phellandrene (60 to 80 per cent) and other terpenes; it also contains a small amount of piperitone (about 5 per cent), piperitol, pinene, esters, sesquiterpenes, and traces of cineole.

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[81] *Proc. Linnean Soc. N. S. Wales* **29** (1904), 752.

[82] "A Key to the Eucalypts," The Worker Trustees, Sydney (1934).

[83] "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 306.

The following constituents have been identified by Baker and Smith,[84] and by Penfold and Morrison:[85]

l-α-Phellandrene. This terpene, the principal component (60 to 80 per cent) of the oil, was identified by means of its nitrosite m. 121°–122°.

Piperitol. Oxidation with Beckmann's chromic acid mixture yielded piperitone, identified by preparation of the β-semicarbazone m. 175°–176°.

Piperitone. About 5 per cent of piperitone.

Cineole. Traces.

Pinene, Esters, and Sesquiterpenes. Small quantities.

Use.—At present the oil is used for mineral flotation purposes, and as a source of phellandrene.

OIL OF *Eucalyptus Numerosa* MAIDEN, VAR. "A"
(Syn. *E. lindleyana* De Candolle, Var. "A")

Introduction.—This tree occurs in association with *Eucalyptus numerosa*, Type, but almost pure stands of this variety have been located and exploited since its discovery in 1932.[86] It has been distilled commercially in the Braidwood District of New South Wales.

Yield of Oil.—The leaves and terminal branchlets yield from 2.3 to 3 per cent of a yellow oil.

Physicochemical Properties.—

Specific Gravity at 15°/15°	0.901 to 0.910
Optical Rotation	−46° 0′ to −65° 0′
Refractive Index at 20°	1.4790 to 1.4820
l-Piperitone Content	50%
l-α-Phellandrene and Other Terpenes	40%
Solubility in 70% Alcohol (W/W)	Soluble in 1.2 to 1.5 vol.

Chemical Composition.—The chemical composition of oil of *Eucalyptus numerosa*, var. "A" closely resembles that of *E. dives*, Type.

The oil contains about 40 per cent of *l*-α-phellandrene and other terpenes, and about 50 per cent of *l*-piperitone. Its odor is characteristic of piperitone.

The above components were identified by Penfold and Morrison:[87]

l-α-Phellandrene. Nitrosite m. 121°–122°.

l-Piperitone. Hydroxylamino-oxime m. 169°–170°, α-oxime m. 118°–119°.

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[84] *Ibid.*, 307, 373 and 345.

[85] *J. Proc. Roy. Soc. N. S. Wales* **66** (1932), 181.

[86] Penfold and Morrison, *ibid.*

[87] *Ibid.*

OIL OF *Eucalyptus Macarthuri* H. DEANE AND J. H. MAIDEN[88]

Botany.—A tree of medium to large size with a coarse bark, whence the common name "Paddy's River Box" or "Camden Woollybutt." *Eucalyptus macarthuri* cannot be confused in the field with any other eucalypt. The odor of the leaves when crushed at once distinguishes the species from practically all others, with the possible exception of *E. acervula* Hook.[89]

Habitat, Range, and Occurrence.—*Eucalyptus macarthuri* prefers swampy or low-lying land and the banks of streams. It is particularly abundant at Mittagong, Bowral, Moss Vale, Wingello on the southern highlands of New South Wales, and Jenolan in the same state.

The tree grows fast and responds readily to cultivation. When felled it quickly throws out new shoots (generally called "suckers") from the stump.

Yield of Oil.—The yield of oil from the leaves and terminal branchlets of forest trees varies from 0.15 to 0.3 per cent (usually 0.2 per cent), although, at certain periods of the year, yields of up to 0.5 per cent have been obtained.

The yields from cultivated trees have varied from 0.5 to 1 per cent. The bark contains an oil similar in composition to that of the leaf but lower in yield (usually about 0.15 per cent).

Physicochemical Properties.—The authors have examined many commercial samples of this oil, as well as oils obtained from leaves from experimental plots, with the following typical properties:

	I	*II*	*III*	*IV*
Specific Gravity at 15°/15°	0.9284	0.9292	0.9238	0.9274
Optical Rotation	+1° 36′	+2° 12′	...	+3° 6′
Refractive Index at 20°	...	...	1.4704	1.4744
Geranyl Acetate Content	72.6%	68.6%	67.9%	67%
Geraniol Content	2.9%	2.6%	7.2%	...
Eudesmol Content	15.7%	17.1%	15.0%	...
Solubility in 70% Alcohol (W/W)	1.2 vol.	1.2 vol.	1.2 vol.	1.2 vol.

The oil is often rectified by users for the purpose of improving the color and odor. Two samples gave the following results:

	I	*II*
Specific Gravity at 15°/15°	0.9164	0.9168
Optical Rotation	+0° 7′	+0° 9′
Refractive Index at 20°	1.4665	1.4660
Geranyl Acetate Content	79%	84%
Solubility in 70% Alcohol (W/W)	1 vol.	1 vol.

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[88] *Proc. Linnean Soc. N. S. Wales* **24** (1899), 448.

[89] Baker and Smith, "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 314.

As an example of an oil, from a tree cultivated near Sydney, the following results are worthy of record:

Age of Tree	7 yr.
Height	45 ft.
Diameter	12 in.
Weight of Foliage	418 lb.
Yield of Oil	0.4%
Specific Gravity at 15°/15°	0.9214
Optical Rotation	+3° 45′
Refractive Index at 20°	1.4697
Geranyl Acetate Content	69.1%
Geraniol Content	5.3%
Eudesmol Content	8.1%
Solubility in 70% Alcohol (W/W)	1.5 vol.

Chemical Composition.—The chemical composition of oil of *Eucalyptus macarthuri*, which contains geranyl acetate as chief constituent, has been investigated by Smith,[90] and Penfold and Morrison,[91] who identified the following compounds:

Aldehydes (Isovaleraldehyde) and Esters (Isoamyl Butyrate, Butyl Butyrate). The two last named authors found that the oil contains small quantities of low boiling aldehydes (isovaleraldehyde, etc.), and the isoamyl and butyl esters of butyric acid. The low boiling aldehydes impart a powerful, unpleasant odor to the first fractions of the natural (crude) oil. They may be removed by fractionation *in vacuo.*

Pinene. Characterized by green color on treatment with nitrous acid (Smith).

Geraniol and Geranyl Acetate. According to the same author, the oil contains about 10 per cent of geraniol and 60 per cent of geranyl acetate. The geraniol was characterized by oxidation to citral.

Phenols(?) and a Sesquiterpene(?). Penfold and Morrison observed phenols and a sesquiterpene in the oil.

Eudesmol. The presence of eudesmol in oil of *Eucalyptus macarthuri* was noted years ago by Smith.

Use.—The crude oil is used in perfumery, but primarily as a denaturant of alcohol for the manufacture of perfumes. It is usually of a reddish color, due to the action of the phenols and free acid upon the iron of the condensers employed in the field stills. If tin, or lead-tin coils are used, the oil is of a pale yellow color.

The residue left in the stills after rectification of the crude oil represents a very good source of eudesmol; this sesquiterpene alcohol constitutes a valuable fixative. Eudesmol forms an acetate, which in Australia was a useful wartime substitute for oil of bergamot and its constituents.

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[90] *J. Proc. Roy. Soc. N. S. Wales* **34** (1900), 142.

[91] *Sydney Technological Museum, Bull.* No. 2, 4th Ed. (1944), 15.

OIL OF *Eucalyptus Citriodora* HOOKER[92]

Botany.—*Eucalyptus citriodora,* also known as "Spotted Gum," "Citron-scented Gum," or "Lemon-scented Gum,"[93] is a large tree, often attaining a great height, with a smooth whitish to pale pink bark, sometimes with gray spots. The tree was originally classified as a variety of *Eucalyptus maculata,* from which it differs only slightly in morphological characteristics, although the latter contains very little oil (and of entirely different composition).

Both trees furnish excellent hardwood timbers.

Eucalyptus citriodora is readily identified by its characteristic fruit and by the deliciously fragrant citronellal odor of the crushed leaves.

Habitat, Range, and Occurrence.—*Eucalyptus citriodora* is essentially a Queensland tree, being particularly abundant in the north coast area of that state. It grows within 10 to 15 miles of the coast and extends from the Maryborough District—the extreme southern limit—to the north of Cairns. The principal areas of distillation are around Gladstone and Maryborough.

Eucalyptus citriodora has been extensively cultivated as an ornamental tree throughout the Commonwealth of Australia. It is grown commercially in the Seychelles Islands, Java, South Africa, Guatemala, the Belgian Congo, and Brazil.

Yield of Oil.—The leaves and terminal branchlets of forest trees yield from 0.5 to 0.75 per cent, those of isolated trees from 1 to 1.3 per cent of oil. Cultivated trees yield up to 2 per cent.

Exploitation.—The utilization of this tree for oil distillation is not encouraged by the Queensland Forest Service. As mentioned above, *Eucalyptus citriodora* is a valuable timber tree, very much sought after for mine props, general construction purposes, and for railway sleepers. Consequently, most of the oil of commerce is distilled from trees growing on privately controlled forest areas.

Forest trees carry very small heads of foliage, and it is only by felling and allowing the "sucker" leaves to grow from the stumps that any considerable quantity of leaves can be obtained for distillation.

The tree responds readily to cultivation, the only way in which regular production of oil may be assured. The tree must be grown as a special crop for oil purposes, and not as a timber tree, if the industry is to be successfully established in Australia.[94]

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[92] T. L. Mitchell, "Journal of an Expedition into the Interior of Tropical Australia," London (1848), 235.

[93] Baker and Smith, "A Research on the Eucalypts and Their Essential Oils," 2d Ed. (1920), 323.

[94] Penfold and Morrison, "Commercial Eucalyptus Oils," *Sydney Technological Museum, Bull.* No. 2 (1944), 16.

Physicochemical Properties.—Good commercial samples, practically colorless, but unrectified, have given the following values:

Specific Gravity at 15°	0.8658 to 0.8740
Optical Rotation	+2° 48′ to −2° 48′
Refractive Index at 20°	1.4510 to 1.4560
Citronellal Content	65 to 80%
Solubility in 70% Alcohol (W/W)	Soluble in 1.3 to 1.7 vol.

Samples of oil freshly distilled by the authors from cultivated trees, also unrectified, have exhibited these properties:

Specific Gravity at 15°	0.8640 to 0.8770
Optical Rotation	+3° to −3°
Refractive Index at 20°	1.4511 to 1.4570
Citronellal Content	65 to 85%
Ester Number	12 to 60
Ester Number after Acetylation	230 to 292
Solubility in 70% Alcohol (W/W)	Soluble in 1.3 to 1.5 vol.

Chemical Composition.—As early as 1888, Schimmel & Co.[95] recognized that oil of *Eucalyptus citriodora* consists chiefly of citronellal. The other constituents of the oil were investigated years later by Chiris.[96]

Citronellal. This aldehyde, the principal constituent of the oil, was identified by means of its semicarbazone m. 82.5°. Citronellal seems to be present in the oil as a mixture of the *d*- and *l*-form; it has these properties:

b_{10}	88°–90°
d_{15}^{15}	0.855–0.856
α_D^{20}	+0° 50′ to −0° 50′
n_D^{20}	1.4480

Citronellol, Geraniol, and Esters. Aside from citronellal, the oil contains from 15 to 20 per cent of *d*- and *l*-citronellol, and about 5 per cent of geraniol. The latter was identified by oxidation to citral, the citronellol by preparation of the semicarbazone of pyrotartaric acid ester, m. 110°.

Citronellol and geraniol occur in the oil chiefly in free form, although partly as acetates. Citronellyl butyrate and citronellyl citronellate have been reported by Chiris.[97]

Pinene, Cineole, and Sesquiterpenes(?). The oil also contains pinene (probably in the *d*- form), traces of cineole (identified by means of the hydrobromide), and sesquiterpene compounds which were not identified.

Isopulegol. Chiris found from 1 to 2 per cent of isopulegol (b_{11} 90°–92°) in the oil. However, it has not yet been proved that the isopulegol occurs naturally in the foliage of the plant. Isopulegol may be formed by enolization of citronellal during storage of the oil. In fact, most of the oils that contain a large amount of citronellal also contain a small percentage of isopulegol.

[95] *Ber. Schimmel & Co.* (1888), 16.

[96] *Parfums France* (1925), 18, 72.

[97] *Ibid.*

Guaiol. This sesquiterpene alcohol $C_{15}H_{26}O$, m. 93°, $[\alpha]_D^{20}$ $-30°12'$, has recently been observed in some oils distilled and examined by the chemists associated with the Museum of Technology and Applied Science, Sydney. (Publication forthcoming.) Re Guaiol, see Vol. II of the present work, p. 278.

The bulk of commercial *Eucalyptus citriodora* oils, including those derived from cultivated trees in the Seychelles Islands, Guatemala, and Brazil, assay from 65 to 80 per cent of citronellal. Recently, however, a number of commercial samples from Queensland have been examined which contained only 40 per cent of citronellal.

Extensive investigations to determine the cause of this lower aldehyde content have been undertaken by the authors, but some time must elapse before they are completed. An indication of the probable cause is suggested under the heading of "Physiological Forms."

Meanwhile, there is some evidence to indicate that the aldehyde content diminishes rapidly soon after cutting of the foliage. Distillers often allow the leaves to remain in heaps from 24 to 48 hr. before they are transferred to the still. This will result in loss of aldehyde according to the conditions prevailing at the time, i.e., whether the leaves have been exposed to the sun, or whether the heaps are unduly bulky and fermentation ("sweating") has taken place.

Other observers[98] have directed attention to a progressive diminution of the oil content when leaves are stored for a lengthy period; but no previous reference seems to have been made to diminution of aldehyde content.

Analysis of the Oil.—Originally the aldehyde content of *Eucalyptus citriodora* oil was determined by the bisulfite method, which indicated a 90 to 95 per cent absorption.

Later[99] it was shown that other constituents are also soluble in the bisulfite-aldehyde solution, and the method had to be abandoned.

The modified Holtappel method of Penfold and Arneman[100] was found to give dependable results, and finally the British Official Method was adopted,[101] the results obtained showing that the oil from *Eucalyptus citriodora* contains from 40 to over 80 per cent of citronellal.

Physiological Forms.—Notwithstanding the exploitation of *Eucalyptus citriodora* oil for nearly fifty years, and the thousands of gallons which have been produced and exported, it is only within the last few months that physiological forms of the species have been definitely observed. There appear to be several forms, and a variety containing only about 7 per cent

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[98] *Perfumery Essential Oil Record* **29** (1938), 126, summarizing data published in Annual Report of Dept. Agr., Colony of Seychelles (1936).

[99] Pfau, *Perfumery Essential Oil Record* **16** (1925), 183.

[100] *J. Proc. Sydney Tech. Coll. Chem. Soc.* **4** (1929), 53.

[101] *Analyst* **57** (1932), 773.

of total aldehyde (calculated as citronellal) has been discovered.[102] The citronellal seems to have been replaced by citronellol and its esters.

Use.—The oil is used for perfumery purposes and as a source of citronellal for the manufacture of citronellol, hydroxycitronellal, and menthol. A small proportion of the oil added to germicides and disinfectants made from other eucalyptus oils greatly improves their odor.[103]

Suggested Additional Literature

A. R. Penfold, F. R. Morrison, and H. H. G. McKern, "Some Sources of Error in the Study of Plant Populations: *Eucalyptus citriodora* Hook.," *Researches on Essential Oils of the Australian Flora* (Museum of Technology and Applied Science, Sydney), Vol. I (1948), 8.

Isolates of the Eucalyptus Oils

Having discussed the commercially important eucalyptus oils, we shall describe briefly those constituents (viz., cineole, piperitone, and phellandrene) which are isolated from some of these oils and offered on the market in large quantities. For further data on these compounds, the reader is referred to Vol. II of this work, pp. 708, 396 and 41, respectively.

Cineole.—Cineole, sometimes called eucalyptol, is the principal constituent of eucalyptus oils prepared and sold for pharmaceutical use.

Commercial eucalyptol containing 98 per cent of cineole is now a regular article of commerce, being exported in large quantities to the United Kingdom and America.

It is prepared by freezing the oils of *E. polybractea* or *E. australiana* (preferably the former, because of its higher content of cineole and the ease with which it freezes).

Cineole is a water-white liquid of strong camphoraceous odor. Its physical properties should fall within these limits:

Specific Gravity at 15°/15°	0.928 to 0.930
Optical Rotation	+0° 18′ to −0° 18′
Refractive Index at 20°	1.4580 to 1.4600
Boiling Point	176° to 177°
Congealing Point	Not below 0°

The most reliable physical test consists in the determination of the congealing point. Any sample with a congealing point lower than 0° C. should be rejected.

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[102] Penfold and Morrison, *Australian J. Sci.* **11** (1948), 29.

[103] Penfold and Morrison, "Uses of Commercial Eucalyptus Oils," *Sydney Technological Museum, Bull.* No. 17 (1938), 2.

Piperitone.—Commercial piperitone, the principal constituent of *Eucalyptus dives,* Type, oil, has been produced for many years and is now a regular article of commerce, available in considerable quantities.

Piperitone is of a pale yellow color and usually contains from 90 to 92 per cent of actual ketone. It possesses the following properties:

Specific Gravity at 15°/15°	0.937 to 0.940
Optical Rotation	−40° 0′ to −46° 0′
Refractive Index at 20°	1.484 to 1.486

Phellandrene.—Considerable quantities of this terpene are now available, as a result of the production of piperitone from the oil of *Eucalyptus dives,* Type.

Practically the whole of the Australian production of commercial phellandrene is utilized for technical purposes, particularly as a solvent.

Commercial phellandrene produced from *E. dives* oil in the process of separation of *l*-piperitone contains about 50 per cent of *l*-α-phellandrene, with cymene, terpinene, α-thujene, and not more than 5 per cent of piperitone (usually 2 per cent).[104] Recent samples have exhibited the following chemical and physical properties:

	I	*II*
Specific Gravity at 15°/15°	0.8592	0.8531
Optical Rotation	−83° 0′	−89° 54′
Refractive Index	1.4713	1.4744
Boiling Point Range	170° to 190°	170° to 190°
Specific Rotation	−96° 36′	−105° 18′
Phellandrene Content	47%	50%

The phellandrene in these specimens was assayed by Kaufmann's method for the determination of diene numbers.[105]

For comparison, the physical properties of optically pure *l*-α-phellandrene found by Hancox and Jones [106] are recorded. This particular sample is considered to be 99.5 to 100 per cent pure:

Specific Gravity at 20°/4°	0.8324
Specific Optical Rotation at 20°	−177° 24′
Refractive Index at 20°	1.4724

EXAMINATION OF EUCALYPTUS OILS

Methods of analysis of essential oils have been fully described in Vol. I of this work, pp. 229 ff. Nevertheless, the authors believe that it will interest

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[104] A. J. Birch, *J. Proc. Roy. Soc. N. S. Wales* **71** (1937–38), 54, 261, 330.

[105] Hancox and Jones, *Univ. Queensland Papers, Dept. Chem.* **1,** No. 14 (1939), 2.

[106] *Ibid.*

the reader to become acquainted with those assays which are used in the scientific and commercial laboratories of Australia for the evaluation of eucalyptus oils.

In common with other essential oils, the following physical and chemical properties of eucalyptus oils are first determined:

1. Specific Gravity at 15°/15° C.
2. Optical Rotation in a 100 mm. tube.
3. Refractive Index at 20° C.
4. Solubility in 70% or 80% alcohol, usually by volume.

The following additional determinations and tests are made, according to the type of eucalyptus oil under examination:

1. Of cineole in oils required for medicinal purposes (various Pharmacopoeias require a minimum of 70 per cent).
2. Of phellandrene; absence or presence by the nitrosite test, and quantitative determination, if required.
3. Of volatile aldehydes (mainly isovaleraldehyde) in oils required for medicinal purposes.
4. Of citronellal in *Eucalyptus citriodora* oil.
5. Of piperitone (*Eucalyptus dives, E. numerosa* var. "A," etc.).
6. Of esters, determined by saponification at room temperature—2 hr. contact—in *Eucalyptus macarthuri* oil.

Specific Gravity, Optical Rotation, Refractive Index and Solubility.—The procedures for determining these physical properties are fully described in Vol. I of this work and need not be further discussed here. These four important properties readily differentiate oils rich in cineole from oils containing phellandrene, as the following table shows:

	Name of Oil	*Specific Gravity*	*Optical Rotation*	*Refractive Index*	*Solubility in 70% Alcohol (V/V)*
Cineole Oils	*E. polybractea*	0.922 to 0.930	0° to +2° 0′	1.4584 to 1.4616	Soluble in 1.8 to 2 vol.
	E. australiana	0.9162 to 0.930	0° to +5° 0′	1.4632 to 1.4644	Soluble in 1.8 to 2 vol.
Phellandrene Oils	*E. dives* (Type)	0.8892 to 0.9063	−58° 0′ to −70° 0′	1.4784 to 1.4812	Insoluble in 10 vol.
	E. numerosa (Type)	0.8904 to 0.8948	−25° 0′ to −35° 0′	1.4775 to 1.4786	Insoluble in 10 vol.

Cineole Assay.—Only two accurate methods for the estimation of this constituent can be recommended:

1. The congealing point method of Kleber and von Rechenberg (*J. prakt. Chem.* [2], **101** (1920), 171).
2. The ortho-cresol method of Cocking (*Perfumery Essential Oil Record* **11** (1920), 281), adopted as a standard method by both the Essential Oil Sub-Committee of the Society of Public Analysts (*Analyst* **52** (1927), 276) and The British Pharmacopoeia of 1932 and 1948.

Results of both methods are comparable. After many years' experience in their use, the authors can confidently recommend the congealing point method. It has the advantage of rapidity, an important consideration in handling a large number of routine samples, e.g., in a works laboratory. (For details see Vol. I of this work, p. 294.)

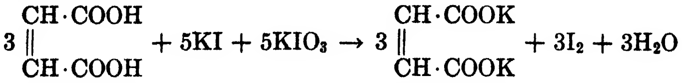
Phellandrene Assay.—The method given in the British Pharmacopoeia is an excellent one for detecting very small amounts of this terpene. It is carried out as follows: [107]

> 1 ml. of the oil under examination is placed in a test tube, 2 ml. glacial acetic acid are added, and then 5 ml. petroleum ether, b. 50°–60° (motor spirit or petrol, etc., will answer as well, when petroleum ether is not available), and finally 2 ml. of a saturated solution of sodium nitrite. On bringing the layers into contact by a gentle shaking or rotary motion, any phellandrene will reveal itself as a flocculent precipitate of the nitrosite at the junction of the liquids. Oils rich in phellandrene, such as *Eucalyptus numerosa* and *E. dives*, solidify to a gel in a few minutes.

α-Phellandrene can be determined quantitatively, if required, by taking advantage of its reaction with maleic anhydride. Since this terpene has conjugated double bonds, whereas the other major constituents of eucalyptus oils have not, it is possible to assay the phellandrene content accurately by the method developed by Kaufmann and applied by Hancox and Jones of Queensland.[108]

The procedure is as follows:

> To a weighed quantity of the material (0.1 g. is convenient for samples rich in phellandrene) is added 10 ml. of a standardized solution of maleic anhydride in toluene (about N/4). The whole is placed in a sealed bottle and heated in a boiling water bath for 4–6 hr. After cooling, the contents are transferred to a 250 ml. conical flask equipped with a ground-glass stopper, and the following reagents added: 15 ml. of a 25% potassium iodide solution, 15 ml. of a 4% potassium iodate solution; then, according to the amount of iodine liberated, a sufficient excess of decinormal thiosulfate. The flask and contents are then shaken for one hour. The excess maleic anhydride is thereby hydrolyzed to the free acid which then reacts with the iodide-iodate mixture according to the following equation:



$$3\begin{array}{l}\mathrm{CH\cdot COOH}\\ \|\\ \mathrm{CH\cdot COOH}\end{array} + 5\mathrm{KI} + 5\mathrm{KIO_3} \rightarrow 3\begin{array}{l}\mathrm{CH\cdot COOK}\\ \|\\ \mathrm{CH\cdot COOK}\end{array} + 3\mathrm{I_2} + 3\mathrm{H_2O}$$

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[107] The wording of the British Pharmacopoeia (1948) is modified here.

[108] *Univ. Queensland Papers, Dept. Chem.* **1**, No. 14 (1939), 2.

the iodine being liberated in quantity equivalent to the excess maleic anhydride. In the presence of excess thiosulfate the reaction goes to completion. Finally, a suitable quantity of decinormal iodine is added, and the residual iodine back-titrated with thiosulfate.

To standardize the maleic anhydride solution, a 10-ml. sample is hydrolyzed and titrated in the manner described above. The strength of this reagent alters fairly quickly with time and should be redetermined every time it is used. To express the result as diene number the following equation can be used:

$$\frac{1.27 \times (a - b)}{w}$$

where a = number of ml. N/10 iodine equivalent to the maleic anhydride in the blank experiment;
b = number of ml. N/10 iodine equivalent to the maleic anhydride with sample;
w = weight in g. of sample.

Since the diene number of 100 per cent phellandrene is 186.6, the percentage of α-phellandrene may be readily calculated.

Assay of Volatile Aldehydes.—The British Pharmacopoeia of 1948 requires a limiting test for the amount of these very objectionable constituents of commercial eucalyptus oils.

The following solutions are required:

Indicator Solution—A 0.2 per cent solution of pure methyl orange in 60 per cent alcohol.

N/2 Alcoholic Potassium Hydroxide—Prepared with pure 60 per cent (by volume) alcohol and standardized against N/2 hydrochloric acid, using methyl orange as indicator and running the alkali *into* the acid until the full yellow color is obtained.

N/2 Hydroxylamine Hydrochloride—Dissolve 3.475 g. of pure hydroxylamine hydrochloride in 95 ml. of pure 60 per cent (by volume) alcohol; add 10 drops of the indicator solution, and adjust to the full yellow color of the indicator with the N/2 alcoholic potassium hydroxide, and make up to 100 ml. with 60 per cent (by volume) alcohol.

The procedure is based upon that recommended by the Essential Oil Sub-Committee of the (British) Society of Public Analysts.[109]

The following method is a combination of that suggested by the Essential Oil Sub-Committee and that of the British Pharmacopoeia 1948:

Measure out into a stoppered tube (approximately 25 mm. in diameter and 150 mm. in length) the following substances:

[109] *Analyst* **55** (1930), 109; **59** (1934), 105. Cf. British Pharmacopoeia (1948), 374, 764.

10 ml. of the eucalyptus oil to be tested
4 ml. of hydroxylamine hydrochloride solution
5 ml. of benzene
1 drop of the indicator solution

Shake and neutralize the liberated acid with N/2 potassium hydroxide in alcohol (60 per cent) until the red color changes to yellow; continue the shaking and neutralizing until the full yellow color of the indicator is permanent in the lower layer, after shaking vigorously for two minutes and allowing separation to take place. The reaction is slow toward the end, but should be completed in about 15 min.

Not more than 2 ml. of N/2 potassium hydroxide solution in alcohol should be required.

The authors have examined many commercial samples of redistilled eucalyptus oil, and not one has failed to pass the above test.

Oils such as *Eucalyptus dives, E. numerosa*, var. "A," *E. citriodora*, and *E. macarthuri*, whose composition differs entirely from the ordinary cineole-containing oils, require a specific determination for each characteristic constituent.

Piperitone Assay—Oils of *Eucalyptus Dives*, Type, and *E. Numerosa*, Var. "A."—The commercial value of these oils is dependent upon their content of piperitone, which varies from 40 to 50 per cent. It is not always practicable to secure large commercial supplies containing 50 per cent of the ketone, owing to the difficulty experienced in bringing over the whole of the piperitone in some of the crude field stills operating in Australia. The majority of the distillers prefer to offer *Eucalyptus dives* oil for sale as containing from 40 to 45 per cent of piperitone.

Quantitative Determination.—The following slightly modified Burgess method [110] for the estimation of aldehydes and ketones gives excellent results with these oils:

Five ml. of the oil are pipetted into a cassia flask of about 150 ml. capacity, with a neck graduated 5 ml. in 1/10ths. A solution of crystallized sodium sulfite (made by dissolving 350 g. of the crystallized salt in 1,000 ml. of water) is added to the flask until about two-thirds full; 0.5 ml. of phenolphthalein indicator is added, and the flask and contents heated in a *vigorously boiling* bath, with constant agitation of the contents. The liberated alkali is neutralized from time to time by means of 10 per cent acetic acid solution until the reaction is completed. The volume is gradually made up with the sulfite solution, and finally the unabsorbed oil is forced up into the neck of the flask. When cold, the volume is read off. The difference in volume between the unabsorbed oil and 5 ml. (original volume taken), represents the amount of piperitone present in that volume, which, when multiplied by 20, gives the percentage present.

When individual samples are shaken by hand, too much stress cannot be laid upon the necessity for heating the flask containing the oil and sulfite solution in a vigorously boiling water bath. With a mechanical shaker, a bath temperature of 90° C. is sufficient for the reaction. The estimation occupies from 15 to 20 min.

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[110] *Analyst* **29** (1904), 78. Cf. Vol. I of this work, p. 283

The hydroxylamine method of Stillman and Read[111] has also been found very satisfactory for estimating piperitone in these oils (cf. Vol. I of this work, p. 287).

Citronellal Assay—Oil of *Eucalyptus Citriodora.*—The principal constituent of this oil is citronellal, which should be present to the extent of 65 to 85 per cent in the freshly distilled oil. This aldehyde can be determined accurately by the Holtappel method modified by Penfold and Arneman,[112] or more rapidly by the method recommended by the Essential Oil Sub-Committee of the (British) Society of Public Analysts.[113] The method outlined in the Sub-Committee's Report No. 10, "The Determination of Citronellal," follows.

These solutions are required:

Indicator Solution—A 0.2 per cent solution of dimethyl yellow (*p*-dimethyl-aminoazobenzene) in 90 per cent alcohol.

N/2 Alcoholic Potassium Hydroxide—Prepared with 90 per cent (by volume) alcohol and standardized against N/2 hydrochloric acid, using dimethyl yellow as indicator and running the alkali into the acid until the full yellow color is obtained.

N/1 Hydroxylamine Hydrochloride Reagent—Dissolve 6.95 g. of pure hydroxylamine hydrochloride in 95 ml. of 90 per cent (by volume) alcohol, add 0.4 ml. of dimethyl yellow solution, adjust to the full yellow color of the indicator with N/2 alcoholic potassium hydroxide, and make up to 100 ml. with 90 per cent (by volume) alcohol.

Method of Determination: Into a stoppered tube (approximately 150 mm. long and 25 mm. in diameter) weigh accurately such a quantity of the oil as contains about 0.8 g. of citronellal, and cool to a temperature of 0° (or lower). Add about 10 ml. of the N/1 hydroxylamine hydrochloride reagent previously cooled to 0°, and titrate the liberated acid *immediately* with N/2 alcoholic potassium hydroxide, adding the alkali very cautiously and *taking great care to avoid going beyond the orange color of the indicator.* Continue the titration as long as the red color develops, then allow the mixture to stand at laboratory temperature for 1 hr., and complete the titration to the full yellow color of the indicator. The number of ml. of N/2 alcoholic potassium hydroxide required, multiplied by the correcting factor 1.008, by the factor 0.077 for citronellal, and by 100, and divided by the weight of oil taken, will give the percentage (by weight) of the aldehydes, calculated as citronellal. The correcting factor (1.008) is necessary owing to the fact that the end point of the titration occurs at a pH different from that of normal hydroxylamine hydrochloride.

$$\%\ \text{citronellal} = \frac{a \times F \times 0.077 \times 100}{w}$$

where a = ml. of N/2 alcoholic KOH used;
F = correction factor (1.008);
w = weight of oil taken in grams.

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[111] *Perfumery Essential Oil Record* **23** (1932), 283.

[112] "The Estimation of Citronellal and Citral in Australian Essential Oils," *J. Proc. Sydney Tech. Coll. Chem. Soc.* **4** (1929), 53.

[113] *Analyst* **57** (1932), 773.

Assay of Ester Content—Oil of *Eucalyptus Macarthuri*.—The oil from *Eucalyptus macarthuri* is valued for its geranyl acetate content, which should be of the order of 60 per cent. This ester is usually determined in the following manner:

About 1.5 g. of the oil are weighed accurately into a stoppered flask, 25 ml. of N/2 alcoholic potassium hydroxide added and the contents well mixed by gentle swirling. The flask is stoppered and let stand at room temperature for 2 hr., a blank being run at the same time in a flask made of similar glass. At the end of the period, 50 ml. of water are added to each, together with ½ ml. of 1 per cent alcoholic phenolphthalein indicator, and the uncombined alkali is neutralized with standard seminormal hydrochloric acid.

The geranyl acetate content is given by the formula:

$$\frac{(b - a) \times 9.81}{w}$$

where b = ml. of N/2 HCl used to neutralize the blank;
a = ml. of N/2 HCl used to neutralize the sample;
w = weight of sample in grams;
1 ml. of N/2 KOH = 0.0981 g. of geranyl acetate.

(Cf. Vol. I of this work, p. 265.)

SPANISH OIL OF *Eucalyptus Globulus* LABILLARDIÈRE[114]

by

ERNEST GUENTHER

Introduction.—The bulk of the so-called "medicinal" eucalyptus oil is supplied by Australia, but for many years Spain, also, has been producing substantial quantities of a high-grade eucalyptus oil. The Spanish product has always found a good market in Europe, because it can be obtained more quickly on demand than the Australian oil, which has to be shipped a long distance.

Botany.—The *Eucalyptus* species exploited in Spain for the extraction of oil is *E. globulus,* which was introduced into Spain in the eighteenth century for the rather strange purpose of drying out swampy depressions in the ground. Another species found in Spain is that commonly known as "Eucalipto negro"; its leaves, however, contain practically no essential oil.

Producing Regions, Planting, and Growth of the Tree.—The area of cultivation lies in the temperate zone of southern Andalusia, particularly in the province of Huelva, the most important centers of production being the villages of Hinojos, Almonte, Rociana, Moguer, Bonares, Trigueros, Beas, Valverde del Camino, and Gibraleon.

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[114] Compare *Am. Perfumer* **48** (April 1946), 41.

It should be mentioned that *Eucalyptus globulus* grows abundantly also in the northern part of Spain, particularly in the provinces of Santander and Asturias, and that the leaves were distilled during World War II, when the price of the oil was high. However, at the present time the eucalypts in northern Spain are used only as a source of timber for shoring in mines and the leaves only for fuel.

In southern Spain *Eucalyptus* grows along the highways, on low sandy or moist land, and on the banks of rivers. It prefers poor but humid soil. The tree does not reproduce itself; it must be planted (to a depth of 35 to 40 cm.). When four years old the trunk has reached a height of about 8 m., with a diameter of about 20 cm. The wood can then be used for construction work and for shoring in mines, and the leaves can be distilled for the extraction of the essential oil. By the seventh year the tree attains a height of about 15 m. and may be considered fully grown, although its maximum is reached in the tenth year, with a height of 20–25 m.

Distillation and Yield of Oil.—For the collection of the leaf material the trees are usually felled as the gathering of leaves from live trees is difficult and costly, and feasible only when the oil brings high prices. Sometimes, however, leaves are collected from old live trees that contain abundant foliage.

The leaves are distilled throughout the year, the period of distillation depending largely upon the use to which the wood can be put; in other words, the leaves are distilled only when the owner of the land decides to fell the trees and sell the wood. The most favorable time for distillation is from April to September, because the yield of oil then averages 0.8 per cent, and the cineole content of the (crude) oil is 63 to 73 per cent. During the winter months the yield of oil drops to about 0.7 per cent and the cineole content to 60 to 65 per cent.

The highest yield of oil comes from the top leaves of the trees; this oil has a better solubility and a higher cineole content than the oil from the lower leaves. A tree six to eight years old yields 20 to 60 kg. of leaves per year.

Distillation is carried out in the usual type of field stills employed in Spain for the production of oils of spike-lavender, rosemary, thyme, pennyroyal, etc. (cf. the monographs on these respective oils in Vol. III of this work). The stills are 2 m. high, and 1.6 to 1.8 m. in diameter, holding 70 to 90 arrobas of leaf material (1 arroba = 11.5 kg. or about 25 lb.). Including the charging of the still, distillation of one batch requires 6 hr.; it is completed when 200 or 240 liters of condensate (water and oil) have been distilled over.

Total Production.—Prior to World War II, Spain produced yearly from 60 to 100 metric tons of eucalyptus oil. After the outbreak of the war, Central Europe, and particularly Germany, France, and Italy, came to depend entirely upon the Spanish oil, since the Australian product had become unavailable. Production in Spain, therefore, rose to 300 tons in 1942. Since then, it has fallen off to about 100 metric tons per year. In 1948 Spain produced 90 metric tons of eucalyptus oil.

Physicochemical Properties.—According to Bordas,[115] the properties of crude (unrectified) Spanish eucalyptus oil vary within these limits:

Specific Gravity at 15°	0.9175 to 0.930
Optical Rotation at 20°	+2° 0′ to +7° 12′
Cineole Content	66.5 to 73.3%
Solubility in 70% Alcohol	Soluble in 2.2 to 11 vol., frequently with separation of paraffins

Since in many instances the properties of the crude oils do not meet the specifications of most pharmacopoeias, the oil has to be rectified, whereby the cineole content is increased and the solubility in 70% alcohol improved. The properties of the rectified oils vary within the following limits:

Specific Gravity at 15°	0.905 to 0.922
Optical Rotation at 20°	+1° 48′ to +9° 0′
Cineole Content	71.3 to 84.5%
Solubility in 70% Alcohol	Soluble in 1.5 to 10 vol.

Chemical Composition.—Oil of *Eucalyptus globulus* was first investigated by Cloez [116] who isolated a substance (b. 175°), which he called eucalyptol, but which was evidently still accompanied by terpenes, and therefore not pure. The true nature of eucalyptol, $C_{10}H_{18}O$ (the main constituent of eucalyptus oil) and its identity with cineole, was recognized by Jahns.[117] Since then oil of *Eucalyptus globulus* has been the subject of many investigations, with the result that today our knowledge regarding the chemical composition of this important oil is fairly well established. The following compounds have been identified in oil of *E. globulus:*

Ethyl Alcohol. In the foreruns, according to Bouchardat and Oliviero.[118]

Isoamyl Alcohol. Isolated by Schimmel & Co.[119] through the calcium chloride addition compound, and identified as phenylurethane m. 52°–53°.

Butyraldehyde, Valeraldehyde, and Caproaldehyde. According to Schimmel & Co.,[120] these aldehydes which occur in the foreruns of the oil are primarily responsible for the disagreeable, stinging, and cough-provoking odor of the crude oil and should be removed by fractionation.

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[115] Private communication from Mr. Ramon Bordas, Sevilla.

[116] *Compt. rend.* **70** (1870), 687. *Liebigs Ann.* **154** (1870), 372.

[117] *Ber.* **17** (1884), 2941. *Arch. Pharm.* **223** (1885), 52.

[118] *Bull. soc. chim.* [3], **9** (1893), 429.

[119] *Ber. Schimmel & Co.*, April (1904), 47.

[120] *Ibid.*

d-α-Pinene. Wallach and Gildemeister[121] isolated *d*-α-pinene from the fraction b. about 165°, and identified it as nitroso compound m. 129°–130°, and as nitrolpiperidine m. 116°.

Camphene. In the fraction b. about 155°, according to Schimmel & Co.[122]

Cineole (Eucalyptol). This chief constituent of the oil was recognized and identified in the fraction b. about 175° by Jahns.[123]

l-Pinocarveol. This laevorotatory alcohol was first observed by Wallach[124] in the fractions of *Eucalyptus globulus* oil boiling above 200°, after these fractions had been saponified. The alcohol then boiled at 215°–220°. Purified through the acid phthalate, *l*-pinocarveol had these properties:

b_{12}	92°
$[\alpha]_D$	$-52° 27'$ (in 12.75% solution)
n_D^{20}	1.49630

The presence of *l*-pinocarveol in Spanish oil of *E. globulus* was later confirmed by Schmidt[125] who also identified the following compounds:

l-Pinocarvone. The bicyclic, *l*-rotatory unsaturated ketone $C_{10}H_{14}O$, which aside from *d*-myrtenol was isolated from the saponified last runs, had the constitution of pinocarvone. It cannot be distilled at ordinary pressure and is completely regenerated from its sulfite compound only by the action of strong alkali.

b_4	67°–69°
d_{15}^{15}	0.985
α_D	$-59° 54'$
n_D	1.49459
Semicarbazone	m. 350°
Oxime (liquid)	α_D $-11° 0'$

The ketone also yielded a solid oxime m. 131°–132°. It showed no melting point depression with nitrosopinene.

Dibromide	m. 73.5°–74°
$[\alpha]_D$	$+130° 0'$

d-Myrtenol. Isolated from the saponified last fractions in the form of its boric acid ester. The phthalate melted at 114°–115°.

d-Myrtenal. Separated as sodium sulfite compound which was decomposed by treatment with alkali. The aldehyde was then isolated by steam distillation.

b.	220°–221°
d_{15}^{15}	0.991
α_D	$+13° 13'$
n_D	1.50302
Semicarbazone	m. 215°
Oxime	m. 69°–70°

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[121] *Liebigs Ann.* **246** (1888), 283.

[122] *Ber. Schimmel & Co.,* April (1904), 47.

[123] *Ber.* **17** (1884), 2941. *Arch. Pharm.* **223** (1885), 52.

[124] *Liebigs Ann.* **346** (1906), 221, 227.

[125] *Ber.* **62** (1929), 2947. *Ber. Schimmel & Co.* (1941), 56. *Ber.* **77** (1944), 167.

i-Terpineol. Schmidt[126] identified this optically inactive alcohol as phenylurethane m. 113° in the last runs of *E. globulus* oil. Treatment with 20 per cent sulfuric acid transformed this terpineol into terpin-hydrate m. 118°.

Globulol(?), ($C_{15}H_{25}OH$).. Schimmel & Co.[127] observed in the last fractions of *E. globulus* oil an almost odorless sesquiterpene alcohol $C_{15}H_{26}O$ which after recrystallization from 70 per cent alcohol had these properties:

m.	88.5°
b_{755}	283°
$[\alpha]_D$	−35° 29′ (in 12% chloroform solution)

Semmler and Tobias[128] named this sesquiterpene alcohol globulol and expressed the view that physically and probably also chemically globulol differs from eudesmol.

According to Schimmel & Co.,[129] globulol on treatment with chromic acid yields a crystalline compound m. 78° (orange red needles). Wienhaus[130] observed similar addition compounds of chromic acid in the case of several sesquiterpenes.

Sesquiterpenes(?), $C_{15}H_{24}$. Ruzicka, Pontalti and Balas[131] found that the last runs of a *E. globulus* oil, after distillation over metallic sodium, yielded an oily substance b_{12} 122°–131° which consisted almost entirely of sesquiterpenes. The same authors separated these sesquiterpenes into two fractions:

(a)	b_{12}	124°–127°
	d_4^{20}	0.9078
	α_D	−12°6′
	n_D^{20}	1.4968

Dehydrogenation with sulfur of this apparently bicyclic sesquiterpene gave two blue oils b_{12} 130°–145° and b_{12} 145°–160°, both of which yielded black picrates m. 122°. Probably these picrates were identical with azulene picrates.

(b)	b_{12}	127°–131°
	d_4^{20}	0.9172
	α_D	−4° 18′
	n_D^{20}	1.5001

Dehydrogenation with sulfur gave cadalene in about 10 per cent yield.

Ruzicka, Pontalti and Balas also observed that a sesquiterpene alcohol fraction b_{12} 150°–160° of *E. globulus* oil, on boiling with 85 per cent formic acid, yielded a sesquiterpene which, on dehydrogenation with sulfur, gave also cadalene. These authors therefore concluded that the sesquiterpene compounds contained in *E. globulus* oil are mainly bicyclic representatives of the cadinene type, contrary to other eucalyptus oils which contain eudesmol.

Sesquiterpene Alcohols. Pfau and Plattner[132] reported that the higher boiling part of oil of *Eucalyptus globulus*, after repeated fractionation (finally over metallic so-

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[126] *Ber.* **62** (1929), 2946.
[127] *Ber. Schimmel & Co.,* April (1904), 45.
[128] *Ber.* **46** (1913), 2030.
[129] *Ber. Schimmel & Co.,* October (1908), 82, footnote.
[130] *Ber.* **47** (1914), 322.
[131] *Helv. Chim. Acta* **6** (1923), 859.
[132] *Ibid.* **19** (1936), 871.

dium), gave 30 per cent of a mixture of sesquiterpenes and sesquiterpene alcohols with these properties:

b_{10}	120°–122°
d_{20}	0.9135–0.9143
$[\alpha]_D$	+4° 56′ to +5° 29′
n_D^{20}	1.4978–1.4983

On dehydrogenation of these compounds with sulfur or selenium S-guaiazulene was obtained.

Aromadendrene, $C_{15}H_{24}$. Briggs and Short,[133] and Naves and Perrottet[134] arrived at the conclusion that the sesquiterpene fraction isolated from oil of *E. globulus* consists mainly of tricyclic aromadendrene. These authors reported the following properties of aromadendrene:

b_{10}	121°
b_6	114°
d_4^{20}	0.9116
d_{20}	0.9166
α_J	+4° 48′
$[\alpha]_{577}^{20}$	−6° 6′
n_D^{20}	1.4980

Dehydrogenation of aromadendrene with sulfur yielded S-guaiazulene, which was identified as picrate m. 122°.

Radcliffe and Short[135] recorded these properties of the sesquiterpene fraction from oil of *E. globulus*, containing aromadendrene:

b_{10}	120°–125°
d_4^{20}	0.9159
α_{5770}	+0° 48′ to +2° 4′
n_D^{20}	1.4990–1.5004

For the configuration of aromadendrene, see Vol. II of the present work, p. 110. Since the publication of that volume, however, Treibs and Barchet [*Liebig's Ann.* **566** (1950), 89] have proposed a new formula.

Carvone, *d*-Verbenone, and 3-Isopropyliden-1-acetyl-5-cyclopentene. More recently Schmidt[136] investigated the high boiling portions of Spanish oil of *Eucalyptus globulus*, and found that these fractions contain a number of carbonyl compounds, viz., carvone, *l*-pinocarvone, *d*-verbenone, *d*- and *dl*-myrtenal and 3-isopropyliden-1-acetyl-5-cyclopentene $C_{10}H_{14}O$, a ketone with a five-membered ring which had never previously been observed in essential oils.

These carbonyl compounds were separated by means of their hydrosulfonic acid compounds, and by steam distillation of the sulfite compounds (first in sodium carbonate and then in sodium hydroxide solutions).

The carvone was separated by preparation of the semicarbazone m. 154°. It consisted of 25 per cent of laevorotatory carvone (b. 229°–230°, d_{15} 0.9608, α_D −16° 12′, n_D^{20} 1.49762) and 75 per cent of racemate.

The *d*-verbenone was identified by means of its oxime m. 119°.

The 3-isopropyliden-1-acetyl-5-cyclopentene was isolated by decomposition of

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[133] *J. Chem. Soc.* (1928), 2524.

[134] *Helv. Chim. Acta* **23** (1940), 914.

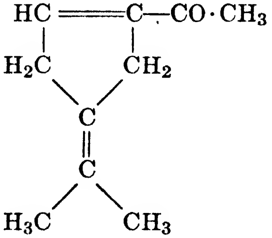
[135] *J. Chem. Soc.* (1938), 1200.

[136] *Chem. Ber.* **80**, No. 6 (1947), 528, 533.

the sulfite compound in a strong sodium hydroxide solution (via steam distillation), and by fractionation *in vacuo*. The resulting oil exhibited a very pleasant anise-like odor and had these properties:

b_{738}	225°–225.5°
d_{15}	0.955
α_D	±0°
n_D^{20}	1.49412
Cong. Point	−0.2°

Schmidt established the following structural formula for 3-isopropyliden-1-acetyl-5-cyclopentene:



Ketones with a five-membered ring and the carbonyl group in the side chain have not heretofore been observed in natural products. In the opinion of Schmidt, their occurrence in essential oils is of special interest because they are related to the valuable jasmone.

PORTUGUESE OIL OF *Eucalyptus Globulus* LABILLARDIÈRE

Meager information from Portugal indicates that *Eucalyptus globulus* grows abundantly to the north of Lisbon, particularly near Abrantes, Gavião, and Coruche (Herdade da Agolada). The leaves are hauled to Lisbon for distillation. The crude (unrectified) oil contains about 55 per cent of cineole and is of poor solubility. Rectification yields an oil of normal properties.

The entire Portuguese production amounts to about 10 metric tons per year, of which much has lately been exported to the United States.

Efforts toward a more intensive cultivation of eucalyptus are being made in the southern part of Portugal.

AMERICAN EUCALYPTUS OILS

by

ERNEST GUENTHER

American Medicinal Eucalyptus Oils

Introduction.—Prior to the outbreak of World War II, the world demand for all kinds of eucalyptus oils was satisfied chiefly by Australia. Shipping difficulties arising during the war, the lack of labor in the interior of Australia, and the greatly increased demand for medicinal and technical eucalyptus oils on the part of the British armed forces resulted in a shortage of the oil in the Western Hemisphere. In consequence, several producers in Central and South America saw an excellent opportunity to develop their own sources and to supply the United States with this oil. Encouraged by the high oil prices then prevailing, a number of producers entered the field, exploiting either old-established stands of eucalyptus or starting new plantings. The new industry prospered for a time, but with the reappearance of the Australian oils its future in some of the Central and South American countries is not too secure. It may be able to retain local markets, but whether it will successfully withstand competition with the Australian oil on the world market is doubtful. It should be kept in mind that in most countries of the Western Hemisphere eucalyptus oil is distilled from *Eucalyptus globulus,* which gives a low yield of oil, whereas in Australia other, high yielding, species of *Eucalyptus* are exploited.

Argentina and Uruguay.—Substantial quantities of eucalyptus oil from these countries have been sold on local markets, and have been exported to the United States, especially during World War II. Some shipments, however, were of substandard quality in regard to solubility and cineole content and had to be rectified in the United States. Because of the difficulties experienced, United States importers no longer consider this oil satisfactory.

Brazil.—The *Eucalyptus* was introduced to Brazil in 1855, the species being *globulus.* However, the importance of *Eucalyptus* for reforestation was only fully recognized much later (about 1900), as a result of the extensive experimental work of Brazil's great eucalyptologist Edmundo Navarro de Andrade. Large areas were then planted with a number of species. In the State of São Paulo alone there are at present about 500,000,000 eucalyptus trees.

The original idea which led to the wide propagation of *Eucalyptus* species in Brazil, particularly in the State of São Paulo, was to supply the railroads with much needed fuel (in the years before some of them were electrified), as most of the primeval forests along the rail tracks had been cut down and wasted. No other forest plant could serve better for reforestation than the quick-growing *Eucalyptus,* which six to seven years after planting yields from 700 to 1,000 sq. m. of fueling wood per alqueira paulista (= 2.5 hectares or about 6 acres). Moreover, after cutting, the tree regrows spontaneously. Years of experimenting have proved that the most suitable *Eucalyptus* species for this purpose are *E. saligna, botryoides, robusta, umbellata (tereticornis), rostrata, alba,* etc. It was only recently that the ever growing demand for timber led to the wide propagation of *E. citriodora,* the wood of which can be used for almost any purpose after the twentieth year of growth. This species also yields an essential oil (oil of *E. citriodora*).

E. globulus, although the first species introduced into Brazil, is no longer propagated (except perhaps for the special purpose of essential oil production), as the wood is not well suited for use as timber.

Despite the fact that *Eucalyptus* has, for the last fifty years, been planted in enormous quantities in Brazil, it was only in the course of World War II that production of essential oils (from *E. citriodora* and *E. globulus* exclusively) was started. At the time of this writing (1949) it cannot be predicted whether the exploitation of these two species for essential oil production will be economically successful in the long run. To produce cineole-containing, medicinal oil in competition with the Australian oils, it will most probably be necessary to introduce *Eucalyptus* species which give a much higher yield of oil than the presently exploited *E. globulus.* Of the latter there are now about 300,000 trees in the State of São Paulo, only some of which are used for the distillation of essential oil. Total annual production varies from 8 to 10,000 kg. of oil, which quantities amply suffice to cover the requirements of the domestic market. Methods of planting and harvesting are the same as those used for *E. citriodora* (see below—American Perfume Eucalyptus Oils); but *E. globulus* is a much faster growing tree and six to seven months after planting often attains a height of more than 3 m. The yield of oil is also a little higher than that from *E. citriodora,* and varies from 1.0 to 1.5 per cent. The cineole content of the crude (unrectified) oil averages 64 to 66 per cent.

Colombia.—E. globulus was introduced into Colombia about a century ago, but the first real plantations were laid out about twenty-five years ago, not far from Bogotá, Colombia's capital, on a fertile, high plateau and in a temperate, rather cool climate chosen by the early conquistadores as best suited for settlement. Since then the tree has escaped cultivation and can now be found semiwild and wild in numerous parts of the plateau. Many settlers plant *Eucalyptus globulus* for the wood, which is used for construction work as the trees grow quickly and can be cut for the first time three years after planting. However, most trees are left to grow for about ten years before cutting. A better procedure would be, perhaps, to fell the trees for the first time five years after planting, when they are not yet thick enough to make transport of the logs difficult. After cutting, the tree grows again spontaneously and can be cut a second time after seven years, and a third and last time after ten years.

The leaf material used for distillation originates partly from these felled trees and partly from wild and semiwild live trees scattered over wide regions. To collect the latter leaf material the natives have to climb the trees to trim them with machetes. The natives then transport and sell the leaves in sacks of about 25 kg. content to the distilleries.

There exist a few field distilleries—for example, there is one near La Tribuna, 48 km. from Bogotá on the road to Villeta. One producer operates 5 square metal stills holding 2 cu. m. each, and 1 square still holding 5 cu. m. One thousand five hundred pounds of fresh (green) leaves are charged into each of the smaller stills above a grid; the water beneath the grid is brought to a boil by direct fire, and the steam blown through the leaf material. Distillation lasts about 3 hr. per batch, but the yield is only about 0.9 per cent—which low yield is a result of the rather ineffective method of distilling. The method of water *and* steam distillation easily causes wetting of the plant charge with a resulting insufficient yield of oil.

Two samples of crude *Eucalyptus globulus* oil distilled in that section and analyzed by Fritzsche Brothers, Inc., New York, had these properties:

	I	*II*
Specific Gravity at 25°/25°	0.910	0.901
Optical Rotation	+9° 50′	+12° 0′
Refractive Index at 20°	1.4647	1.4633
Cineole Content	57.9%	56.3%
Solubility at 25°	Soluble in 1 vol. and more of 80% alcohol. Hazy in 10 vol. of 70% alcohol	Opalescent in 1.5 to 2 vol. and more of 80% alcohol
Test for Heavy Metals	Negative	Positive (traces)

Two samples of rectified *Eucalyptus globulus* oil of identical origin had the following properties:

	I	*II*
Specific Gravity at 25°/25°	0.907	0.900
Optical Rotation	+9° 37′	+10° 47′
Refractive Index at 20°	1.4644	1.4622
Cineole Content	61.2%	61.2%
Solubility at 25°	Cloudy in 10 vol. of 70% alcohol. Soluble in 1 vol. and more of 80% alcohol	Turbid in 10 vol. of 70% alcohol
Test for Heavy Metals	Negative	Negative

None of the four oils described above met the specifications of the United States Pharmacopoeia.

Total production of eucalyptus oil in Colombia is still very limited but could be increased to several tons per month if sufficiently high prices and demand on the part of the United States should warrant it.

Guatemala.—Eucalyptus globulus has been known in this Central American republic for some years. A hacienda owner near Guatemala City[137] started large plantings of various *Eucalyptus* species, particularly *E.*

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[137] Interview with Mr. Rafael Pinol Batres in Guatemala City.

citriodora, in 1910. The soil there consists of volcanic ash and sand. The altitude is about 5,000 ft. above sea level. The temperature varies from +6° C. to +28° C. with fairly heavy rainfalls from May to October, and a dry period from November to April. *Eucalyptus globulus* may be easily uprooted by the strong winds prevailing in this region between November and February. The originally small acreage of *Eucalyptus smithii* and *E. australiana,* which give medicinal eucalyptus oils very similar to that of *E. globulus,* has therefore been enlarged.

In Guatemala *Eucalyptus* species are planted, harvested, and distilled as follows: The seed capsules are cut when ripe and about ready to open, then dried in the sun for a day or two, or until the seeds fall out of the capsules. For best results the seed should be sown as fresh as possible, although it will retain its germinating power for a year. Because of the length and fragility of their root system, the plants are sown in pots, then placed into the fields when they have reached a height of about 6 in. The planting is done either quincuncially or in rows (fence form). With quincuncial arrangement the square is 7 m. wide; if fence arrangement is used, the distance between the plants should be 2 m., and the distance between the rows 7 m., in order to give the roots sufficient room for development. Corn, beans, or other leguminous plants sown between the rows keep the land free of weeds and provide green manure.

When the trees are three to four years old the tops are lopped off in order to force the branches to spread out. This is repeated until the trees are seven to eight years old, by which time the trunk has grown to fairly large size and has developed numerous low branches which are easy to cut. Trees thirty years old show no sign of exhaustion.

The leaves of a well-developed tree may be cut twice a year. The branches are lopped off by one straight cut of the machete, then piled between the trees. Two branches are left on each tree to keep it alive. A cart passes between the rows, picks up the branches as soon as they are cut, and hauls them to the distillery. There the leaves and terminal branchlets (not more than ½ in. in diameter) are cut from the branches with machetes. Thus, the distillation material consists only of leaves and terminal branchlets. One hundred pounds of freshly cut material will dry in the shade to about 80 lb. in two days and will, in each case, produce the same amount of oil.

Three to four-year-old trees, reckoning from the time of planting the field, produce 8 to 10 lb. of leaf material yearly; fully grown (ten to twelve-year-old) trees, if well cultivated and properly cut to form bushes, yield on the average 100 lb. of leaves per year. When planted in rows, one acre contains about 350 trees. One acre will thus produce up to 35,000 lb. of leaf material. After the tree has reached full maturity at ten to twelve years, the yield of leaves will no longer increase.

Distillation is carried out in the usual way, the steam pressure in the generator varying from 30 to 40 lb. Distillation of one batch lasts about 1½ hr., but must be modified according to the different species. The plant material is packed into the stills very loosely, which in the opinion of the producer shortens the time of distillation substantially and increases the yield of oil. The apparatus should be cleaned frequently to prevent rusting and also to remove deposits which form inside of the still and condenser. In fact, because of these deposits, and to avoid contamination, each individual species of *Eucalyptus* should be distilled in separate apparatus.

The yield of oil from leaves that are too young or too old is below average. The presence of flowers and seeds in the distillation material alters the composition of the oil and such matter should therefore be eliminated. Whenever the trees are allowed to go into seed, the yield of leaves decreases. During the rainy season the trees develop more leaf material, but the yield of oil is lower and the composition of the oil somewhat different.

On the average, *Eucalyptus smithii* yields about 1.75 per cent of oil from fresh leaf material.

A sample of Guatemala *Eucalyptus smithii* oil, examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 25°/25°	0.916
Optical Rotation	+4° 8′
Refractive Index at 20°	1.4618
Cineole Content	78.4%
Solubility at 25°	Soluble in 2 to 2.5 vol. and more of 70% alcohol
Test for Heavy Metals	Negative

The properties of this oil met the specifications of the United States Pharmacopoeia.

Mexico.—Introduced probably by the Emperor Maximilian about eighty years ago, if not by the early Spanish settlers, eucalyptus trees (*Eucalyptus globulus* and closely allied species) grow wild and semiwild in the great valley of Mexico City, in a radius of 12 to 30 km. of the capital.

Principal growing centers lie near Tlanepantla, 30 km. from Mexico City, and around the Hacienda Echegaray. The trees there have reached great height and the Indians must climb high in order to cut the branches with the adhering leaves. After harvesting, the leaf material is trucked to the distillery and while fresh (green) distilled for about 3 hr., the yield of oil being less than 1 per cent. Production in this distillery approximates 600 kg. monthly.

The long haulage of the distillation material to the distillery increases the cost of production, for which reason the establishment of portable field stills in the State of Chalisco would be advisable, where eucalyptus grows abundantly.

Under the present system of distillation as practiced in Atzcapotzalco (outside of Mexico City), the oil is fractionated into three fractions:

1. The forerun (about 25 per cent of the total oil) is sold to the local candy makers.
2. The main run (about 65 per cent of the total oil) is employed by local pharmaceutical manufacturers. It contains about 90 per cent cineole.
3. The last run (about 10 per cent of the total oil) is also sold to candy makers.

A sample of crude (not fractionated) Mexican eucalyptus oil, examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 25°/25°	0.912
Optical Rotation	+6° 45′
Refractive Index at 20°	1.4683
Cineole Content	53.5%
Solubility at 25°	Cloudy in 10 vol. of 70% alcohol
Test for Heavy Metals	Positive

Obviously this oil did not meet the specifications of the United States Pharmacopoeia.

United States (*California*).—Large numbers of eucalyptus trees have been planted at various times, and at various places, in southern and central California. About forty-five years ago, for instance, some 30,000 acres in the Oceano region were laid out with *E. globulus.* Another planting, of 90,000 trees, was made near Fontana about thirty years ago. These, and other large plantations, have, however, been broken up into small home and farm sites, with the result that no large stand of the trees remains. About 90 per cent of the trees left belong to the species *globulus.*

There are miles and miles of *E. globulus* windbreaks planted along the roadsides in the southern counties of California; but, since the trees are planted on private land, and have attained such a height as to make harvesting of the leaves uneconomical, there is little likelihood that commercial production of eucalyptus oil will be undertaken. Any producer interested in the project would have to deal with such a multitude of landowners, and pay such a high price for labor in order to collect leaf material for distillation, that costs would become prohibitive. For these reasons, and for the additional one that Australian species give much higher yields of oil, the California product could not possibly compete with Australian eucalyptus oils.

American Perfume Eucalyptus Oils

Introduction.—What was said in the introduction to the monograph on American Medicinal Eucalyptus Oils applies also to the so-called Perfume Eucalyptus oils which, since the outbreak of World War II, have been produced in Guatemala and Brazil—particularly in the latter.

Brazil.—The importance of *Eucalyptus citriodora* for reforestation and as a source of timber was recognized in Brazil only recently. The tree grows fast, straight, and to a considerable height, so that the felled trunks can be used for masts on small sailing vessels, for buildings, bridges, and all kinds of construction work. Moreover, the leaves yield an essential oil containing a high percentage of citronellal. When World War II caused a serious shortage of the Java citronella oil, the Brazilian soap, cosmetic, and perfume industries accepted oil of *Eucalyptus citriodora* as an effective substitute. Hundreds of thousands of trees were planted, particularly in the State of São Paulo.

Since the sensitive root system of *Eucalyptus citriodora* does not easily withstand transplanting, propagation is carried out as follows: [138] The seeds are planted in well-prepared, protected, humus-containing seedbeds, three to four months before the beginning of the rainy season. After the plants have attained a height of about 1 in. they are transplanted, 2 in. apart, into well-prepared nursery beds. Another method, according to Dierberger,[139] is to plant the seedlings in small wooden boxes or pots made of thin wood shavings. In the former case the young plants, when 4 to 8 in. high, are lifted from the nursery bed and transplanted on a rainy day, with careful preservation of the earth adhering to the delicate root system. With the second method, the procedure is about the same, except that the seedlings can be left to grow taller. Prior to transplanting, the small wooden boxes or pots have to be removed.

It is advisable to transplant the seedlings into the fields at the beginning of the rainy season, from November to January, so that at the beginning of the dry season (April to May) the plants have reached a height of usually 1.5 to 2 m. and can develop further throughout the winter, without suffering from the dry weather.

If the trees are to serve later as timber, they should be planted 2 m. apart in each direction; but if they are planted for the distillation of the leaves, the trees should be spaced 1.0 to 1.5 m. apart, in rows 3 m. apart. This will permit circulation of loading carts within the plantation and substantially reduce the cost of harvesting. To profit from a maximum of sunlight, the

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[138] Private communication from Mr. João Dierberger, São Paulo.
[139] *Ibid.*

plantations should be laid out in an east-west direction, effecting a better development of the leaf system.

The leaves can be harvested for the first time six to eight months after planting. For this purpose it is advisable to cut off only the young side branches and to preserve the main growth. In the second year the whole tree can be felled, which practice yields not only all the leaves, but also the trunk and the branches as wood for fuel purposes. After the second year of growth, numerous branches will develop on the stump. Depending upon weather conditions these can be cut once or twice a year, one vigorous branch being left on the tree on the occasion of each cutting. The nature of the soil, the age of the planting, the distance between the trees, the cultural care, and prevailing weather influence the annual yield of leaves, which may range from 2 to 5 kg. of leaves per tree. In other words, one hectare produces from 4,000 to 10,000 kg. of leaf material. According to the experience of Dierberger, there are several plantations of *Eucalyptus citriodora* in the State of São Paulo, which even after five years of harvesting have retained their vigor and full productivity, the reason being that the harvesting was carried out in the above described manner.

The leaves can be harvested and distilled at any time of the year, but the optimum yield of leaf material and oil is obtained toward the end of the rainy season. The stills used for distillation hold from 300 to 1,000 kg. of leaves. In most cases they are equipped for distillation with indirect steam. Distillation of one batch requires from 1 to 1½ hr.; the yield of oil varies from 0.8 to 1.2 per cent.

The first distillation experiments were undertaken in 1941 and 1942; since then the following quantities of oil of *Eucalyptus citriodora* have been produced in Brazil (chiefly in the State of São Paulo):

	Kilograms
1944	1,500 to 2,000
1945	3,000
1946	12,000
1947	20,000

In 1948 the production capacity in the State of São Paulo alone was 30,000 kg. of oil, but, because of a greatly reduced demand from abroad, only 5,000 kg. of oil were actually produced. A part of this quantity was exported, the balance consumed by the domestic market.

As regards the physicochemical properties of the Brazilian oil of *Eucalyptus citriodora:* the content of citronellal usually varies from 70 to 75 per cent; in a few cases a citronellal content as high as 82 per cent has been observed.

Two samples of Brazilian oil of *Eucalyptus citriodora* examined by Fritzsche Brothers, Inc., New York, had these properties:

	I	*II*
Specific Gravity at 15°/15°	0.867	0.867
Optical Rotation	+0° 47′	+1° 5′
Refractive Index at 20°	1.4512	1.4515
Aldehyde Content, Calculated as Citronellal (Hydroxylamine Hydrochloride Method)	79.7%	74.6%
Solubility in 70% Alcohol, at 20°	Soluble in 3 vol. and more	

Guatemala.—This prosperous Central American republic has also been producing limited quantities (about 350 to 400 lb. per month) of *Eucalyptus citriodora* oil. The plantings, located on the outskirts of Guatemala City, now comprise about 60,000 trees.

The methods of planting, harvesting, and distilling are the same as those described under Guatemala *Eucalyptus globulus* oil. The yield of oil amounts to about 1.5 per cent (Pinol Batres [140]).

A sample of *Eucalyptus citriodora* oil distilled on these plantations and analyzed by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 15°/15°	0.863
Optical Rotation	+0° 27′
Refractive Index at 20°	1.4512
Aldehyde Content, Calculated as Citronellal (Hydroxylamine Hydrochloride Method)	80.5%
Solubility	Soluble in 4.5 vol. and more of 70% alcohol
Color	Practically colorless

The oil was normal and of excellent quality.

The same producer near Guatemala City has also started to grow *Eucalyptus staigeriana*. The leaves yield about 2.6 per cent of oil, several hundred pounds of which have been produced.

A sample of Guatemala *Eucalyptus staigeriana* oil examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 25°/25°	0.880
Optical Rotation	−31° 36′
Refractive Index at 20°	1.4798
Citral Content (Neutral Sulfite Method)	31.2%
Ester Content, Calculated as Geranyl Acetate	13.69%
Total Geraniol Content	19.1%

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[140] Private communication from Mr. Rafael Pinol Batres, Guatemala City.

Solubility	Hazy in 10 vol. of 70% alcohol. Clearly soluble in 0.5 vol. of 90% alcohol

The oil had a very agreeable, somewhat lemon-like odor accompanied by a fruity note. The oil might be employed in all kinds of flavors, perfumes, toilet preparations, and soaps.

United States (California).—The growing of *Eucalyptus citriodora* in California is in the nature of an experiment; this tree does not stand cold temperatures, 28° F. being about the critical point. (There is one tree, perhaps the northernmost of its kind, growing at Belvedere on San Francisco Bay, at some 150 ft. above sea level; it is about 60 ft. high.) *E. citriodora* has been planted only in the coastal areas of Southern California. So far, there exist in California comparatively few *citriodora* trees, probably two or three thousand, as compared with several millions of *E. globulus*. For instance, three or four miles of *E. citriodora* trees have been planted along the curbs of Cajon Boulevard in San Diego. These trees have grown very tall and are now beyond the economical pruning stage for any oil recovery. The only organized *E. citriodora* planting in California is located near Oceanside, but it consists of only one acre, the trees being planted in squares of 8 by 8 ft. The leaf material is collected three times a year by cutting the plants back like a hedge.

An oil of *Eucalyptus citriodora* produced experimentally in California and examined in the New York laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 15°/15°	0.871
Optical Rotation	−1° 7′
Refractive Index at 20°	1.4547
Aldehyde Content, Calculated as Citronellal (Hydroxylamine Hydrochloride Method)	65.8%
Solubility at 20°	Opalescent in 3 to 3.5 vol. and more of 70% alcohol
Color	Yellow

Owing to the high cost of labor in California, commercial production of this oil is practically impossible.

SUGGESTED ADDITIONAL LITERATURE

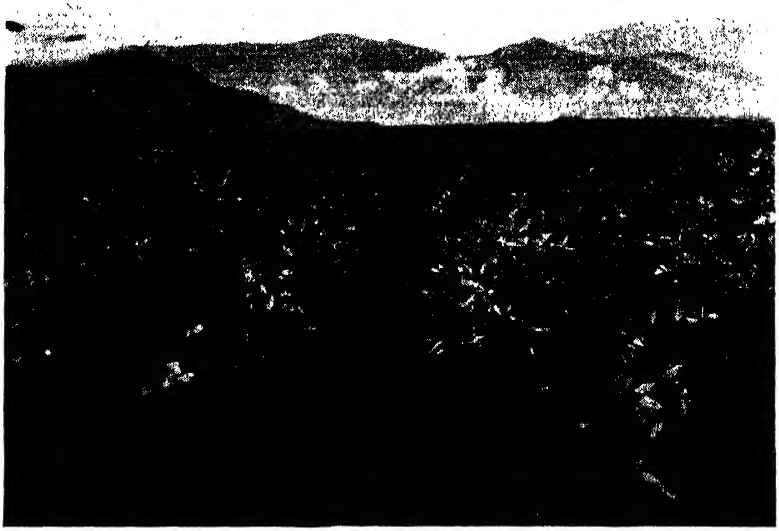
A. Hoffmann, "Comparative study of some methods used for the determination of citronellal in the oils of *Eucalyptus citriodora*," *Anais assoc. quím. Brasil* **6** (1947), 240. *Chem. Abstracts* **42** (1948), 8417.

EUCALYPTUS OILS FROM THE BELGIAN CONGO[141]

by

ERNEST GUENTHER

General.—According to various government reports,[142] eucalyptus oils in the Belgian Congo were first produced in 1944. The principal producing regions are located in the eastern part of the colony, particularly in the province of Kivu, northwest of Lake Kivu between Sake and the Mokotos lakes, at altitudes ranging from 1,500 to 2,100 m. Rainfall in these sections is regular, averaging 1.8 m. per year. Because there is no prolonged dry season, termites do not flourish to attack the plants, and, as yet, no other insects or major diseases affect the trees. The soil is fertile, varying from recent volcanic ash to the alluvium of small rivers and decomposed slate.



Courtesy of Gerard J. Danco, Inc., New York.

FIG. 34. Production of eucalyptus oil in the Belgian Congo. A young eucalyptus plantation.

Although essential oils are not generally regarded as a primary crop in

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[141] The author is indebted to Mr. Gerard J. Danco, New York, for much of the information contained in this monograph.

[142] U. S. Dept. Comm., Off. Intern. Trade, "World Trade in Commodities." Vol. 7, Pt. 3 (1949), No. 16—"The Belgian Congo as a Source of Crude Drugs and Essential Oils." Further data supplied by the Ministère des Colonies, Bruxelles. Office des Produits Agricoles de Costermansville. Institut National pour l'Etude Agronomique du Congo Belge, Yangambi. All through the courtesy of Mr. Gerard J. Danco, New York.

the Belgian Congo, they occupy an important place in the agricultural economy of the Kivu area. To the coffee planter, the subsidiary crops represent some insurance against a sudden collapse in the price of Arabica coffee. Of the 1946 production of 12,734 kg. of eucalyptus oil in the Belgian Congo, 12,434 kg. were distilled in the Kivu section. In 1947 and 1948 the production of eucalyptus oils in the Congo amounted to about 26,000 kg. each year.

Labor in the essential oil industry of the colony is supplied by the European growers who recruit local help. These workers, paid by daily wages, are housed on the plantations.

The trees are planted in nurseries and set out in the field when sufficiently strong. From 4,000 to 10,000 trees may be planted on one hectare. Cutting of the leaves commences when the young trees have attained a height of 2 to 3 m. By regular trimming the plants are kept in bush form. Many producers make it a practice to cut only a part of the foliage of each bush, in order to maintain the plants in good health and thereby increase production. Frequent, but only partial, trimming (two to three times per year) is therefore preferred. Because of the relatively uniform climate prevailing in the Kivu section, this can be done at any time of the year, except during the short dry seasons. Care of a eucalyptus plantation in full production consists of two weedings per year (by mowing).

As regards distillation equipment, the stills used in the Congo are of local construction and are made of bricks and concrete. Of large capacity (8 to 30 cu. m.) they hold up to 10 metric tons of plant material. The condensers consist of galvanized iron tubes. Drums holding 200 liters of water each, and fed at constant level, are housed in a solid brick enclosure and serve as steam generators. Because of the low-pressure steam employed, the practice is to intersperse the leaf material in the retort with branches. This arrangement allows for easy passage of the steam through the plant charge and prevents back-pressure in the drums of the steam generator, permitting the water to remain at constant level. Exhausted plant material, dried in the sun, serves as fuel.

The following will briefly describe the various types of eucalyptus oils produced in the Belgian Congo, commercially and experimentally:

Medicinal Eucalyptus Oils.—The most important and profitable species grown in the Kivu section of the Belgian Congo is *Eucalyptus smithii.*

One hectare planted with this species is said to produce, with two cuttings, from 150 to 600 kg. of oil per year. The yield of oil from fresh plant material amounts to 0.9 per cent only. This low yield results partly from the practice of interspersing the leaf material in the stills with inert branches (see above), and partly from the moist, rainy climate prevailing in the Kivu section. The yield does not seem to be influenced by conditions of soil and altitude, except insofar as low altitudes adversely affect the development of leaves.

Distillation of one charge of the leaves requires 3 to 4 hr. The two principal producers in the Kivu section rectify the crude oil in commercial stills, whereby about 20 per cent of oil is lost. The purpose of rectification is to produce oils which will satisfy the requirements of the various pharmacopoeias, in respect to cineole content and other properties.

Total production of rectified oil per year amounts to more than 20 metric tons. Because of the low and unprofitable prices prevailing in 1949, no expansion of production was planned at that time. It should, however, be kept in mind that the eucalyptus trees in the Belgian Congo were planted originally for the purpose of oil production only. It is quite possible that new plantations will be started at some future date with a view toward the production of wood for fuel and timber, and that the essential oil will then be only a low-priced by-product. Since *Eucalyptus smithii* is a fast-growing tree, plantings undertaken for the purpose of wood production would probably be profitable.

Another type of medicinal eucalyptus oil produced in the Belgian Congo is that of *Eucalyptus globulus*. In the Kivu section the crude oil contains, on the average, 55 per cent of cineole. Production per cutting amounts to 24 metric tons of leaves per hectare, which yield 180 liters or 165.6 kg. of oil after rectification. With two cuttings per year, 332 kg. of oil can be produced on each hectare.

As the cineole content of the natural oil is too small for commercial pharmaceutical use, the oil must be rectified. During this process the oil loses about 35 per cent of its weight. Thus, annual production of commercially acceptable oil amounts to 216 kg. per hectare.

As regards the physicochemical properties of medicinal eucalyptus oils from the Belgian Congo, the analytical laboratories of Fritzsche Brothers, Inc., New York, have collected the following data for commercial shipments:

Specific Gravity at 25°/25°	0.907 to 0.909
Optical Rotation at 25°	+4° 19′ to +5° 15′
Refractive Index at 20°	1.4598 to 1.4607
Cineole Content (*o*-Cresol Method)	71 to 74.2%
Phellandrene Test	Negative
Heavy Metals Test	Negative
Solubility	Soluble in 3 vol. and more of 70% alcohol

All oils were almost colorless; they met the U.S.P. specifications for rectified oils. The odor and quality of the oils were normal.

Industrial Eucalyptus Oils.—The most important type of industrial eucalyptus oil produced in the Belgian Congo (Kivu section) is that of *Eucalyptus* *dives* Schauer. It contains piperitone and phellandrene as chief constituents. In the Kivu section this species grows much more slowly than the other species described above. The leaves can be cut for the first time two years after transplanting into the field.

Distillation of one charge lasts 8 to 10 hr. The yield of oil from fresh leaf material varies from 1.8 to 2.0 per cent. One hectare is said to produce about 125 kg. of oil per year; higher figures have been reported, however. In general, data on this type of oil are vague, because of lack of experience. Total production per year amounts to only 3 metric tons of oil. No increase of production was planned in 1949, but a project for locally converting the piperitone isolated from the oil into synthetic menthol was under consideration. If realized, this may lead to an expansion of the *Eucalyptus dives* plantings which at present comprise only 20 to 30 hectares.

Perfumery Eucalyptus Oils.—The principal species are *Eucalyptus citriodora* and *E. macarthuri*, about 50 hectares of which were planted during the years of World War II. Annual production of oil, for each species, has been approximately one metric ton, but seems to be diminishing. It has been observed that on clayey soil *E. citriodora* does not grow well, and does not withstand trimming of the leaves. Old leaves of *E. citriodora* have yielded 0.516 per cent of oil, young leaves 0.528 per cent.

Future Outlook.—Several features combine to make the future of the eucalyptus oil industry in the Belgian Congo an uncertain one In the first place, Australian oils have re-entered the field as strong competitors on the world market. Since they are produced in quantity, they tend to replace the Congo oils, which are available only in small lots, and hence difficult to handle.

In the second place, the Congo oils suffer from certain deficiencies, which must be overcome if the industry is to flourish. The most serious of these is the lack of uniformity among the lots offered on the market. The rectification now practiced by only the principal producers must be universally adopted before the Congo oils can be accepted without reservation. As soon as the Congo can offer large lots of oil, of uniform quality, a substantial improvement in the industry may be expected.

EUCALYPTUS OILS OF LESSER IMPORTANCE

by
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In the foregoing we have discussed the commercially important eucalyptus oils. There are a great many other eucalyptus species and varieties, the essential oils of which have been produced on an experimental basis but which have not attained any commercial importance. The majority of these oils have been reported fully by R. T. Baker and H. G Smith in their monumental work, "A Research on the Eucalypts and Their Essential Oils." For completeness' sake, these oils will now be reviewed briefly in tabular form.

The authors are greatly indebted to Mr. H. H. G. McKern, Assistant Chemist, Museum of Technology and Applied Science, Sydney, Australia, for compiling the data on these oils.

NOMENCLATURE USED BY BAKER AND SMITH(1)	NOMENCLATURE ADOPTED BY BLAKELY(2)	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D[100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL. [% by weight]	PRINCIPAL CONSTITUENTS(3)	REFERENCE(4)
E. acaciaeformis Deane & Maiden		0.20	0.8864	+35.7°	1.4713	Insol. 10 vol. 80%	d-α-Pinene; sesquiterpene; geranyl acetate.	
E. accedens Fitz.		0.87	0.9084	+13.4°	1.4691	9 vol. 70%	Cineole [43%]; d-α-pinene; eudesmol; sesquiterpene.	
E. acervula Hook. f. See also E. paludosa, footnote.	**E. ovata** Labill.	0.22	0.8957 to 0.9300	-1.1° to -1.4°	1.4724 to 1.4870	1 vol. 80%	Cineole [21%]; d-α-pinene, phellandrene; geraniol & geranyl acetate.	
E. acmenioides Schau.	**E. triantha** Link.	0.09	0.9252	Not taken	1.5008	1 vol. 80%	Sesquiterpene; α-pinene; phellandrene.	
E. affinis Deane & Maiden		0.26	0.9259	+5.6°	1.4864	1 vol. 80%	Sesquiterpene; α-pinene; cineole [14-19%].	
E. aggregata Deane & Maiden		0.04	0.9474 to 0.9560	+11.2°	1.4977 to 1.5005	Insol. 10 vol. 80%	Amyl eudesmate and/or amyl phenylacetate, d-α-pinene.	
E. albens Miq.		0.11	0.9044	-6.5°	1.4679(6)	1 vol. 80%	Cineole [30%]; aldehydes(5), pinene; p-cymene.	
E. alpina Lindl.		0.36	0.8973	-2.8°	1.4756	Insol. 10 vol. 80%	α-Pinene; cineole [10%]	
E. amygdalina Labill.	**E. salicifolia** [Sol.] Cav.	1.80	0.8668 to 0.8848	-59.1° to -75.1°	1.4752 to 1.4781	7 vol. 70% to 1 vol. 80%	ℓ-α-Phellandrene; cineole [12-24%]; piperitone	
E. amygdalina Labill. Var. "A" *	**E. salicifolia** [Sol.] Cav.	0.7 to 0.8 *	0.897 to 0.906 *	-57.2° to -64.2° *	1.4727 to 1.4819 *	0.55 vol. 80%	Piperitone [36-46%]; α-phellandrene.*	
E. amygdalina Labill. var. nitida Benth.	**E. radiata** Sieb.	1.6	0.8625 to 0.8665	-45.74° to -57.8°	1.4805 to 1.4833	Insol. 10 vol. 80%	ℓ-α-Phellandrene; eudesmol, cineole.	

E. anceps [R. Br.] Blakely see **E. conglobata** var. anceps Maiden

E. andrewsi Maiden		1.25	0.8770 at 15.5°	-60.9°	1.4810		*l*-α-Phellandrene; p-cymene; piperitone; piperitol.	Jones & White Proc.Roy.Soc. Queensland Vol.40[1928], 132.
		1.27	0.8646	-41.5°	1.4831	Insol. 10 vol. 80%	*l*-α-Phellandrene; piperitone;sesquiterpene.	Baker & Smith
E. angophoroides Baker		0.19	0.9049	-11.5°	1.4824	1 vol. 80%	*l*-α-Phellandrene; pinene; cineole [18%]; sesquiterpene.	
E. apiculata Baker & Smith		0.70	0.9056 to 0.9112	-7.8° to -8.4°	1.4877	1 vol. 80%	*l*-Piperitone; d-α-pinene; cineole; sesquiterpene.	
	E. astringens Maiden	0.5 to 0.6 [air-dried material].	0.911 at 20°	+7.3°	1.469	1.1 vol. 80%	Cineole [50%]; α-pinene; aromadendrene.	Marshall & Watson, J. Roy. Soc. W. Australia Vol.24 [1937-8], 65.
E. australiana Baker & Smith "Type" [Penfold and Morrison's nomenclature]	E. radiata Sieb. var. australiana Blakely	3.0 to 3.5 *	0.916 to 0.930 *	+1° to +5° *	1.463 to 1.465 *	1.2 to 1.5 vol. 70% *	Cineole [65-72%]: α-pinene; α-terpineol; geraniol; citral [0.8 to 5.8%] *	See separate monograph on E. australiana oil in this volume; also "Composition of Commercial Eucalyptus Oils"

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[1] "A Research on the Eucalypts Especially in Regard to Their Essential Oils," 2nd Ed., Sydney, Govt. Printer (1920).

[2] "A Key to the Eucalypts." The Worker Trustees, Sydney (1934). This book is the most recent complete work on the genus available. It is by no means free of errors in nomenclature, but Blakely's terminology has been followed to preserve uniformity.

[3] For minor constituents the reader is referred to the original literature.

[4] Unless otherwise mentioned, all references are to Baker & Smith's monograph.

[5] The term "aldehydes" used in this table denotes the presence of one or more of that group of carbonyl constituents whose principal components are cuminal, phellandral and cryptone, and which nearly always occur together in eucalyptus oils, usually in association with *p*-cymene. They are not to be confused with the term "volatile aldehydes," used here to denote the low-boiling aliphatic aldehydes, of which isovaleric aldehyde is typical and the most common.

[6] This refractive index is believed by the present authors to be too low (in view of the composition of this oil). It probably is a transcription or typographical error in Baker & Smith's monograph. Unpublished data (A. R Penfold) give a range of 1.4871–1.4890, thus bringing it into line with figures for oils of *E hemiphloia* and *E. woollsiana*, with which *E. albens* oil is almost identical.

* Properties, constituents, or percentages of constituents marked with an asterisk are data additional to those in the original literature. They represent the findings of the Museum of Technology and Applied Science since 1920 on oils of the various individual species; and in the case of oils of commerce (e.g., *E dives*) are based on many hundreds of analyses. Asterisks on all future entries in this table refer to this note.

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D[100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL. [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
E. australiana variety "A" [Penfold and Morrison's nomenclature]	E. radiata Sieb.	1.5 to 2.3	0.8762 to 0.9013	-19.6° to -58.75°	1.4762 to 1.4787	1.8 vol. 70% to 5.0 vol. 80%	α-and γ-Terpinene; β-phellandrene; terpinen-4-ol.	Penfold and Morrison, J. Proc.Roy.Soc. N.S.W. Vol.69 [1935], 111
E. australiana variety "B" [Penfold and Morrison] = E. phellandra Baker & Smith	E. radiata Sieb.	3.0 to 4.5 *	0.902 to 0.905 *	-13.4° to -28.3° *	1.466 to 1.4695 *	1.3 to 10 vol. 70% *	Cineole [20-50%]; * ℓ-α-phellandrene; terpineol; citral.	See separate monograph on E. phellandra oil in this volume; also "Composition of Commercial Eucalyptus Oils"
E. australiana variety "C" [Penfold and Morrison's nomenclature]	E. radiata Sieb.	0.4 to 3.9	0.8686 to 0.9036	-43.8° to -68.5°	1.4766 to 1.4830	1.4 vol. 70% to 3.5 vol. 80%	ℓ-Piperitone; ℓ-piperitol; ℓ-α-phellandrene.	Penfold and Morrison, J. Proc.Roy.Soc. N.S.W. Vol.74 [1940], 277.
E. australiana var. latifolia Baker and Smith, see E. dives, var. "C"								
E. baeuerleni F.v.M.		0.33	0.8895	+4.05°	1.4784	4 vol. 80%	α-Pinene; cineole [20%]; eudesmol; sesquiterpene.	
E. baileyana F.v.M.		0.82	0.8928	+14°	1.4767	10 vol. 80%	d-α-Pinene; ℓ-aromadendrene.	
	E. bakeri Maiden	1.0	0.9257 to 0.9335	-1.2° to +1.0°	1.4629 to 1.4642	1 vol. 70%	Cineole [70-76%]; phloracetophenone dimethyl ether; aldehydes; p-cymene; esters; p-isopropylphenol.	Penfold, Ibid. Vol.61[1927], 179.
E. bancrofti Maiden		0.50	0.8982	-14.4°	1.4721	1 vol. 80%	Cineole [30%]; ℓ-α-phellandrene; ℓ-α-pinene.	
E. behriana F.v.M.		0.62	0.9237	+3.7°	1.4708	1.5 vol. 70%	Cineole [45%]; α-pinene.	

E bicolor Cunn.		0 85	0 9155	+5 5°	1 4675	1.5 vol. 70%	Cineole [48%]; pinene, volatile aldehydes	
	E. bicostata Maiden, Blakely and Simmonds.	1.14 to 2.40 [dry material]	0.9171 to 0 9336	+6 4° to +20°	1 4657 to 1.4804	1.1 to 1.5 vol. 70%	Cineole [38-65%]; d-α-pinene; eudesmol.	Penfold and Morrison, Ibid. Vol.64[1930],218.
E. blaxlandi Maiden & Cambage		0.83	0.8881	+11.0°	1 4653	6 vol. 80%	d-α-Pinene. cineole [21%]	
E. bosistoana F.v.M.		0 97	0.9078	+9 26°	1.4675	5 vol. 70%	Cineole [35%]; α-pinene, volatile aldehydes, sesquiterpene; terpineol.	
E botryoides Sm.		0.11	0.8774 to 0.8778	+23.75° for fraction 160°-190° [87% of oil]	1.4730	7 to 9 vol 80%	d-α-Pinene; sesquiterpene.	
E. bridgesiana § Baker	**E. stuartiana F.v.M.**	0.67	0.9120 to 0.9246	+1 8° to +3.35°	1.4655 to 1.4672	1.5 vol. 70%	Cineole [65%]; α-pinene.	
E. caerulea Baker & Smith	**E. caleyi Maiden**	0 4	0.9158	+12.7°	1.4827	1 vol. 80%	α-Phellandrene, cineole [17%]; α-pinene; eudesmol.	
E. calophylla R. Br.		0.25	0.8756	+22.9°	1.4731	Insol. 10 vol. 80%	d-α-Pinene; p-cymene; sesquiterpene.	
E. calycogona Turcz.		1 0	0 9152	+7.6°	1.4659	5 vol. 70%	Cineole [50%]; d-α-pinene, sesquiterpene	
E. campanulata Baker & Smith		0.85	0 8804	-25 8°	1.4847	10 vol 80%	α-Phellandrene, eudesmol	
	E. campaspe Moore	0.72	0.9118	5.43° [No sign given]	1.4762	5 vol. 80%	α-Pinene, p-cymene, cineole [15%]; alcohols [18.65%]	Phillips, J.Roy. Soc.W.Australia Vol.9[1923],107
		1.22	0.9225	+7 15°	1.465	1 vol. 80%	Cineole [64%]; geraniol [7%]; aromadendrene.	Watson, Ibid. Vol. 31[1944-45], 33

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§ *E. bridgesiana* Baker, the oil of which is described by Baker and Smith (p. 141), is synonymised by Blakely with *E. stuartiana* F.v.M. However, in another place (p. 100), Baker and Smith describe a species and its oil which they call *E. stuartiana* F.v.M.

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D[100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL. [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
E. camphora Baker		1.34	0.9071 to 0.9167	+1.3°	1.4676	1.5 vol. 70%	Cineole [30-50%]; α-pinene; eudesmol.	
E. capitellata Sm.		0.11	0.9175	+4.4°	1.4771	1 vol. 80%	Cineole [25%]; α-pinene; α-phellandrene; sesquiterpene.	
E. carnea Baker		0.16	0.8901 to 0.8963	+37.2° to +39.0°	1.4681	7 vol. 80%	d-α-Pinene; terpinyl acetate; cineole [5-10%]	
E. cinerea F.v.M.		1.20	0.9113 to 0.9225	+2.5° to +4.1°	1.4649	1.5 vol. 70%	Cineole [54%]; α-pinene; butyraldehyde; valeraldehyde.	
E. citriodora Hook.		0.5 to 2.0 *	0.862 to 0.874 *	-1.0° to +6.5° *	1.450 to 1.459 *	1.5 to 4.2 vol. 70% *	Citronellal [65-80%]; citronellol [15-20%]; esters.*	See separate monograph on E. citriodora oil in this volume, also "Composition of Commercial Eucalyptus Oils."
E. cneorifolia DC.		About 2.0 *	0.915 to 0.925 *	-1° to -5° *	1.4654 to 1.4681 *	1.5 vol. 70% *	Cineole [70%]; * p-cymene; α- and β-phellandrene; aldehydes [ℓ-cryptone]	See separate monograph on E. cneorifolia oil in this volume; also "Composition of Commercial Eucalyptus Oils."
E. coccifera Hook. f.		0.61	0.8810	-35.8°	1.4849	Insol. 10 vol. 80%	ℓ-α-Phellandrene; sesquiterpene.	
	E. concinna Maiden & Blakely	1.7 to 1.8 [dry material]	0.923 at 20°	-0.18°	1.4650	2 vol. 70%	Cineole [65%]; aromadendrene; α-pinene; geraniol; volatile aldehydes.	Marshall & Watson, J.Roy. Soc. W. Australia Vol.26 [1939-40], 15.

E. conica Deane & Maiden		0.59	0.9057	+5.24°	1.4676	6 vol. 70%	α-Pinene; cineole [35%]; sesquiterpene; volatile aldehydes.	
		1.0 *	0.9235 *	+2.8° *	1.4618 *	1.1 vol. 70% *	Cineole [75%] *	
	E. conglobata var. anceps Maiden = E. anceps [R. Br.] Blakely	0.69 to 0.74	0.907 to 0.908	+13.37° to +14.11°			Cineole [57.2-58%]; d-α-pinene.	Berry & Swanson, J.Proc. Roy. Soc.N.S.W. Vol.76[1942], 53.
	E. conglomerata Maiden & Blakely	0.12 to 0.2	0.9451 to 0.9547 at 15.5°	5.7° to 7.3° [Sign not given]	1.4936 to 1.4980	Not determined.	ℓ-α-Phellandrene; 2 sesquiterpenes; a sesquiterpene alcohol; conglomerone.	Lahey & Jones Proc.Roy.Soc. Queensland Vol.50[1938], 10.
E. consideniana Maiden		1.20	0.9027	+2.9°	1.4737	2 vol. 70%	Cineole [40%] α-phellandrene; α-pinene; eudesmol.	
E. cordata Labill.		2.3	0.9138	+8.5°	1.4638	1.5 vol. 70%	Cineole [55%]; d-α-pinene; volatile aldehydes.	
E. coriacea Cunn.	E. pauciflora Sieb.	0.61	0.8947 to 0.8983	-27.0° to -29.3°	1.4845 to 1.4890	1 vol. 80%	ℓ-α-Phellandrene; eudesmol; piperitone.	
E. cornuta Labill.		1.20	0.9043	+10.1°	1.4601	2 vol. 70%	Cineole [31%]; d-α-pinene: volatile aldehydes.	
E. corymbosa Sm.	E. gummifera [Gaertn.] Hochr.	0.06	0.883	-8.4°	1.4838	Insol. 10 vol. 80%	α-Pinene; sesquiterpene.	
E. corynocalyx F.v.M.	E. cladocalyx F.v.M.	0.096	0.8945	+8.1°	1.4779	4 vol. 80%	Cineole [20%]; d-α-pinene.	
E. cosmophylla F.v.M.		0.62	0.9108	-3.2°	1.4659	7 vol. 70%	Cineole [43%]; α-pinene; volatile aldehydes.	
E. costata R. Br.	E. angulosa Schau.	0.90 to 1.20	0.9023	+4.8° to +11.8°	1.4657 to 1.4676	1.5 vol. 70% to 1.0 vol. 80%	Cineole [35-60%]; d-α-pinene; sesquiterpene.	
E. crebra F.v.M.	E. racemosa Cav.	0.16	0.8986	-10.8°	1.4787	Insol. 10 vol. 80%	ℓ-α-Phellandrene; cineole [22%]; α-pinene; sesquiterpene.	

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D[100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL. [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
E. dalrympleana Maiden		0.48	0.9133 to 0.9145	+4.6° to +6.7°	1.4639 to 1.4645	2 vol. 70%	Cineole [50%]; α-pinene.	
E. dawsoni Baker		0.18	0.9418	-23.5° [1st Fraction]	1.5077	2 vol. 80%	Sesquiterpene; ℓ-α-phellandrene.	
E. dealbata Cunn.		0.86	0.9261	+3.8°	1.4648	1.75 vol. 70%	Cineole [52%]; α-pinene, sesquiterpene.	
E. deanei Maiden		0.60	0.9216	-3.2°	1.4896	2 vol. 80%	α-Pinene, p-cymene, cineole [8-10%]; aldehydes, sesquiterpene.	
E. delegatensis Baker	**E. gigantea Hook. f.**	1.70	0.8596 to 0.8676	-47.4° to -58.6°	1.4812 to 1.4863	Insol. 10 vol 80%	ℓ-α-Phellandrene, piperitone.	
E. dextropinea Baker	**E. muelleriana Howitt**	0.85	0.8758 to 0.8778	About +30°	1.4684	Insol. 10 vol 80%	d-α-Pinene.	
E. diversicolor F.v.M.		0.80	0.8948 to 0.9145	+20.5° to +30.1°	1.4671 to 1.4748	1 to 4 vol. 80%	d-α-Pinene; d-α-terpineol; butyl butyrate; volatile aldehydes.	
E. dives Schau. "Type" [Penfold and Morrison's nomenclature]		3.0 to 4.0 *	0.8892 to 0.9063 *	-43.8° to -78.0° *	1.4784 to 1.4812 *	1.3 to 10 vol. 70% *	ℓ-Piperitone [40-52%]; ℓ-α-phellandrene [20-30%] *	See separate monograph on E. dives oil in this volume; also "Composition of Commercial Eucalyptus Oils".
E. dives Schau. Variety "A" [Penfold and Morrison's nomenclature]		1.5 to 5.1	0.8630 to 0.8879	-43.75° to -66°	1.4750 to 1.4792	Insol. 10 vol 70%	ℓ-α-Phellandrene [60-80%]; ℓ-piperitone [2-8%]	Penfold & Morrison, J. Proc.Roy.Soc. N.S.W. Vol. 61 [1927],54; Vol.63[1929],79.

E. dives Schau. Variety "B" [Penfold and Morrison's nomenclature]		2.9 to 3.9	0.9062 to 0.9148	-13.4° to -28.3°	1.4669 to 1.4711	1.1 to 1.3 vol. 70%	l-α-Phellandrene; cineole [25-45%]; piperitone [12-18%]	Penfold & Morrison, Ibid., Vol.61[1927],54.
E. dives Schau. Variety "C" [Penfold and Morrison's nomenclature]		3 to 4*	0.917 to 0.923*	Up to +4°*	1.4609 to 1.4640*	1 to 1.5 vol. 70%*	Cineole [68-75%];* terpineol; geraniol; citral.	See separate monograph on E. dives Var. "C" oil in this volume; also "Composition of Commercial Eucalyptus Oils."
E. dumosa Cunn.		1	0.9016 to 0.9151	+2.2° to +16.4°	1.4667 to 1.4703	1.75 vol. 70% to 1.0 vol. 80%	Cineole [33-44%]; d-α-pinene; aldehydes; sesquiterpenes.	
		1	0.9187	+5.5°	1.4620	5 vol. 70% [by volume]	Cineole [66%]	Penfold & Morrison, Bull. No.2, "Commercial Eucalyptus Oils," Technological Museum, Sydney, 4th Ed., [1944] 11, Govt. Printer.
	E. dundasi Maiden	0.2	0.9075 at 20°	+10.65°	1.4694	1 vol. 80%	Cineole [32%]; α-pinene; ester [13%] aromadendrene.	Marshall & Watson, J.Roy.Soc. W. Australia, Vol. 21 [1934-35],107.
E. elaeophora F.v.M.		1.5 to 2.5*	0.916 to 0.926*	+2° to +5.7°*	1.4610 to 1.4624*	2 vol. 70% [by Volume]	Cineole [65-80%];* α-pinene; aldehydes.	
	E. eremophila [Diels] Maiden	1.75	0.9040 [No temperature given]	+11.1°	1.4724 [No temperature given]	7 vol. 80%	Cineole [33%]; α-pinene: eudesmol [7%]; alcohols as geraniol [12%]	Marshall & Watson, Ibid., Vol.23[1936-37], 1.
	E. erythronema Turcz.	2.5 [air-dry material]	0.923 at 20°	-0.22°	1.466	2 vol. 70%	Cineole [70.9%]; geraniol.	Watson, Ibid., Vol. 28[1941-42], 247.

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D [100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
E. eugenioides Sieb.	**E. scabra** Dum.-Cours.	0.75	0.9122 to 0.9132	+3.4° to +4.8°	1.4694	6 to 7 vol. 70%	α-Pinene; cineole [30%]; sesquiterpene.	
E. eximia Schau.		0.46	0.8998	+28.8°	1.4832	Insol. 10 vol 80%	d-α-Pinene; sesquiterpene; eudesmol.	
		0.81 *	0.8898 *	+31.65° *	1.4859 *	10.2 vol. 80% *		
E. exserta F.v.M.		0.82	0.8977	+12.2°	1.4729	5 vol. 80%	Cineole [29%]; d-α-pinene; sesquiterpene; aldehydes.	
E. fasciculosa F.v.M.		0.02	0.9041	+6.3°	1.4789	10 vol. 80%	Cineole [less than 15%]	
E. fastigata Deane & Maiden		0.12	0.8925 to 0.9001	+2.8° to -9.5° [1st fraction]	1.4816	5 vol. 80% to insol.	d-α-Pinene; α-phellandrene; cineole.	
		0.43 to 2.4 *	0.9044 to 0.9128 *	-7.5° to -17.7° *	1.4687 to 1.4857 *			
E. fletcheri Baker	**E. baueriana** Schau.	0.30	0.8805 to 0.895	-12.5°	1.4824	2 vol. to insol. 80%	α-Phellandrene; cineole [5-10%]; sesquiterpene.	
	E. flocktoniae Maiden	1.75	0.9216 at 20°	+0.32°	1.4728	2 vol. 70%	Cineole [46%]; aromadendrene; α-pinene [10%]; alcohols [25%]	Watson, Ibid., Vol.21[1934-35], 101.
E. fraxinoides Deane & Maiden		0.98	0.8687	-27.5°	1.4851	Insol.10 vol. 80%	ℓ-α-Phellandrene; cineole [5-10%]; eudesmol; piperitone.	
E. globulus Labill.		0.75 to 1.25 *	0.910 to 0.930 *	+0.3° to +15° *	1.460 to 1.470 *	1.5 to 3.0 vol. 70% *	Cineole [65-75%];* d-α-pinene; volatile aldehydes; sesquiterpenes; globulol.	See monograph Spanish & American E. globulus oils by E. Guenther.
E. gomphocephala DC.		0.03	0.8759	-10.2°	1.4758	Insol. 10 vol. 80%	α-Phellandrene; α-pinene.	

E. goniocalyx F.v.M.		1.0	0.9117 to 0.9125	+4.35° to +7.2°	1.4689	1.5 vol. 70%	Cineole [55-56%]; d-α-pinene; volatile aldehydes; eudesmol; sesquiterpene.	
E. goniocalyx F.v.M. [cont.]		0.82 to 0.95	0.923 to 0.9252	+3.2° to +6.2°	1.4646 to 1.4793		Cineole [25-64%]	
E. gracilis F.v.M.		0.9	0.9098	+1.35°	1.4714	1 vol. 80%	Cineole [19%]; d-α-pinene; aldehydes; p-cymene.	
E. gullicki[‡] Baker & Smith	E. maculosa Baker	0.38	0.9285	+6.7°	1.4717	1.1 vol. 70%	Cineole [46%]; α-pinene; eudesmol.	
E. gunnii Hook.		0.68	0.8984 to 0.9014	-4.3° to +4.7°	1.4743 to 1.4799	4 to 8 vol. 80%	d-α-Pinene; l-α-phellandrene; cineole [20-26%]	
E. haemastoma Sm.		0.3 to 0.5	0.9295 to 0.9571	+3.3° to +15.5°	1.4861 to 1.4957	2 to 10 vol. 70%	Eudesmol; sesquiterpenes; d-α-pinene; cineole [10-15%]	Penfold & Morrison, J. Proc.Roy.Soc. N.S.W. Vol.61 [1927], 275.
E. hemilampra[§] F.v.M.	E. resinifera Sm.	0.37	0.9282	+7.09°	1.4678	1.5 vol. 70%	Cineole [35%]; α-pinene; sesquiterpene; valeraldehyde.	
E. hemiphloia F.v.M.		0.4 to 0.9*	0.924 to 0.931*	-24° to -29°*	1.491 to 1.495*	1.3 to 1.5 vol. 70%*	p-Cymene; cuminal; l-phellandral; l-cryptone; cineole [5-15%]*	
E. intermedia Baker		0.13	0.8829 to 0.8881	+9.9° to +12.2°	1.4821	Insol. 10 vol. 80%	d-α-Pinene; aldehydes; sesquiterpene.	
E. intertexta Baker		0.2	0.9076 to 0.9078	+9.71° to +10.25°	1.4691	1.75 to 2.5 vol. 70%	Cineole [35%]; α-pinene; sesquiterpene.	
E. irbyi Baker & Smith		0.15	0.9021	-1.7°	1.4829	4 vol. 80%	Cineole [15%]; α-pinene; α-phellandrene; sesquiterpene.	

[‡] *E. gullicki* and *E. lactea* are both synonymised by Blakely with *E. maculosa*: Baker and Smith, however, regarded them as three separate species and described their oils separately.

[§] Synonymous with *E. resinifera* Sm. var. *grandiflora* Benth.

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D [100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
	E. kesselli Maiden & Blakely	1.23	0.9248 @ 20°	Inactive	1.4728	2 vol. 70%	Cineole [45%]; d-α-pinene; aromadendrene.	Marshall & Watson, J.Roy. Soc.W. Australia Vol. 21 [1934-35],107.
	E. kochii Maiden & Blakely	2.1 [Fresh material] 3.9 [dry material]	0.921 to 0.925 [Temp. not given]	+0.54° to +3.8°	1.4595 to 1.460	1.8 to 2.1 vol. 70%	Cineole [87.5-92%]	Watson, Ibid. Vol.31[1944-45], 33.
E. lactea‡ Baker	**E. maculosa** Baker	0.56	0.8752 to 0.8826	Inactive	1.4845	2 to 5 vol. 80%	α-Pinene; p-cymene; cineole [10%]	
E. laevopinea Baker		0.61	0.8755 to 0.8875	-30.7° to -37.8°	1.4686 to 1.4704	Insol. 10 vol. 80%	ℓ-α-Pinene; cineole [ca. 10%]	
E. laseroni Baker		0.37	0.9095	-8.1°	1.4790	6 vol. 80%	α-Pinene; α -phellandrene; cineole [5-8%]; sesquiterpene.	
E. lehmanni Preiss.		0.86	0.8964	+17.5°	1.4653	1 vol. 80%	Cineole [20%]; d-α-pinene; volatile aldehydes.	
	E. leptopoda Benth.	1.3	0.9200 [No temp. given]	-0.94°	1.4662 [No temp. given]	1.8 vol. 70%	Cineole [68%]; α - pinene; geraniol [11%]; aromadendrene; volatile aldehydes.	Marshall & Watson, Ibid. Vol.23[1936-37], 1.
E. leucoxylon F.v.M.		1.5 to 2.5 *	0.910 to 0.920 *	+2.0° *	1.4612 to 1.4624 *	6 vol. 70% [V/V] *	Cineole [65-75%]; * α-pinene; limonene.	
E. ligustrina DC.		0.12	0.9499	+22.4°	1.4974	1 vol. 80%	Eudesmol; sesquiterpene; geraniol and geranyl acetate [7%]	
E. linearis Cunn.	**E. linearis** Dehn.	1.5	0.9036 to 0.9096	-9.9' to -23.1°	1.4677 to 1.4734	6 to 8 vol. 70%	ℓ-α-Phellandrene; cineole [44-51%]; eudesmol; piperitone.	

E. longicornis F.v.M.		1.2	0.9203	+5.0°	1.4670	1.5 vol. 70%	Cineole [56%]; α-pinene; sesquiterpene.
E. longifolia Link & Otto		0.54	0.9226	+2.86°	1.4681	1.25 vol. 70%	Cineole [61%]; α-pinene; sesquiterpene.
E. luehmanniana F.v.M.	E. virgata Sieb.	0.30	0.879	-27.5°	1.4880	Insol. 10 vol. 80%	l-α-Phellandrene; eudesmol; cineole [ca. 10%]
E. macarthuri Deane & Maiden		0.2 to 1.0 *	0.921 to 0.935 *	+1.0° +6.0° *	1.469 to 1.477 *	1.25 to 1.50 vol. 70% *	Geranyl acetate [60-70%]*; geraniol; eudesmol; d-α-pinene.
E. macrorhyncha F.v.M.		0.29	0.929	Not taken	1.4745	2 vol. 70%	Cineole [30%]; α-pinene; α-phellandrene; eudesmol.
E. maculata Hook.		0.23	0.8959 to 0.9201	+5.1° to +7.7°	1.4804	1 to 4 vol. 80%	d-α-Pinene; cineole [18%]; sesquiterpene.
E. maculosa Baker		1.1	0.9158 to 0.9229	+2.3° to +3.35°	1.4684	1.75 vol. 70%	Cineole [46-58%]; α-pinene; eudesmol.
E. maideni F.v.M.		1.0	0.9247	+5.8°	1.4679	1.5 vol. 70%	Cineole [50%]; α-pinene.
E. marginata Sm.		0.22	0.8889 to 0.9117	-8.5° to -10.4°	1.4889	1 to 5 vol. 80%	p-Cymene; aldehydes; α-pinene; sesquiterpene.
E. marsdeni Hall	E. penrithensis Maiden	0.7	0.9469	+4.8°	1.4989	Insol. 10 vol. 80%	Sesquiterpenes.
E. megacarpa F.v.M.		0.5	0.8852	-31.2°	1.4719	10 vol. 80%	l-α-Pinene; l-limonene; cineole [15%]; α-terpinene.
E. melanophloia F.v.M.		0.11	0.8959	-23.5°	1.4893	Insol. 10 vol. 80%	α-Phellandrene; α-pinene; p-cymene; cineole [5-10%]; sesquiterpene; eudesmol.
E. melliodora Cunn.		0.87	0.9042 to 0.9321	+5.0° to +6.5°	1.4649	1.5 to 6.0 vol. 70%	Cineole [52-60%]; α-pinene; α-phellandrene.

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‡ *E. gullicki* and *E. lactea* are both synonymised by Blakely with *E. maculosa:* Baker and Smith, however, regarded them as three separate species and described their oils separately.

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D[100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
	E. micrantha DC. "Type" [Penfold & Morrison's nomenclature]	0.62 to 0.9	0.8883 to 0.9122	+5° to -25.5°	1.4701 to 1.4892	1 to 8 vol. 80%	ℓ-α-Phellandrene; cineole [up to 33%]; piperitol; α-pinene.	Penfold & Morrison, J. Proc.Roy.Soc. N.S.W. Vol.61 [1927], 267.
	E. micrantha DC., Variety "A" [Penfold & Morrison's nomenclature]	1.2 to 1.5	0.8949 to 0.9011	-48.2° to -57.0°	1.4820 to 1.4837	4.5 to 10.0 vol. 70%	Piperitone [41-47%]; ℓ-α-phellandrene; piperitol.	Penfold & Morrison, Ibid., Vol.67[1933], 359.
	E. micrantha DC. Fraser Island Form [Penfold & Morrison]	2.0	0.8775	-23.0°	1.4869	10 vol. 80%	β-Phellandrene; Δ^4-carene; phellandral; ℓ-cryptone.	Ibid., Vol. 61 [1927], 354.
E. microcorys F.v.M.		0.71 to 0.73	0.8953 to 0.9069	+17.9° to +18.6°	1.4671 to 1.4690	Not determined	d-α-Pinene; cineole [43.9-46%]; borneol and its esters; isovaleric aldehyde.	Jones & Lahey, Proc.Roy.Soc. Queensland Vol.50[1938], 43.
E. microtheca F.v.M.	E. coolabah Blakely & Jacobs	0.48	0.8855	-27.2°	1.4838	Insol. 10 vol. 80%	ℓ-α-Phellandrene; α-pinene; sesquiterpene.	
E. moorei Maiden & Cambage		0.8	0.9289	+6.12°	1.4699	1.1 vol. 70%	Cineole [56%]; eudesmol; α-pinene.	
E. morrisii Baker		1.65	0.9097 to 0.9164	+3.76° to +6.1°	1.4636	1.5 vol. 70%	Cineole [59-63%]; α-pinene.	
E. muelleri Moore	E. johnstoni Maiden	1.28	0.9096	+10.4°	1.4647	4 vol. 70%	Cineole [57%]; d-α-pinene.	
E. nepeanensis‡ Baker & Smith	E. bosistoana F.v.M.	0.52	0.9259	+1.1°	1.4677	1.25 vol. 70%	Cineole [56%]; α-pinene; sesquiterpene.	
E. nigra Baker		0.04	0.8744	-34°	1.4706	Insol. 10 vol. 80%	ℓ-α-Pinene; cineole [11%]	

Deane & Maiden			0.9301	+14.5°	1.4932	80%	dendrene.	
E. numerosa Maiden "Type" [The actual specific name used by Baker and Smith is E. radiata Sieb.]	**E. lindleyana DC.**	1 to 3*	0.876 to 0.905*	-25° to -42°*	1.477 to 1.481*	Sol. to insol. in 70%*	ℓ-α-Phellandrene; piperitol [10-15%]; piperitone [5-10%]	Penfold & Morrison, J. Proc.Roy.Soc. N.S.W. Vol.66[1932],181.
E. numerosa Maiden Variety "A" [Penfold & Morrison's nomenclature.]	**E. lindleyana DC. var. stenophylla Blakely**	1 to 3*	0.895 to 0.910*	-45° to -65°*	1.479 to 1.482*	1.3 to 10.0 vol. 70%*	ℓ-Piperitone [40-52%]; ℓ-α-phellandrene	Ibid.
E. numerosa Maiden Variety "B" [Penfold & Morrison's nomenclature.]	**E. lindleyana DC.**	1.7 to 2.7	0.9009 tc 0.9034	-40.2° to -42.1°	1.4737 to 1.4740	1.2 to 1.4 vol. 70%	ℓ-Piperitone [20-30%]; cineole [12-15%]; ℓ-α-phellandrene; piperitol.	Ibid.
E. obliqua L'Her.		0.7	0.8836 to 0.8902	-24.2° to -28.8°	1.4835 to 1.4877	1.0 to 4.0 vol. 80%	ℓ-α-Phellandrene; aldehydes; p-cymene; cineole [15%]	
E. obtusiflora DC.		No oil obtained from 280 lb.	-	-	-	-		
E. occidentalis Endl.		0.95	0.9135	+9.0°	1.4717	1 vol. 80%	d-α-Pinene; cineole [36%]; aldehydes.	
E. odorata Behr.	**E. odorata Behr. & Schlecht**	1.87	0.9193	-1.1°	1.4639	1.25 vol. 70%	Cineole [63%]; aldehydes.	
E. oleosa F.v.M. [New South Wales Form]		1.1	0.925	-1.5°	1.4689	1.25 vol. 70%	Cineole [52%]; α-pinene; aldehydes.	
E. oleosa F.v.M. [West.Aust. Form]		1.0	0.936 [No temp. given]	-7.42°	1.4754 [No temp. given]	1.3 vol. 70%	Cineole [45%]; geraniol [20%]; aldehydes; aromadendrene.	Marshall & Watson, J.Roy. Soc. W.Australia Vol.23 [1936-37], 1.

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‡ Blakely synonymises Baker & Smith's *E. nepeanensis* with *E. bosistoana* F.v.M. However, Baker and Smith describe separately the oil of *E. bosistoana* F.v.M.

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D[100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
E. oreades Baker		1.2	0.8869	-22.7°	1.4888	1 vol. 80%	ℓ-α-Phellandrene; eudesmol; sesquiterpene.	
E. ovalifolia[§] **Baker**	**E. polyanthemos Schau.**	0.27	0.9058	-8.9°	1.4864	1 vol.80%	ℓ-α-Phellandrene; sesquiterpene.	
E. ovalifolia Baker var. lanceolata Baker & Smith		0.58	0.9083	-4.26°	1.4654	2 vol. 70%	Cineole [45%]; α-pinene; α- phellandrene; sesquiterpene.	
E. paludosa[¶] **Baker**	**E. ovata Labill.**	0.24	0.9056	+10°	1.4716	1 vol. 80%	d-α-Pinene; cineole [23%]; sesquiterpene.	
E. paniculata Sm.		0.1	0.901	+7.8°	1.4744	1 vol. 80%	α-Pinene; cineole [29%]; esters & alcohols.	
E. parramattensis Hall		0.57	0.9223	+2.7°	1.4629	1.25 vol.70%	Cineole [75%]; volatile aldehydes; α-pinene.	
E. parvifolia Cambage		0.7	0.9177	+3.6°	1.4644	1.2 vol. 70%	Cineole [69%]; α-pinene; volatile aldehydes; eudesmol.	
E. patentinervis Baker	**E. kirtoniana F.v.M.**	0.26	0.8735	-15.2°	1.4891	Insol. 10 vol. 80%	Terpenes [limonene ?]; citral; sesquiterpenes.	
E. perriniana F.v.M.	**E. perriniana [F.v.M.] Rodway**	1.1	0.9082 to 0.9119	+5.7° to +8.90°	1.4612 to 1.4628	2 to 7 vol. 70%	Cineole [58%]; α-pinene; butyl butyrate: volatile aldehydes.	
E. phellandra Baker & Smith	**E. radiata Sieb.**	See **E. australiana** variety "B"						
E. phlebophylla F.v.M.	**E. pauciflora Sieb.**	1 to 1.5 *	0.876 to 0.913 *	-19° to -33° *	1.4679 to 1.4836 *	Insol. 10 vol. 80% *	ℓ-α-Pinene [60%]; eudesmol [20-30%]; cineole [under 10%] *	

E. pilularis Sm		0.11	0.885 to 0.903	-4.2° to +11.1°	1.4904	8 vol. 80% to insol. 80%	ℓ-α-Phellandrene; d-α-pinene; sesquiterpene; eudesmol; cineole [5-10%]	
E. piperita Sm. "Type" [Penfold and Morrison's nomenclature]		2 to 2.5	0.8924 to 0.9016	-52.0° to -62.75°	1.4805 to 1.4821	5 to 10 vol. 70%	ℓ-Piperitone [40-50%]; ℓ-α-phellandrene.	Penfold & Morrison, J. Proc.Roy.Soc. N.S.W. Vol.58 [1924], 124.
E. piperita Sm. Variety "A" [Penfold and Morrison's nomenclature]		0.8	0.8785 to 0.9111	-2.7° to -35.5°	1.4772 to 1.4781	1 vol. 80% to insol.	α-Phellandrene; cineole [10-20%]; piperitone; eudesmol.	
E. planchoniana F.v.M.		0.014	0.9039	Not determined.	Not determined.	1 vol. 80%	α-Phellandrene; sesquiterpene.	
E. platypus Hook.		0.82	0.9103	+10.2°	1.4639	1.75 vol. 70%	Cineole [48%]; d-α-pinene; volatile aldehydes; sesquiterpene.	
E. polyanthemos Schau.		0.83	0.9281	+5.4°	1.4679	1.25 vol. 70%	Cineole [54%]; α-pinene.	
E. polybractea Baker	**E. fruticetorum F.v.M.**	1.5 to 2.5*	0.922 to 0.927*	+0.5° to +2.0°*	1.458 to 1.4616*	1 to 1.2 vol. 70%*	Cineole [77-84%];* p-cymene; cuminal; phellandral; cryptone.	See separate monograph on E. polybractea oil in this volume; also "Composition of Commercial Eucalyptus Oils."
E. populifolia Hook.		0.76	0.9207 to 0.923	+0.4° to +1.2°	1.4652	1.25 vol. 70%	Cineole [57-62%]; α-pinene; sesquiterpene.	
E. propinqua Deane & Maiden		0.24	0.8980	+4.4°	1.4731	8 vol. 70%	α-Pinene; cineole [32%]; aldehydes.	
E. pulverulenta Sims		2.22	0.9236	+2.12°	1.4629	1.25 vol. 70%	Cineole [60%]; α-pinene.	

|| *E. ovalifolia* Baker is synonymised by Blakely with *E. polyanthemos* Schau. However, Baker and Smith describe separately *E. ovalifolia* and *E. polyanthemos* Schau., as different oils were obtained from them.

¶ Both *E. paludosa* Baker and *E. acervula* Hook. f. are synonymised by Blakely with *E. ovata* Labill. However, Baker and Smith describe separately the two different oils distilled from material ascribed by them to *E. paludosa* Baker and *E. acervula* Hook. f., respectively.

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D[100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
E. pumila Cambage		1.6	0.9237	+2.3°	1.4683	1.1 vol. 70%	Cineole [74%]; d-α-pinene; volatile aldehydes.	
E punctata DC.		0.63 to 1.19	0.9129 to 0.9220	-2.30° to +4.07°	1.4717	1.25 vol. 70%	Cineole [46-64%]; α-pinene.	
E. punctata DC. variety didyma Baker & Smith		0.18 to 0.37	0.9033 to 0.9070	-4.2° to -5.9°	1.4811	7 vol. 70% to 2 vol. 80%	α-Pinene; aldehydes; cineole [10-15%]	
	E. pyriformis Turcz.	1.0 to 1.1	0.920 at 20°	+8.4°	1.469	1 vol. 80%	d-α-Pinene; cineole [56%]; eudesmol; aromadendrene; both low & high boiling aldehydes.	Marshall & Watson, J.Roy. Soc.W. Australia Vol.24 [1937-38], 65.
E. quadrangulata Deane & Maiden		0.68	0.9064	+10.7°	1.4625	2 vol. 70%	d-α-Pinene; cineole [32%]	
E. radiata Sieb.	E. lindleyana DC.	See under E. numerosa Maiden						
	E. rariflora Bailey	2.5 [Air-dry material]	0.9072 to 0.9154	-8.5° to -10°	1.4872 to 1.4909	0.8 vol. to partially sol. 10 vol. 80%	Δ^4-Carene; β-phellandrene; ℓ-α-pinene; β-pinene, p-cymene; cineole [ca.10%]; aromadendrene; dehydroangustione.	Penfold, Radcliffe & Short, J.Proc. Roy.Soc.N.S.W. Vol.64[1930],101.
E. redunca Schau.		1.2	0.9097	+13.5°	1.4663	6 vol. 70%	Cineole [38%]; α-pinene; sesquiterpene.	
E. regnans F.v.M.		0.81	0.8802 to 0.8879	-28.4° -31.1°	1.4882 to 1.4901	5 vol. 80%	ℓ-α-Phellandrene; eudesmol.	
E. resinifera Sm.		0.42	0.9098	+2.25°	1.4698	1.75 vol. 70%	Cineole [50%]; α-pinene.	
E. risdoni Hook. f.		1.4	0.9045 to 0.9079	-9.9° to -14.6°	1.4656 to 1.4677	3 to 5 vol. 70%	Cineole [56-58%]; ℓ-α-phellandrene; amyl acetate.	

E. robusta **Sm**		0.16	0.8777	+4.0°	1.4744	8 vol. 80%	α-Pinene, sesquiterpene; cineole; α-phellandrene.	
E. rodwayi[§] **Baker & Smith**	**E. aggregata** **Deane & Maiden**	0.48	0.9075	+10.6°	1.4671	6 vol. 70%	Cineole [64%]; α-pinene.	
E. rossii **Baker & Smith**		0.61	0.9168 to 0.9215	+7.2° to +9.8°	1.4684	1.25 to 1.5 vol. 70%	Cineole [40-42%]; α-pinene; eudesmol.	
E. rostrata **Schlecht.**	**E. camaldulensis** **Dehn.**	0.27	0.8953 to 0.9047	-11.8° to -14.5°	1.4839 to 1.4890	1 vol. to 2 vol. 80%	p-Cymene; phellandrene; cuminal; phellandral; geraniol; cineole [8-10%]	See also Gandini, Ann. chim. applicata Vol.26[1936],344 for composition of an Italian oil.
E. rostrata **Schlecht** **var. borealis** **Baker & Smith**		0.8	0.9109	+5.46°	1.4654	1.75 vol. 70%	Cineole [45%]; α-pinene.	
E. rubida **Deane & Maiden**		0.07	0.9067 to 0.9209	-1.1° to +4.4°	1.4892	Insol. 10 vol. 80%	α-Pinene; α-phellandrene; sesquiterpene; cineole [10-20%]	
E. rudderi **Maiden**		0.31	0.9042	-8.5°	1.4841	1 vol. 80%	p-Cymene; aldehydes.	
E. rudis **Endl**		1.2	0.9068	+10.1°	1.4695	1 vol. 80%	Cineole [38%]; d-α-pinene, volatile aldehydes.	
E. rydalensis[§] **Baker & Smith**	**E aggregata** **Deane & Maiden**	0.26	0.8854	+24.7°	1.4717	Insol. 10 vol. 80%	d-α-Pinene; esters, sesquiterpene; cineole [8%]	
E. saligna **Sm**		0.12	0.8731	+1.1°	1.4789 to 1.4795	10 vol. 80%	α-Pinene; p-cymene.	
E. saligna **Sm. var.** **pallidivalvis** **Baker & Smith**	**E. grandis** **[Hill] Maiden**	0.12 to 0.26	0.8860 to 0.8937	+32.4° to +34.5°	1.4703	7 to 9 vol. 80%	d-α-Pinene; esters & alcohols.	

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§ *E. rodwayi* and *E. rydalensis* of Baker and Smith are both synonymised by Blakely with *E. aggregata* Deane and Maiden. However, Baker and Smith describe them as three distinct species both morphologically and chemically.

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D[100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
E. salmonophloia F.v.M.		1.40	0.9137 at 20°	-4.12°	1.4731	1.75 vol. 70%	Cineole [46.4%]; α-pinene; aromadendrene.	Watson, J.Roy. Soc. W. Australia Vol.22 [1935-36], 113.
E. salubris F.v.M.		1.39	0.902	-5.8°	1.4784	1 vol. 80%	p-Cymene, α-pinene; aldehydes; cineole [10%]	
E. santalifolia F.v.M.	**E. diversifolia Bonpl.**	0.41	0.884	-37.7°	1.4736	8 vol. 80%	Terpenes [ℓ-limonene?]; sesquiterpenes [20%]; cineole [12%]	
E. seeana F.v.M.		0.78	0.91	+5.6°	1.4649	1.25 vol. 70%	Cineole [52%]; α-pinene.	
E. siderophloia Benth.		0.06	0.9067	+14.5°	1.4943	Insol. 10 vol. 80%	Phellandrene; pinene.	
E. sideroxylon Cunn.	**E. sideroxylon [Cunn.] Benth.**	1.5 to 2.5 *	0.915 to 0.919 *	+2.0° *	1.4612 to 1.4624 *	4 vol. 70% [by volume]	Cineole [65-75%] ; * α-pinene; sesquiterpene.	
E. sieberiana F.v.M.		0.5	0.8880	-43.3°	1.4829	Insol. 10 vol. 80%	ℓ-α-Phellandrene; piperitone; cineole [5-10%]	
E. smithii Baker		1.14 to 2.2	0.9133 to 0.9198	+4.7° to +6.4°	1.4616 to 1.4672	1.1 to 1.25 vol. 70%	Cineole [70-77%]; α-pinene; eudesmol.	
	E. spathulata Hook.	1.43	0.9239	+1.18°	1.4700	4 vol. 70%	Cineole [65%]; d-α-pinene; aromadendrene; aldehydes.	Phillips, Ibid. Vol. 9[1923], 107.
E. squamosa Deane & Maiden		0.65	0.9182	Inactive	1.4635	1.25 vol. 70%	Cineole [51%]; α-pinene; volatile aldehydes.	
E. staigeriana F.v.M.		1.2 to 1.5 *	0.871 to 0.883 *	-26.4° to -37.5° *	1.4793 to 1.4814 *	1 to 8 vol. 80% *	ℓ-Limonene; citral [16-40%]; geraniol and geranyl acetate; sesquiterpene. *	See also Naves, Perfumery Essential Oil Record Vol.39[1948],345. Anon.,Ibid. Vol.29 [1938], 127.

E. stellulata **Sieb.**		0.3	0.871	-22.7°	1.4845	Insol. 10 vol. 80%	ℓ-α-Phellandrene, cineole; sesquiterpene.	
E. stricta **Sieb.**		0.5	0 9246	-0.35°	1 4654	1 25 vol. 70%	Cineole [58%]; α-pinene, aldehydes, eudesmol.	
E. stuartiana **F.v M.**		0.4	0.916	+4.8°	1.4652	1 25 vol. 70%	Cineole [53%], α-pinene.	
E. stuartiana **F.v.M. var. cordata** **Baker & Smith**		1.13	0 934	+4.0°	1 4652	1.5 vol. 70%	Cineole [50%]; α-pinene.	
E. taeniola **Baker & Smith**		0.66	0.8864	-27 6°	1.4844	5 vol. 80%	ℓ-α-Phellandrene, eudesmol, sesquiterpene	
E. tereticornis **Sm.**	**E. umbellata** **[Gaertn.] Domin.**	0.5	0 9158 to 0.9218	-9.4° to -11 8°	1.4877 to 1.4906	1 vol. 80%	p-Cymene, cuminal, phellandral; α-pinene, cineole.	
E. tereticornis **var. cineolifera** **Baker & Smith**		0.9	0 9112	+0.6°	1.4703	1.75 vol. 70%	Cineole [45%]; α-pinene; aldehydes.	
E. tesselaris **F.v.M**		0.16	0 8757	+8.6°	1.4824	Insol. 10 vol. 80%	α-Pinene, aromadendrene; cineole [5-10%]	
	E. tetragona **[R. Br.] F.v.M**	0.48 [Air-dry material]	0.9390 at 20°	+3 65°	1.4954	1 vol. 80%	Aromadendrene; eudesmol [32%]; d-α-pinene; ℓ-α-phellandrene, cineole [15.4%]	Watson, Ibid. Vol. 22 [1935-36], 113.
E trachyphloia **F v.M.**		0.2	0.8873 to 0.8929	+8.4° to +9.8°	1.4844	Insol. 10. vol. 80%	d-α-Pinene; aromadendrene; aldehydes.	
E. umbra **Baker**		0.6	0.8970	+18.7°	1.4639	5 vol. 80%	Cineole [28%]; d-α-pinene; sesquiterpene.	
E uncinata **Turcz.**		1.4	0.9111	-2.4°	1.4754	5 vol. 70%	Cineole [20%]; p-cymene; aromadendrene, aldehydes, d-α-pinene	

NOMENCLATURE USED BY BAKER AND SMITH	NOMENCLATURE ADOPTED BY BLAKELY	AVERAGE PERCENTAGE YIELD	SPECIFIC GRAVITY @ 15°/15°	OPTICAL ROTATION α_D [100 mm]	REFRACTIVE INDEX AT 20°	SOLUBILITY IN AQUEOUS ALCOHOL [% by weight]	PRINCIPAL CONSTITUENTS	REFERENCE
E. unialata Baker & Smith		0.89	0.9179	+3.1°	1.4681	1.75 vol. 70%	Cineole [62%]; d-α-pinene; sesquiterpene.	
E. urnigera Hook. f.		1.13	0.9088	+11.8°	1.4652	5 vol. 70%	Cineole [53%]; d-α-pinene.	
E. vernicosa Hook. f.		0.8	0.9038	+11.3°	1.4642	1 vol. 80% insol. 10 vol. 70%	Cineole [52%]; d-α-pinene; volatile aldehydes.	
E. viminalis Labill.		0.55	0.9044 to 0.9162	+3.7° to +4.2°	1.4707 to 1.4798	1 to 2 vol. 80%	Cineole [28-41%]; d-α-pinene; α-phellandrene; sesquiterpene.	
E. viminalis Labill. variety "A" [Baker & Smith's nomenclature]		0.8	0.9122 to 0.9141	+6.2° to +6.7°	1.4654 to 1.4655	1.5 to 1.6 vol. 70%	Cineole [48-60%]; α-pinene; benzaldehyde; sesquiterpene.	
E. virgata Sieb. The identity of the species from which Baker & Smith obtained their material is not certain.		0.54	0.8883 to 0.9154	-20.9°	1.4810 to 1.4958	1 to 3 vol. 80%	Eudesmol; α-phellandrene; cineole [10-12%]; piperitone; sesquiterpene.	
	E. virgata Sieb. see E. luehmanniana F.v.M.							
E. viridis Baker		1.5	0.926	+0.88	1.4632	2 vol. 70% [by volume]	Cineole [80%]; α-pinene.	Penfold & Morrison Bull. No. 2 "Commercial Eucalyptus Oils," Technological Museum, Sydney, 4th Ed. [1944], 11, Govt. Printer.

E. vitrea Baker	1.5	0.886	-30.1°	1.4771	1 vol. 80%	*l*-α-Phellandrene; cineole [26%]; sesquiterpene.
E. wilkinsoniana Baker	0.98	0.8944	-21.4°	1.4717	Insol. 10 vol. 80%	*l*-α-Pinene; cineole [15-20%]
E. woollsiana Baker	0.5	0.8890 to 0.9051	-9.5° to -15.8°	1.4838	1 vol. 80%	α-Pinene; p-cymene; cuminal; phellandral; cineole [10-12%]

"TEA TREE" OILS

by
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Introduction.—Australia is rich in myrtaceous shrubs and small trees belonging to such genera as *Leptospermum*, *Melaleuca, Kunzea, Baeckea*, etc., which are collectively known by the vernacular term of "Tea Trees" (not "Ti-Trees").

This popular name arose from the story of Captain Cook's sailors having used the leaves of a species of *Leptospermum* as a substitute for tea.

Hundreds of species of "Tea Tree" occur in Australia. The essential oils of many have been examined, but only a few have attracted commercial attention.

Oil of Leptospermum Citratum Challinor, Cheel and Penfold

Botany.—This species was raised to specific rank by Challinor, Cheel and Penfold[1] in 1918. It had previously been described as *Leptospermum flavescens*, var. *citratum*. *Leptospermum citratum* is a glabrous shrub or small tree, varying in height from 4 to 25 ft., the main stem often exceeding 3 in. in diameter, the bark of light brown color, comparatively thin and smooth on the upper branches, and fibrous and furrowed on the lower part of the stem. The flowers are white, solitary in the axils of the leaves, or occasionally terminal on the lateral branchlets, sessile, or very shortly pedicellate.

Habitat, Range, and Occurrence.—This small tree grows on rocky ledges in inaccessible parts of the Dividing Range of eastern Australia, and is very sparsely distributed. Small stands occur at Copmanhurst, Macpherson Range, Punchbowl, Whiteville, and Baryulgil, all in northern New South Wales, and at Springbrook and Palmwood in Queensland.

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* The authors are greatly indebted to Mr. H. H. G. McKern, Assistant Chemist, and Mr. J. L. Willis, Botanical Research Officer, Museum of Technology and Applied Science, Sydney, Australia, for their assistance in the preparation of this chapter.

[1] *J. Proc. Roy. Soc. N. S. Wales* **52** (1918), 175.

Planting and Cultivation.—It was early realized that this attractive shrub, which had been grown as a garden hedge, would have to be cultivated if commercial demands for its essential oil were to be met.

Many experimental plots have been established in Australia, and much information on cultivation is available.[2] The only commercial plantations in the British Empire are located in Kenya Colony,[3] although Naves[4] reports an analysis of an oil sent to him from Rhodesia by the distiller. Outside of the Empire, the tree is grown in Guatemala (C. A.).

Yield of Oil.—One thousand pounds of leaves and terminal branchlets yield from 10 to 15 lb. of a pale lemon colored oil containing from 75 to 85 per cent of the aldehydes citral (45 to 50 per cent) and citronellal (35 per cent).

Distillation.—Portable field stills, similar to those described in the monograph on Australian Eucalyptus Oils, are employed for the distillation of *Leptospermum citratum.* The general procedure of distillation resembles that of the eucalyptus oils in every respect.

Physicochemical Properties.—

Specific Gravity at 15°/15°........	0.8792 to 0.8856
Optical Rotation..............	+3° 30′ to +5° 0′
Refractive Index at 20°	1.4688 to 1.4757
Total Aldehyde Content (Citral and Citronellal)....................	75 to 85%
Solubility in 70% Alcohol (W/W)..	Soluble in 1 to 1.2 vol.

Chemical Composition of the Type Oil.—Challinor, Cheel and Penfold[5] observed the following constituents in oil of *Leptospermum citratum:*

Citral. Identified by means of the naphthocinchoninic acid compound m. 200°. The oil contains from 40 to 50 per cent of citral b_{12} 110°–112°, d_{15}^{15} 0.8929, α_D ±0°, n_D^{20} 1.4875.

Citronellal. Identified by means of the naphthocinchoninic acid compound m. 225°, and of the semicarbazone m. 78°–79°. The oil contains about 35 per cent of citronellal b_{12} 93°–94°, d_{15}^{15} 0.8577, α_D^{20} +8° 36′, n_D^{20} 1.4482.

Eugenol. Identified by preparation of the benzoate m. 67°.

Geraniol(?), Citronellol(?), Esters (Formates and Acetates), Sesquiterpenes(?) and Sesquiterpene Alcohols(?). Aside from the above named compounds, the oil contains small quantities of other constituents, probably geraniol, citronellol, formic and acetic acid esters, sesquiterpenes and sesquiterpene alcohols; but their identity was not definitely established.[6]

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[2] "Australian Tea Trees of Economic Value," *Sydney Technological Museum, Bull.* No. 14, Part II (1936).

[3] *Bull. Imp. Inst.* **40** (1942), 1.

[4] *Perfumery Essential Oil Record* **39** (1948), 346.

[5] *J. Proc. Roy. Soc. N. S. Wales* **52** (1918), 175.

[6] In an oil from Rhodesia, Naves (*Perfumery Essential Oil Record* **39** (1948), 346) found 8.2 per cent of alcohols (geraniol and citronellol) in equal amounts.

Use.—The oil is an excellent source of citral and citronellal. The citral isolated from it is superior to that from any other source, with the possible exception of *Backhousia citriodora.* The oil has also been used as a fortifier or modifier in perfume compounds where citral or citronellal-containing oils are employed. It has proved helpful in eaux de Cologne, toilet waters, hair oils, powder perfumes, hair washes, and shampoo preparations.[7]

Physiological Forms.—Aside from the Type oil discussed above, two physiological forms of *Leptospermum citratum* were described in 1942.[8] The two forms are readily distinguished in the field by crushing the leaves between the fingers. The leaves of variety "A" emit a terpene-like odor resembling γ-terpinene, whereas the foliage of variety "B" gives a rose-like odor characteristic of geraniol and its esters.

Physicochemical Properties.—

	Oil of Leptospermum citratum	
	Var. "A"	*Var. "B"*
Specific Gravity at 15°/15°.....	0.862 to 0.8634	0.881 to 0.884
Optical Rotation at 20°.	+2° 5′ to +2° 21′	+1° 41′ to +1° 45′
Refractive Index at 20°........	1.4789 to 1.4795	1.4760 to 1.4780
Total Aldehyde Content (Citral and Citronellal).............	Nil	16 to 20%
Solubility in Alcohol (W/W)....	Insoluble in 10 vol. of 80% alcohol	Soluble in 1.4 to 1.8 vol. of 70% alcohol

Chemical Composition of Oil of *Leptospermum Citratum* Var. "A" and "B."—Penfold, Morrison and Smith-White[9] reported the following compounds in oil of *Leptospermum citratum* var. "A" and "B":

Variety "A"

γ-Terpinene. Identified by means of the erythritol m. 235°–236°. The γ-terpinene had these properties: b. 179°–181°, d_{15}^{15} 0.851, α_D^{20} +0° 14′, n_D^{20} 1.4781.

d-α-Pinene. Characterized by oxidation to pinonic acid m. 69°–70°.

p-Cymene. Characterized by oxidation to *p*-hydroxyisopropylbenzoic acid m. 155°–156°.

Terpenes(?), Cineole, Linaloöl(?), Eugenol, and Sesquiterpenes(?). The oil also contains unidentified terpenes, cineole, linaloöl(?), small quantities of sesquiterpenes, and about 0.6 per cent of eugenol, identified by means of its benzoate m. 69°–70°.

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[7] *Perfumery Essential Oil Record* **20** (1929), 155.

[8] A. R. Penfold, F. R. Morrison and S. Smith-White, *J. Proc. Roy. Soc. N. S. Wales* **76** (1942), 93. Cf. Penfold, Morrison and McKern, *Researches on Essential Oils of the Australian Flora* (Museum of Technology and Applied Science, Sydney), Vol. I (1948), 12.

[9] *J. Proc. Roy. Soc. N. S. Wales* **76** (1942), 93

Variety "B"

Citral. The oil of variety "B" contains from 16 to 20 per cent of citral d_{15}^{15} 0.8928, n_D^{20} 1.4883. The citral yielded two semicarbazones m. 163°-164°, and m. 135°–136°, respectively.

Geraniol (Free and as Formate and Acetate). Identified by means of the silver salt of the phthalic acid ester m. 133°, and of the diphenylurethane m. 82°-83°. The geraniol d_{15}^{15} 0.880, α_D^{20} $+1° 26'$, n_D^{20} 1.4699 occurs in the oil both free and as formate and acetate.

Citronellol. Citronellol is also present in free and in ester form.

OIL OF MELALEUCA ALTERNIFOLIA CHEEL

Botany.—This species was raised to specific rank by Cheel.[10] It had previously been described by Maiden and Betche [11] as a variety of *Melaleuca linariifolia.* The tree bears a superficial resemblance to *Melaleuca linariifolia,* but is distinct botanically. Both trees are "Narrow-leaved" paper bark "Tea Trees," but *Melaleuca alternifolia* is not as tall as *M. linariifolia,* the height not exceeding 20 ft. The leaves are alternate, narrower, and usually shorter than those of *M. linariifolia.* The whole plant is glabrous and the flowers are generally scattered in an interrupted spike.

Habitat, Range, and Occurrence.—*Melaleuca alternifolia* follows watercourses and flourishes in swampy situations. The tree occurs in fairly large stands in the Northern Rivers districts of New South Wales, from the southern limit at Stroud, through the coastal rivers to southern Queensland.

Planting and Cultivation.—*Melaleuca alternifolia* responds readily to cultivation from seed, and good results have been obtained in experimental plantations. Notwithstanding the export demand for the oil of *M. alternifolia,* the existing stands have so far met all requirements. However, fairly large areas of country are destroyed from time to time by bush fires.

Collection of Leaf Material.—To collect the leaf material the trees are cut down to within 5 or 6 ft. of the ground, and the limbs are cut off. The leaves are removed with a cane knife, and allowed to drop upon squares of hessian, each holding from 40 to 80 lb. The foliage is then carted to the distillery.

Within eighteen months to two years after cutting of the original trees, new growth, known as "ratoon," makes its appearance. Depending upon climatic conditions, this new growth is ready for cutting within eighteen months to two years.

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[10] "Notes on *Melaleuca,* with Descriptions of Two New Species and a New Variety," *J. Proc. Roy. Soc. N. S. Wales* **58** (1924), 189.

[11] *Proc Linnaean Soc. N. S. Wales* **29** (1904), 742.

Distillation.—Two methods are employed in distilling the leaves of this species—namely, distillation in directly fired stills, and distillation of the foliage with live steam generated in a separate boiler. The stills used for direct firing resemble those described in the monograph on "Australian Eucalyptus Oils," in the section on "Production." Made of mild steel, and holding from 1½ to 2 tons of leaves, they are connected to a water tank of approximately 1,500 gal. capacity, in which the condenser coil for cooling of vapors is placed. The distillation occupies about 6½ hr.

The large plants using live steam employ boilers ranging from 24 to 40 h.p. The stills used in this operation are slightly smaller than those employed for direct firing, as they do not require a water space in the bottom of the stills. A wire tray to support the foliage rests immediately on top of the steam pipes, and live steam of about 15 to 20 lb. pressure is passed through the leaves. The oil and steam are condensed in the same manner as in the case of the directly fired still. The methods of packing and emptying the still are essentially the same, and there is no difference in the yield and quality of the oil.

The live steam unit consists of a steam boiler with three stills, each with its separate condenser tank. Overhead derricks or endless chain blocks are used to empty the stills rapidly.

Directly fired stills are used where the stands of *Melaleuca alternifolia* are not sufficiently large to warrant steady all-year-round operation of a still. In order to keep a large steam plant busy it is necessary to have sufficient stands of the tea tree within a radius of about 12 miles of the distillery.

Yield of Oil.—One thousand pounds of leaves and terminal branchlets yield about 18 lb. of a pale lemon-tinted oil possessing a pleasant nutmeg odor. The yield of oil is lower in the winter months than in the summer, a sudden increase appearing in November, the first month of summer. The yield declines again about June, the first winter month in Northern New South Wales.

As regards the cineole content of the oil, an increase appears to occur in the winter months, corresponding to the lowered yield.

Physicochemical Properties.[12]—

Specific Gravity at 15°/15°	0.8950 to 0.9050
Optical Rotation	+6° 48′ to +9° 48′
Refractive Index at 20°	1.4760 to 1.4810
Ester Number	2 to 7
Ester Number after Acetylation	80 to 90
Cineole Content	Under 10%
Solubility in 80% Alcohol (W/W)	Soluble in 0.6 to 0.8 vol.

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[12] Penfold and Morrison, "Australian Tea Trees of Economic Value," *Sydney Technological Museum, Bull.* No 14, Part I, 3d Ed. (1946), 12.

Chemical Composition.—The chemical composition of the oil of this species was investigated by Penfold[13] and by van Hulssen and Meijer,[14] who identified the following constituents:

d-α-Pinene. Identified via the nitrosochloride m. 109°, and the nitrobenzylamine m. 122°–123°.

α- and γ-Terpinene. Identified by means of the hydrochloride m. 53°–54° and by oxidation with potassium permanganate and potassium hydroxide to erythritol m. 238°–239°, and to α,α′-dihydroxy-α-methyl-α-isopropyladipic acid m. 188°–189°.

p-Cymene. Characterized by oxidation with hot potassium permanganate solution to *p*-hydroxyisopropylbenzoic acid m. 156°–157°.

Cineole(?). Characterized by chemical and physical constants, after purification through the phosphoric acid compound. Van Hulssen and Meijer could not isolate any cineole from their oil.

Δ^1-Terpinenol-4 (1-Terpinen-4-ol). Identified by means of the nitrosochloride m. 115°–116°, the naphthylurethane m. 104.5°–105.5°, and by oxidation with cold potassium permanganate to *p*-menthane-1,2,4-triol.

Sesquiterpenes. Apparently a complex mixture, in which cadinene was identified by means of its dihydrochloride m. 118°–119°, $[\alpha]^{20}_{D}$ −51° 24′.

Sesquiterpene Alcohols. Identified as corresponding to the sesquiterpene cadinene by dehydration with formic acid. The dihydrochloride melted at 118.5°.

Use.—The complex mixture of substances constituting this oil possesses a high germicidal value when tested against pure phenol, with *B. typhosus* as test organism.[15] The germicidal activity, the pleasant odor, and nonpoisonous, nonirritant, and noncorrosive properties of the oil have resulted in its extensive application in surgical and dental practice. The great value of the oil in medical practice is due to its property of penetrating pus, and of mixing with it in a manner which causes it to slough off, leaving a healthy surface. The following pathological conditions have responded to treatment, either with the oil alone or with it in a water soluble emulsion:[16]

Perionychia, empyema, gynaecological conditions, skin conditions (epidermophyton infection [psoriasis], impetigo contagiosa, pediculosis, ringworm, tinea [albuginea]), throat and mouth conditions (acute nasopharyngitis, catarrh, thrush, and "aphthous" stomatitis, tonsilitis and ulcers of the mouth, sore throat, pyorrhoea, gingivitis), diabetic gangrene, etc.

It has also been demonstrated that the water soluble emulsions of *Melaleuca alternifolia* oil not only retain their activity in the presence of blood and organic matter, but actually increase in effectiveness.

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[13] *J. Proc. Roy. Soc. N. S. Wales* **59** (1925), 306.

[14] *Mededeeling Lab. voor scheikundig Onderzoek, Buitenzorg* (Java), No. **75** (1941).

[15] Penfold and Grant, *J. Proc. Roy. Soc. N. S. Wales* **56** (1922), 219; **59** (1925), 346.

[16] Penfold and Morrison, *Sydney Technological Museum, Bull.* No. 14, Part I, 3d Ed. (1946), 14.

An interesting technical application of the oil is its incorporation (about 1 per cent) in machine "cutting" oils, whereby skin injuries, especially abrasions to the hands by metal filings and turnings, have been reduced to a minimum. Large quantities of the oil were used for this purpose in munitions factories during World War II.

The oil has also found use in perfumery as a toner and blender, and as a flavoring and antiseptic agent in denture and mouth washes.[17]

Physiological Forms.—The occurrence of physiological forms was observed in 1946,[18] when investigations revealed oils containing a high content of cineole. (A normal distillate of *Melaleuca alternifolia* contains about 10 per cent of cineole.) Since that date it has been noted [19] that oils obtained from various trees of *Melaleuca alternifolia* fall into the following three groups: [20]

Type	6 to 14 per cent of cineole
Variety "A"	31 to 45 per cent of cineole
Variety "B"	54 to 64 per cent of cineole

Warning on the Use of Oils Other than "Type" for Medicinal Purposes.—Recent analyses have shown that the cineole content may vary from 5 to 15 per cent in the Type oil, although the average of commercial consignments has been approximately 10 per cent.

In view of clinical evidence that the oil should contain a minimum of cineole, it is imperative that the Type oil *only* be used for medicinal and dental purposes.

OIL OF MELALEUCA LINARIIFOLIA SMITH

Botany, Habitat, Range, and Occurrence.—This tall, "Narrow-leaved" paper bark "Tea Tree" has been fully described by Bentham.[21] It occurs abundantly throughout the coastal districts of New South Wales and Queensland, following watercourses and flourishing in all swampy situations.

Yield of Oil.—One thousand pounds of leaves and terminal branchlets yield from 15 to 20 lb. of a pale lemon colored oil.

Distillation.—The procedure is fully described in the monograph on "Oil of *Melaleuca alternifolia.*"

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[17] *Perfumery Essential Oil Record* **20** (1929), 155.

[18] Penfold and Morrison, *Sydney Technological Museum, Bull.* No. 14, Part I, 3d Ed. (1946), 12.

[19] Cf. Penfold, Morrison and McKern, *Perfumery Essential Oil Record* **40** (1949), 149.

[20] Penfold, Morrison and McKern, *Researches on Essential Oils of the Australian Flora* (Museum of Technology and Applied Science, Sydney), Vol. I (1948), 5, 18.

[21] "Flora Australiensis," Vol. 3, Lovell Reeve & Co., London (1866), 140.

Physicochemical Properties.[22]—The physical and chemical properties are as follows:

Specific Gravity at 15°/15°	0.8927 to 0.8992
Optical Rotation	+3° 18′ to +6° 48′
Refractive Index at 20°	1.4752 to 1.4780
Ester Number	1.3 to 2.7
Ester Number after Acetylation	58 to 82
Cineole Content	16 to 20%
Solubility (W/W)	Soluble in 0.8 vol. of 80% alcohol

Chemical Composition.—The chemical composition of the oil derived from this species was investigated by Penfold,[23] who identified the following constituents:

α- and γ-Terpinene (First recorded occurrence in an Australian essential oil). Identified through the dihydrochloride m. 53°–54°, and by oxidation with potassium permanganate and potassium hydroxide to erythritol m. 238°–239°, and to α,α′-dihydroxy-α-methyl-α-isopropyladipic acid m. 188°–189°.

p-Cymene. Characterized by oxidation with hot potassium permanganate solution to *p*-hydroxy-isopropylbenzoic acid m. 156°–157°.

Cineole. Characterized by chemical and physical constants after purification through the phosphoric acid compound: iodol compound m. 112°–113°.

Δ^1-Terpinenol-4 (1-Terpinen-4-ol) (First recorded occurrence in an Australian essential oil). Identified by means of its nitrosochloride m. 115°–116°, naphthylurethane m. 104°–105°, and by oxidation with cold potassium permanganate to *p*-menthane-1,2,4-triol.

Sesquiterpenes. Apparently a complex mixture, in which cadinene was identified as dihydrochloride m. 118.5°–119°, $[\alpha]_D^{17}$ −36° 52′.

Sesquiterpene Alcohols. Identified as corresponding with the sesquiterpene cadinene by dehydration with formic acid. The dihydrochloride had m. 118.5°, $[\alpha]_D^{17}$ −36° 51′.

A more recent examination of an oil of *Melaleuca linariifolia* has been made by Davenport, Jones and Sutherland.[24] The particular sample examined had the following characteristics: d_4^{25} 0.8875; $[\alpha]_D^{28}$ +9° 12′; n_D^{25} 1.4785; esters and acids, traces only; ester number after acetylation 24.0; cineole 4 per cent. In addition to the compounds found by Penfold,[25] these authors have identified the following substances:

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[22] Penfold and Morrison, *Sydney Technological Museum, Bull.* No. 14, Part I, 3d Ed. (1946), 7.

[23] *J. Proc. Roy. Soc. N. S. Wales* **59** (1925), 306.

[24] "The Essential Oils of the Queensland Flora. Part 23. A re-examination of the Essential Oil of *Melaleuca linariifolia*," *Univ. Queensland Papers, Dept. Chem.*, Vol. I, No. 36 (1949), 1.

[25] *J. Proc. Roy. Soc. N. S. Wales* **59** (1925), 306.

Terpinolene. Dibromide m. 67°–70°, tetrabromide m. 116°–117°.

l-α-Thujene. Thujaketone semicarbazone m. 139°–140°.

d-α-Pinene. Pinonic acid m. 100°–103°.

β-Pinene. Nopinic acid m. 123°–124°.

d-α-Terpineol. Phenylurethane m. 108°–109°.

Aromadendrene. Ozonolysis to aromadendrone m. 83°–84°.

Melalilol. A new sesquiterpene alcohol $C_{15}H_{26}O$, m. 87°–88°, phenylurethane m. 140°–141°.

Myrcene(?). The presence of myrcene appears probable from a consideration of the physical properties of two of the terpene fractions.

From all data available, the authors conclude that their sample had the following approximate composition, by volume:

(1) Total terpenes (45 per cent), consisting of—
    α- and γ-terpinenes and associated unidentified material (40 per cent)
    terpinolene (4 per cent)
    α-pinene (1 to 2 per cent)
    α-thujene, β-pinene, myrcene, *p*-cymene (less than 1 per cent each)
(2) Cineole (4 per cent)
(3) Terpinen-4-ol (37 per cent)
(4) α-Terpineol (4 per cent)
(5) Sesquiterpenes (6 per cent)
(6) Sesquiterpene alcohols (2.5 per cent)
(7) Phenols (0.1 to 0.2 per cent)

Use.—Although the oil possesses a high germicidal value,[26] the presence of cineole in quantity renders it unsuitable for many of the applications described under *Melaleuca alternifolia*. Nevertheless, the composition of the oil closely resembles that of *Melaleuca alternifolia*, with the exception that cineole largely replaces the alcohol 1-terpinen-4-ol. The applications of the oil, therefore, are restricted to those where a high percentage of cineole is unimportant, as, for example, in the manufacture of some germicides and soaps other than those required for surgical, medical, and dental work.

Physiological Forms.—Many samples of this oil have been observed by the authors to contain cineole in excess of 20 per cent, the figure often reaching 60 per cent of cineole. As in the case of *Melaleuca alternifolia* this wide variation in cineole content indicates the definite occurrence of physiological forms of the species. We have already mentioned that physiological forms of essential oil-yielding plants are those which are identical morphologically but which yield oils of different composition. The oil from such a form was examined by Jones.[27] It had the following physicochemical constants:

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[26] Penfold and Grant, *ibid.* **56** (1922), 219; **59** (1925), 346.
[27] *Proc. Roy. Soc. Queensland* **48** (1936), 48.

$d_{15.5}$ 0.9180; $[\alpha]_D$ +4° 18′; n_D^{20} 1.4650; ester number 19.6; ester number after acetylation 49; cineole (Cocking's method) 61.5 per cent. The compounds present were found to be pinene (nitrosylchloride m. 103°); dipentene (tetrabromide m. 125°); cineole (physical constants and *o*-cresol addition compound m. 55°); α-terpineol (nitrosylchloride m. 115°–116°, phenylurethane m. 113°, naphthylurethane m. 146°); a sesquiterpene (not aromadendrene); a sesquiterpene alcohol. No trace of 1-terpinen-4-ol could be found.

Davenport, Jones and Sutherland[28] also record an oil from this species containing 44 per cent of cineole, so that it appears probable that the three physiological forms observed with *M. alternifolia* exist also with *M. linariifolia.*

OIL OF MELALEUCA VIRIDIFLORA GAERTNER[29]

Introduction and Botany.—This species was named by Gaertner in 1788 on the basis of specimens collected by Banks and Solander during Captain Cook's voyage to Australia in 1770. The species has generally been described as *Melaleuca leucadendron,*[30] and some authors still retain this nomenclature.

Baker and Smith,[31] in a critical study of the so-called "Broad-leaved Tea Trees," not only separated the Australian tree from the New Caledonian, but declared *Melaleuca leucadendron* Linn. extra-Australian.

By reason mainly of differences in chemical composition of the essential oils obtained from *M. viridiflora* growing in different localities, Baker and Smith[32] established two new species, *Melaleuca maideni* and *M. smithii.*

The present authors agree with the views of the botanists, Cheel and White, that these are not distinct species but are closely related forms of *Melaleuca viridiflora.*

Origin, Habitat, and Range.—*Melaleuca viridiflora* is one of the largest trees of the genus, reaching a height of 60 ft. It is usually found in low-lying, sandy, swampy country, not far from the sea. With its paper bark and compact bushy foliage, consisting of rather stiff, flat, parallel-veined leaves, the species presents little difficulty in identification. This broad-leaved "Tea Tree" is widely distributed, occurring all along the eastern

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[28] "The Essential Oils of the Queensland Flora. Part 23. A Re-examination of the Essential Oil of *Melaleuca linariifolia,*" *Univ. Queensland Papers, Dept. Chem.,* Vol. I, No. 36 (1949), 1.

[29] J. Gaertner, "De Fructibus et Seminibus Plantarum," I (1788), 175.

[30] G. Bentham and F. von Mueller, "Flora Australiensis," Vol. 3, Lovell Reeve & Co., London (1866), 142.

[31] *J. Proc. Roy. Soc. N. S. Wales* **47** (1913), 198.

[32] *Ibid.,* 199.

coastline of Australia from Port Jackson in the south to the Gulf of Carpentaria in the north. The tree produces an excellent, pale, hard, close-grained timber, suitable for boat and carriage building and general cabinet work.

Physiological Forms.—Although *Melaleuca viridiflora* Gaertner is a distinct botanical entity based on morphological evidence, the variations in the chemical composition of the essential oil warrant its classification, for commercial purposes, according to physiological forms. This procedure has already been adopted with other essential oil-yielding plants which are botanically identical, but which yield essential oils of diverse chemical composition. The evidence available justifies the establishment of two distinct physiological forms of *Melaleuca viridiflora* based upon differences in chemical composition of the essential oils, viz., the *Type,* similar in chemical composition to cajuput oil of commerce (containing cineole and α-terpineol), and *Variety "A"* (containing nerolidol and/or linaloöl).

Yield of Oil.—The yield of oil obtained from the leaves and terminal branchlets varies from 1 to 2.6 per cent, according to the physiological form.

Physicochemical Properties.—The results obtained from many analyses of the Type oil during the past twenty-five years fall within the range given below. The close resemblance of these figures with those of commercial cajuput oil, obtained from *Melaleuca minor,* and of niaouli oil are noteworthy.

	Type	*Variety "A"*	
	Queensland and N. S. W. Trees	*Queensland Trees* *	*N. S. W. Trees* †
Specific Gravity at 15.5°/15.5°	0.913 to 0.930	0.8764 to 0.8800	0.8806 to 0.8857
Optical Rotation	−1° 36′ to −5° 12′	$[\alpha]_D$ +14° 16′ to +15° 30′	+13° 18′ to +14° 36′
Refractive Index at 20°.......	1.4658 to 1.4764	1.4700 to 1.4719	1.4720 to 1.4763
Ester Number..	Up to 5	Nil	2.8 to 4.8
Ester Number after Acetylation.........	20 to 60	146 to 150	163 to 193
Cineole Content	46 to 60%		
Solubility in 70% Alcohol (W/W)......	Up to 2.5 vol.	Up to 2.5 vol.	Up to 2.5 vol.
Solubility in 80% Alcohol (V/V)	Up to 1 vol.	Up to 1 vol.	Up to 1 vol.

* Jones and co-workers, *Proc. Roy. Soc. Queensland* **48** (1936), 41; **49** (1937), 95.

† Penfold, Morrison and McKern, *Perfumery Essential Oil Record* **39** (1948), 141.

Chemical Composition.—

Type.—The following constituents have been identified by various workers: Cineole (46 to 60 per cent), *d*-α-pinene, *l*-limonene, dipentene, α-terpineol, sesquiterpenes, and traces of benzaldehyde. A crystalline sesquiterpene alcohol m. 71° has been described by Jones and Haenke.[33]

Variety "A."—The following constituents have been identified: Linaloöl, nerolidol, some linaloöl monoxide, sesquiterpenes, citral, traces of phenol and benzaldehyde.

The Queensland oil contains about 50 per cent of linaloöl, whereas oil distilled in New South Wales contains about 30 per cent of linaloöl and 70 per cent of nerolidol.[34]

Oil of Niaouli

Introduction and Botany.—The "Tea Tree," *Melaleuca viridiflora* (fam. *Myrtaceae*), is characteristic of large areas of New Caledonia. The naming of this species was formerly attributed to Brongniart and Gris, but according to Baker and Smith,[35] the real authority for the New Caledonian tree should be Solander. This was accepted until quite recently, when the Australian botanists, Cheel and White, expressed a belief that the authority should be Gaertner (1788). Edwin Cheel, in a recent private communication, emphasized that the trees growing in New South Wales and Queensland are botanically identical with the New Caledonian trees. (Cf. the preceding monograph on "Oil of *Melaleuca viridiflora* Gaertner.")

In New Caledonia, a French island possession in the Pacific, about 800 miles off the east coast of Australia, the tree forms patches and sparse forests covering approximately two-fifths of the island (Guenther[36]). Hardy, resistant, and of great vitality, it flourishes on swampy and rocky soil alike, in the coastal lowlands as well as on mountain slopes up to an altitude of about 1,000 ft. Its sturdy, widespread roots split the schistaceous soil and in a way prepare the ground for cultivation.

It is almost impossible to exterminate the tree by root pulling or burning, because new shoots soon reappear from those parts of the prolific root system which have been left in the ground. The tree quickly invades uncultivated land, and planters consider it a nuisance—also because it is liable to spread bush fires. *Melaleuca viridiflora* is quite a decorative tree and occasionally reaches great dimensions.

During certain periods of the year large quantities of fallen leaves cover the ground, and, since they contain an essential oil which acts as a strong disinfectant, the native population attributes the healthy air of New Caledonia and the absence of malaria in certain sections to the occurrence of *Melaleuca viridiflora* in these localities (Guenther[37]).

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[33] Jones and co-workers, *Proc. Roy. Soc. Queensland* **48** (1936), 41; **49** (1937), 95.

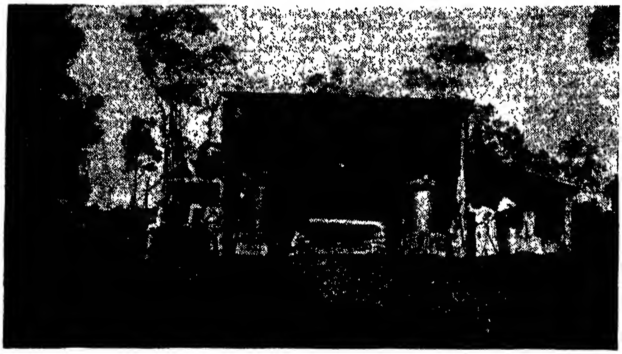
[34] Penfold, Morrison and McKern, *Perfumery Essential Oil Record* **39** (1948), 141.

[35] *J. Proc. Roy. Soc. N. S. Wales* **47** (1913), 200.

[36] *Soap* **18** (August, 1942), 23.

[37] *Ibid.*

Production of Oil.—The tree is not cultivated, as it grows profusely over wide areas of the island. Since labor is quite scarce and relatively high priced (it has to be imported from French Indo-China and the Netherlands East Indies), the production of niaouli oil has remained a small family industry among the settlers—some of them French, some Asiatic. Children and women collect the leaf material, while the men attend to the actual distillation. The center of production is in Gomen, whence the French term "Gomenol" for niaouli oil.



Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 35. Production of niaouli oil in New Caledonia. A typical field distillation post of niaouli leaves.

Distillation.—Most of the stills, particularly those of small size, are directly heated. From 500 to 1,000 kg. of freshly cut leaves are packed into a still, trampled down, some water is poured in, and the contents are distilled for about 6 hr. The leaves are said to contain about 2.5 per cent of essential oil, but in the rather primitive stills employed in New Caledonia the yield of oil from fresh leaves ranges from only 0.6 to 1.0 per cent (Guenther[38]). It varies greatly and depends upon climatic and seasonal conditions, the location, and most of all upon the type of still used. Yields of about 2.5 per cent have been obtained from the leaves of Australian trees.

Physicochemical Properties.—Oil of niaouli closely resembles oil of cajuput as regards physicochemical properties and chemical composition. The oil possesses a slight by-odor of bitter almonds (due to the presence of benzaldehyde), which perhaps accounts for its popularity in France.

Gildemeister and Hoffmann[39] recorded these properties for niaouli oil:

Specific Gravity at 15°...	0.910 to 0.929
Optical Rotation........	Slightly dextro-, or (usually) laevorotatory, +0° 42′ to −3° 34′

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[38] *Ibid.*

[39] "Die Ätherischen Öle," 3d Ed., Vol. III, 437.

Refractive Index at 20°	1.465 to 1.472
Acid Number	Up to 2
Ester Number	2 to 9
Cineole Content	50 to 60%
Solubility	Soluble in about 1 vol. of 80% alcohol; of 70% alcohol 4 to 25 vol. are required for clear solution

In the experience of the present authors the cineole content of niaouli oil ranges from 40 to 65 per cent.

Shipments of niaouli oil received and examined by Fritzsche Brothers, Inc., New York, had properties varying within the following limits:

Specific Gravity at 15°/15°	0.912 to 0.922
Optical Rotation	−0° 10′ to +1° 18′
Refractive Index at 20°	1.4670 to 1.4722
Saponification Number	3 to 5
Cineole Content (*o*-Cresol Method)	52 to 57.8%
Solubility	Soluble in 1 vol. and more of 80% alcohol

Adulteration.—In the producing regions oil of niaouli is occasionally adulterated with kerosene or with fatty oils. A very high cineole content may indicate the addition of eucalyptus oil, which is usually lower priced than niaouli oil.

Chemical Composition.—According to Bertrand[40] and Voiry,[41] oil of niaouli contains these constituents:

d-*α*-Pinene. Whereas oil of cajuput contains *l*-*α*-pinene, oil of niaouli contains *d*-*α*-pinene, which yields a dextrorotatory solid monohydrochloride $C_{10}H_{16}HCl$.

Cineole. Cineole, the principal constituent of niaouli oil (40 to 65 per cent), is accompanied by a laevorotatory compound (*l*-limonene?) possessing the same boiling point.

α-Terpineol, Terpinyl Valerate, Acetates, and Butyrates. About 30 per cent of the oil consists of crystalline *α*-terpineol m. 35°, and its valeric ester. The oil also contains traces of acetates and butyrates.

Benzaldehyde and Valeraldehyde(?). Treating the oil with bisulfite solution, Bertrand isolated two aldehydes, one of which had the odor of valeraldehyde, the other that of benzaldehyde. The latter aldehyde boiled at 180°.

Sulfur-containing Compounds(?). The rather disagreeable odor of the crude oil is caused probably by sulfur-containing substances which, however, the above-named authors could not identify.

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[40] *Bull. soc. chim.* [3], **9** (1893), 432. *Compt. rend.* **116** (1893), 1070.

[41] "Contribution à l'étude chimique des huiles essentielles de quelques Myrtacées." Thèse de l'Ecole supérieure de Pharmacie de Paris (1888). Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 437.

Total Production and Trade.—The annual production of niaouli oil in New Caledonia has varied from 10 to 30 metric tons. In the years prior to World War II it averaged 20 tons per year.

The oil is exported from Noumea, the capital of New Caledonia, usually to Marseilles, for distribution to various parts of Europe and transshipment to the United States.

Use.—Because of its antiseptic properties, the oil is used, particularly in France, as a substitute for oil of cajuput and oil of eucalyptus in the treatment of coughs, rheumatism, and neuralgia. Internally, it is given by mouth or in the form of intramuscular injections, one part of niaouli oil being diluted with four to ten parts of a sterilized fixed oil. The oil has been recommended also in the treatment of chronic catarrhs of the pulmonary membrane and especially of whooping cough.

Behrens[42] reported on the application of a mixture of 5 g. of niaouli oil and 95 g. of paraffin oil when building an oleothorax. Morin[43] has claimed that a solution of 0.5 g. of niaouli oil in 100 cc. of olive oil retards development of the tuberculosis bacillus. Bernou[44] recommends stronger solutions, ranging from 2 to 4 per cent, for blocking the development of the tuberculosis bacillus, and 4 to 10 per cent solutions in cases of tubercular empyema.

The oil has always brought a high price in France, a matter of surprise to the authors in view of the lower prices prevailing for medicinal eucalyptus oils produced in Australia and Spain. Perhaps niaouli oil is simply a part of old pharmaceutical formulas, and manufacturers hesitate to change them to eucalyptus oil.

Another reason for the consistently high price of niaouli oil may be that the oil is a medium of exchange between France and New Caledonia. This factor has probably encouraged the export of niaouli oil from the colony to France. From a strictly technological point of view, the authors consider present-day medicinal eucalyptus oils to be at least the equivalent of niaouli oil.

This oil could also be produced in Australia (New South Wales and Queensland) from *Melaleuca viridiflora* growing there abundantly, but production has been restricted because of the lower yield of oil compared with that obtained from *Eucalyptus* species.

OIL OF MELALEUCA BRACTEATA F. VON MUELLER

Introduction and Botany.—This tree, commonly known as the "Black Tea Tree," occurs in small stands in the northern parts of New South Wales and

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[42] Through *E. Merck's Jahresbericht* **46** (1932), 246.

[43] *Ibid.*

[44] *Ibid.*

southern Queensland. It flourishes in favorable locations such as creeks and watercourses. In general appearance it closely resembles another "Tea Tree," viz., *Melaleuca trichyostachya.* The leaves are small, being about 1 in. in length. The tree possesses long terminal branchlets and calyxes; the bark is hard, compact, and furrowed; these characteristics distinguish it from other paper bark "Tea Trees." The species was first described by Baron von Mueller.[45] The tree attains a height of 30 to 40 ft.

Yield of Oil.—The leaves and terminal branchlets yield from 0.4 to 1.0 per cent of a light amber colored oil, heavier-than-water.

Physicochemical Properties.—

Specific Gravity at 15°/15°	1.025 to 1.039
Optical Rotation at 20°	$-1° 24'$ to $-4° 0'$
Refractive Index at 20°	1.529 to 1.535
Acid Number	0.7 to 1.3
Ester Number	5.3 to 17.1
Ester Number after Acetylation	17.0 to 32.9
Solubility in 70% Alcohol (W/W)	Soluble in 1.0 vol.

Chemical Composition.—The oil consists principally of methyl eugenol (70 to 90 per cent), characterized through the tribromide m. 77° and by oxidation to veratric acid m. 178°–179°. The oil also contains *l*-α-phellandrene, characterized by the nitrosite m. 120°.[46]

Other constituents, identified by Baker and Smith, are eugenol (benzoate m. 68° to 69°), cinnamic acid m. 133°, an ester (cinnamyl ?) of this acid, and perhaps cinnamic aldehyde.

According to a more recent investigation by van Hulssen and Meijer,[47] oil of *Melaleuca bracteata* contains about 90 per cent of methyl eugenol, 3 to 5 per cent of *l*-α-phellandrene, about 3 per cent of esters of cinnamic acid, cinnamyl cinnamate, and traces of free cinnamic acid and presumably cinnamyl alcohol.

Use.—As a source of methyl eugenol, as an insect repellent, and for purposes similar to those described under "Huon Pine Wood Oil" (see Vol. V of this work).

Economics.—The comparatively low yield of oil (less than 1 per cent) militates against the extensive use of this oil as a source of methyl eugenol in competition with oil of Huon pine. The wood of this latter yields from 4 to 6 per cent of oil.

Huon pine wood oil is becoming scarce, and an alternative Australian

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[45] "Fragmenta Phytographiae Australiae," Vol. 1, Melbourne (1858), 15.

[46] Baker and Smith, *J. Proc. Roy. Soc. N. S. Wales* **44** (1910), 601.

[47] *Mededeeling Lab. voor scheikundig Onderzoek, Buitenzorg* (Java), No. 75 (1941). Cosgrove, Islip and Thain [*Bull. Imp. Inst.* **46** (1948), 46] and Mitchell (*ibid.*, 50) expressed the opinion that the cinnamic ester is more likely that of a tertiary alcohol, perhaps of linaloöl.

source of methyl eugenol is urgently required. Experimental plantations of *Melaleuca bracteata* are therefore being established by the authors for the purpose of obtaining high yielding strains for commercial plantations. That the potentialities of the oil are realized is evident from reports on samples of oil distilled from *Melaleuca bracteata* grown in Kenya from seeds sent from Australia.[48]

Physiological Forms.—Recent work at the Museum of Technology and Applied Science, Sydney, has shown the occurrence of physiological forms within this species. Investigating the essential oils from the foliage of selected trees of *Melaleuca bracteata* occurring throughout the eastern coast of Australia, the present authors recently obtained very interesting results. A number of the oils examined contained from 85 to 90 per cent of methyl eugenol, whereas other oils contained equivalent percentages of methyl isoeugenol and elemicin, respectively. This is the first recorded occurrence of methyl isoeugenol in Australian essential oils, and the first time elemicin has been identified in oil of *Melaleuca bracteata.* As the trees, from which the oils were obtained, grow in close proximity to each other, there would appear to be no doubt about the occurrence of two physiological forms of *Melaleuca bracteata.* The separate occurrence of different phenol ethers as major components, and without admixture with each other, in oils derived from individual trees of this species is a matter of considerable biological and economic significance.

The results of the completed investigation of these oils by Penfold, Morrison, McKern and Willis will be published later.

OIL OF CAJUPUT

(Oil of Cajeput)

Botany and Description.—Cajuput oil is distilled from the fresh leaves and terminal branchlets of several species of *Melaleuca,* myrtaceous shrubs and trees growing abundantly in the East Indian Archipelago, the Malay Peninsula, and a few other places. The exact identity of the species which yields the commercial oil of cajuput remained obscure for many years, and several species were suggested, among them *Melaleuca leucadendron* Linn., *M. cajeputi* Roxb., and *M. viridiflora* Gärtn. However, in the opinion of Baker and Smith,[49] *Melaleuca minor* Sm. is the species from which the commercial oil of cajuput is derived. There also exists a variety, growing mostly in marshy regions, which yields an oil of different chemical composition.

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[48] *Imperial Institute London,* Annual Report (1947), 21. *Bull. Imp. Inst. London* **46** (1948), 46.

[49] *J. Proc. Roy. Soc. N. S. Wales* **47** (1913), 198.

Since this variety contains little or no cineole, its oil has no commercial importance.

The cajuput tree may reach a height of 45 ft. Extremely vigorous and resistant, it crowds out other plants and cannot be exterminated by cutting or burning. In many sections the bush or tree has thus become a real nuisance to growers of agricultural crops. Extended forests of cajuput cover wide areas in the coastal plains and mountains on some of the islands in Malaya. On Boeroe and Ceram such large quantities of leaf material from wild growing bushes and trees are available that the plant does not have to be cultivated. The forests are frequently ravaged by fire, but spontaneous new growth soon makes up for the loss.

Producing Regions.—The principal producing regions of cajuput oil are located on some of the outer islands of the Netherlands East Indies, particularly Boeroe and the adjacent island of Ceram (Moluccas). According to Guenther,[50] several attempts have been made to cultivate the tree in Java and Sumatra, but with no success, as the oil derived from the planted trees had entirely different properties. It is possible that the wrong variety of plant material had been used.

Collection of the Leaf Material.—The leaves and terminal branchlets are cut from shrubs and low trees not more than six months old; collection of distillation material from older and taller trees would be too difficult. The harvest continues throughout the year.

Production of Oil.—The production of cajuput oil is entirely in the hands of natives. An intricate system of arrangements between moneylenders, middlemen, Chinese and Arabian distillers, and Malayan cutters has always blocked any advancement of the industry. Moreover, Boeroe is still a rather wild and unhealthy island, not readily accessible. Few steamers—and only small ones at that—stop at Boeroe, and then only irregularly. There are no cable connections with Java. It was only in 1938 that a European operator, holding large forest concessions, started to produce cajuput oil by technically more advanced methods and actually succeeded in exporting an oil of the highest quality. The venture, however, was interrupted by World War II, the Japanese occupation, and the civil strife upon conclusion of the war. The production of cajuput oil thus remains a very primitive native industry. As Guenther[51] has pointed out, the bulk of cajuput oil is consumed in the Netherlands East Indies (Indonesia), particularly in Java, and British Malaya, India, and southern China, where the oil forms one of the most popular and general household medicines. The poor natives pay no attention to physicochemical properties and quality, as long as the oil has a strong, pungent odor, and is cheap enough for their means. The European

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[50] *Soap* **18** (August, 1942), **23**; **18** (September, 1942), **25**.
[51] *Ibid.*

and American markets represent only a small percentage in the total consumption of this oil. If buyers were willing to pay a premium for a better quality, the means of production of the oil could perhaps be improved.

Distillation.—Lack of roads and shortage of labor prevent transport of plant material over any appreciable distances. A modern steam distillery could never compete with the simple movable stills which the natives set up in the interior. After the trees of one section have been exploited, the stills are carried, on bamboo poles, to a new location. The distillers then erect a palm leaf shed as shelter and living quarters for themselves.

Prior to the outbreak of World War II there were about 600 small distillation posts on the island of Boeroe (Guenther). The stills, usually 3.5 ft. high, are constructed of sheet iron or copper and heated by direct fire. The top of the still, as well as the simple condenser (immersed in, or diagonally passing through, a barrel) are often also made of copper. The freshly cut plant material is tramped into the still (kettle), the latter being half filled with water. The yield of oil averages about 1 per cent, but could probably be appreciably increased by the use of modern stills provided with efficient condensers. Depending upon the capacity of the condenser, a native still produces up to 6 liters of oil in 24 hr. The oil is collected in wine or beer bottles of 0.6 to 1.5 liters capacity. For shipment abroad, from 15 to 25 such bottles are wrapped in spent cajuput leaves and packed into cases made of nipa palm stalks. Since no large bulking tanks are available on Boeroe, the shipments usually consist of small lots distilled at different times of the year and in different sections of the island. Thus, the lots reaching the market vary considerably in regard to their physicochemical properties. This wide range in the properties of even genuine cajuput oils has led to much confusion as to their actual limits (Guenther[52]).

More recently, the oil has been exported in galvanized iron drums, which caused another variation—i.e., in color (see below). In Java—provided the lot is first shipped there—the oil is usually bulked, analyzed in the government laboratories of Buitenzorg, and exported to Europe, America, or ports in the Far East, particularly Singapore.

Color of the Oil.—The color of cajuput oil and its variation during recent years have caused much controversy. Formerly, the bulk of oil of cajuput usually possessed a green color, and for many years buyers abroad insisted upon this color, associating it with purity of the oil. The controversy as to whether this green color is caused by the presence of chlorophyll or traces of copper has never been settled. Examining genuine lots of imported cajuput oil, Guenther[53] found heavy metals; yet, the green color of some of these oils was caused not by copper but by organic compounds, perhaps

[52] *Ibid.*

[53] *Ibid.*

chlorophyll, mechanically carried over in the primitive stills. In former years the stills used in Boeroe consisted of copper, or at least had copper tops (still heads) and copper condensers. Since the crude oil contains small quantities of aliphatic acids, the copper is kept in solution and, when the oils are exported in glass bottles, as was the practice in former years, they arrive abroad with their original greenish-blue color. The green color of essential oils, if resulting from the presence of copper, can be removed by treatment with concentrated solutions of tartaric acid. If, on the other hand, the green color is caused by chlorophyll or other organic matter, the oil can be decolorized by treatment with a small quantity of active carbon. Of course, rectification of the oils also eliminates the color, of whatever origin. However, rectification of cajuput oil is not carried out in the producing regions, nor in Java or Singapore; the oil is invariably exported in crude form.

For a number of years oil of cajuput has been imported in galvanized iron drums, with the result that upon arrival it has lost its green tint. It is a fact that cajuput oil, when stored in galvanized iron drums for two or three months, loses its original green color and turns yellow. An investigation made by the government laboratories in Buitenzorg, Java, showed that this change of color is caused by an exchange of copper for zinc from the galvanized walls of the drums, and that otherwise the intrinsic properties of the oil are unchanged.

Thus, a lot of cajuput oil of light yellow color has either been distilled in iron stills and therefore had no contact with copper, or else the originally green oil has been in galvanized iron drums for a certain length of time. Perhaps the green-bluish tint of some lots of cajuput oil is caused by the presence of azulenic compounds in the high boiling portions. In order to comply with demands of those buyers who insist upon the greenish tint, exporters in Java sometimes restore the original green color simply by suspending small copper sheets in the oil for several days.

Physicochemical Properties.—Gildemeister and Hoffmann[54] reported these properties for cajuput oil:

Specific Gravity at 15°	0.917 to 0.930
Optical Rotation	Slightly laevorotatory, up to −3° 40′
Refractive Index at 20°	1.466 to 1.472
Cineole Content (Solid Resorcinol Compound)	50 to 60% (on the average)
Solubility	Soluble in 1 vol. and more of 80% alcohol; occasionally soluble in 2.5 to 3 vol. of 70% alcohol

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[54] "Die Ätherischen Öle," 3d Ed., Vol. III, 432.

The oil possesses an agreeable camphoraceous odor reminiscent of cineole, and a slightly burning flavor with a cooling aftereffect.

Two samples of crude (unrectified) cajuput oil, collected by Guenther[55] during a visit to the Netherlands East Indies, exhibited the following values:

	I	*II*
Specific Gravity at 15°	0.919	0.922
Optical Rotation	−1° 36′	−0° 54′
Refractive Index at 20°	1.4703	1.4670
Saponification Number	9.3	6.5
Cineole Content (*o*-Cresol Method)	53.8%	64.0%
Solubility in 80% Alcohol	Soluble in 1 vol. and more	

Sample II was of exceptionally good quality.

Shipments of cajuput oil received and examined by Fritzsche Brothers, Inc.,[56] New York, in the course of years had these properties:

Specific Gravity at 15°/15°	0.915 to 0.926
Optical Rotation	−1° 0′ to −4° 0′
Refractive Index at 20°	1.4640 to 1.4720
Saponification Number	6.5 to 12.0
Cineole Content (*o*-Cresol Method)	50 to 65%
Solubility in 80% Alcohol	Soluble in 1 vol. and more

Adulteration.—Oil of cajuput is sometimes adulterated by the native producers and intermediaries with fatty oils or with kerosene. The odor of this oil is so strong that a moderate addition of kerosene is hardly noticeable. A simple test employed by the native dealers in the East Indies consists in shaking the bottle violently. If the air bubbles rising to the surface do not disappear quickly, and if there is a formation of foam, the oil has very likely been cut with fatty oils or kerosene. Eucalyptus oils are occasionally added in Europe and America, but not in Boeroe where very little eucalyptus oil is imported. Addition of eucalyptus oil would increase the cineole content of the cajuput oil to an abnormally high percentage. A lot containing, let us say, 70 per cent of cineole should give rise to suspicion.

Chemical Composition.—The first investigation of the chemical composition of cajuput oil dates back more than a century, when Blanchet[57] found that the principal constituent of the oil possesses the empirical molecular formula $C_{10}H_{18}O$. In subsequent investigations by several other authors this compound was named variously "cajuput hydrate" and "cajuputol," or "cajeputol." Wallach,[58] and Wallach and Gildemeister[59] finally established the identity of "cajeputol" with cineole. The other components of the oil

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[55] *Soap* **18** (August, 1942), 23.

[56] Private communication from Dr. Ernest Guenther, New York.

[57] *Liebigs Ann.* **7** (1833), 161.

[58] *Ibid.* **225** (1884), 315.

[59] *Ibid.* **246** (1888), 276.

were investigated by Voiry,[60] Schimmel & Co.,[61] Duyster,[62] and Spoelstra.[63] The following constituents have been identified:

Valeraldehyde and Benzaldehyde. The forerun of the oil contains several aldehydes, which can be separated by treatment with sodium bisulfite, among them valeraldehyde (Voiry), and benzaldehyde.

The latter was identified by means of the phenylhydrazone m. 156° (Duyster).

Cineole. The principal constituent of the oil is cineole (50 to 65 per cent), characterized by oxidation of the corresponding fraction to cineolic acid $C_{10}H_{16}O_5$, m. 196°–197° (Wallach and Gildemeister).

α-Terpineol and Esters. Optically inactive α-terpineol m. 35°, the next most important constituent of the oil, is present in the free form, as well as in the form of acetic, propionic, and valeric ester (Voiry, Schimmel & Co., and Duyster).

The presence of laevorotatory α-terpineol in the oil has been reported by Spoelstra.

l-α-Pinene, *l*-Limonene, Dipentene, Sesquiterpenes, Azulene, and Sesquiterpene Alcohols. The same author also found that the oil contains *l*-α-pinene, *l*-limonene, dipentene, a mixture of mostly bicyclic and some monocyclic sesquiterpenes (which on dehydrogenation with sulfur yielded cadalene), some azulene, and sesquiterpene alcohols b_{20} 160°–165°. The latter, on boiling with formic acid (85 per cent), gave a mixture of sesquiterpenes $C_{15}H_{24}$, which consisted of equal parts of monocyclic and bicyclic hydrocarbons, and on treatment with sulfur yielded cadalene.

Exports.—Before World War II oil of cajuput was exported from Namlea, the capital of Boeroe, via Amboyna and Macassar, either to Java and the outlying islands, or to Singapore, the principal port for transshipment to other countries. According to the interregional trade statistics of the outer islands, the annual interisland shipments of the Netherlands East Indies have averaged about 100 tons of cajuput oil annually.

The quantities shipped to foreign countries during the same period averaged about 70 tons. At one time they were subject to great fluctuations. In 1937 the exports in tons net were as follows:

	Metric Tons
Singapore	43
Holland	6
Great Britain	5
Germany	5
France	3
U.S.A.	2
Other countries	9
Total	73

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[60] *Compt. rend.* **106** (1888), 1538. *Bull. soc. chim.* [2], **50** (1888), 108. *J. Pharm.* [5], **18** (1888), 149.

[61] *Ber. Schimmel & Co.,* April (1892), 7.

[62] *Pharm. Tijdschr. Nederland. Indië* **2** (1925), 327. *Ber. Schimmel & Co.* (1926), 10.

[63] *Rec. trav. chim.* **48** (1929), 372.

Of this quantity, more than 71 tons were shipped from the outer islands, and only a little more than one ton from Java.

From 1939 to 1941 inclusive and in 1948 the exports in gross weight and metric tons were as follows:

1939	81
1940	145
1941	116
1947	...
1948	7

For years, the chief port of destination was Singapore from where a large part used to be transshipped to Indo-China, India, and other parts of the Far East, and to the United States and Europe. The Netherlands East Indies have always been the principal users; they could, in fact, absorb much larger quantities if the price were low enough for the natives to purchase the oil more freely.

Use.—As has been pointed out, the natives of Malaya use the oil as a panacea in the treatment of all kinds of diseases—internally as a medicine for stomachic and intestinal troubles, externally for skin diseases. Rubbed on the forehead, it is alleged to relieve headache, probably because of its cooling effect. Internally it acts as an anthelmintic, particularly effective against roundworms. Introduced into a carious tooth, it relieves toothache. In western countries the oil was formerly used externally for rheumatism; moreover, it has been recommended as an expectorant in cases of laryngitis and bronchitis.

According to native belief, it is a very effective insecticide. Lice and fleas (but not ticks) fall off cats and dogs when they are rubbed down with cajuput oil. The oil is also employed in Malaya as a room spray against bedbugs and all kinds of insect pests.

On this the present authors would like to comment that in their opinion oil of cajuput could readily be replaced by eucalyptus oil.

CHAPTER V

ESSENTIAL OILS OF THE PLANT FAMILY *UMBELLIFERAE*

OIL OF AJOWAN

Essence d'Ajowan *Aceite Esencial Ajowan* *Ajowanöl*

Description.—*Carum ajowan* or *C. copticum* Benth. et Hook., a native of Europe, North Africa, and North Asia, is an annual plant, the grayish-brown fruit (seed) of which resembles that of parsley except for its rougher surface and very different aroma. Two types of seed are known in India, viz., one of larger size grown widely in many parts of India as a garden crop and another of smaller size grown mainly in Indore. The latter is cultivated largely for export; whereas the former serves extensively in curry powders and as a general household remedy for intestinal ailments. The distillation water, the essential oil, and the thymol separated therefrom are used in India as medicine, particularly for cases of cholera.

Although it grows also in Persia, Afghanistan, and Egypt, ajowan is produced chiefly in India, from the Punjab to Bengal and to south Deccan.

Distillation.—A substantial amount of the seed is distilled in India, partly in primitive native stills resembling those used for palmarosa and partly in more modern and large-scale distilleries located in Rao (Indore State).[1] Prior to and during World War I, considerable quantities of ajowan seed were exported from India for distillation in Europe and the United States. The oil was for a long time the principal source of thymol. However, since the introduction of synthetic thymol, the distillation of ajowan oil outside of India has practically ceased, and the oil has lost its former importance.

The yield of volatile oil from the crushed seed varies from 3.0 to 4.0 per cent. The residual dried seed contains a considerable amount of proteins (15 to 17 per cent) and fat (25 to 32 per cent), and thus may be used as cattle feed.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[2] the properties of oil of ajowan seed vary within the following limits:

Specific Gravity at 15°	0.910 to 0.930
Optical Rotation	Slightly dextrorotatory, to +5° 0′
Refractive Index at 20°	1.498 to 1.504
Content of Phenols (Determination with 5% NaOH aq. sol.)	45.0 to 57.0%
Solubility	Soluble in 1 to 2.5 vol. and more of 80% alcohol

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[1] Cf. Sadgopal, *Indian Soap J.*, October-December (1943).

[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 496.

Oil of ajowan is an almost colorless to brownish liquid, possessing a characteristic thyme odor and a sharp burning taste. On standing, a part of the thymol may separate from the oil in the form of crystals.

Chemical Composition.—Oil of ajowan seed is composed of about 50 per cent of phenols, mainly thymol, and about 50 per cent of terpenes, which years ago were marketed under the name of "thymene." Commercial "thymene" consists of *p*-cymene and several other terpenes, which were identified by the Schimmel chemists.[3]

The presence of the following compounds has been established in ajowan seed oil.

α-Pinene. In the fraction b. 165°–170°. Identified as nitrosochloride m. 103°–104°, and nitrolbenzylamine m. 123°–124°.

p-Cymene. The presence of this terpene in ajowan seed oil was first reported by Haines.[4] It occurs in all fractions of "thymene" and is the main constituent of the fraction boiling about 175°. Identified as hydroxyisopropylbenzoic acid m. 155°–156°, and as *p*-propenylbenzoic acid m. 159°–160°.

Dipentene. In the fraction b. 179°–181°. Dihydrochloride m. 48°–49°, nitrosochloride m. 104°–105°, nitrolpiperidine m. 152°–153°.

γ-Terpinene. The fraction b. 179°–181° on oxidation with potassium permanganate, according to Wallach's[5] method, yielded the corresponding erythritol m. 236°–237°.

The Schimmel chemists[6] proved that γ-terpinene predominates among the three terpenes, viz., α-pinene, dipentene, and γ-terpinene.

Murayama[7] expressed the opinion that ajowan seed oil contains still another terpene, viz., moslene, but according to Richter and Wolff,[8] this compound is very probably identical with γ-terpinene.

Thymol. The main constituent of ajowan seed oil was identified almost simultaneously by Haines,[9] and by Stenhouse.[10]

Carvacrol. Sobti and Singh[11] isolated from the oil small quantities of another phenol viz., carvacrol, which gave a nitroso compound m. 153°.

Use.—As has been pointed out, in past years oil of ajowan was used for the isolation of thymol.

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[3] *Ber. Schimmel & Co.*, October (1909), 14.

[4] *J. Chem. Soc.* **8** (1856), 289. *Jahresber. Chem.* (1856), 622.

[5] *Liebigs Ann.* **362** (1908), 303.

[6] *Ber. Schimmel & Co.*, October (1909), 15.

[7] *J. Pharm. Soc. Japan* No. 475 (1921), 786. *Chem. Abstracts* **16** (1922), 1568.

[8] *Ber.* **60** (1927), 477; **63** (1930), 1714.

[9] *J. Chem. Soc.* **8** (1856), 289. *Jahresber. Chem.* (1856), 622.

[10] *Liebigs Ann.* **93** (1855), 269; **98** (1856), 309.

[11] *Perfumery Essential Oil Record* **14** (1923), 399.

OIL OF ANGELICA

Essence d'Angélique *Aceite Esencial Angelica* *Angelicaöl*
Oleum Angelicae

Introduction.—*Archangelica officinalis* Hoffm. (*Angelica archangelica* L.), is a hapaxanthic plant, native to Europe, grown there and in the United States as garden angelica. In the eastern United States one finds also a native wild growing species, *Angelica atropurpurea* L., our common masterwort. This root, however, has little commercial significance, being quite different in odor and flavor from true angelica. It must not be confused with true *Archangelica officinalis.*

Courtesy of Dr. Jules de Bittera, Budapest, Hungary.

FIG. 36. Production of angelica oil in Hungary. Fully developed angelica plants in Tihany near Lake Balaton.

Botany.—*Archangelica officinalis* Hoffm. possesses thick, fleshy taproots (the upper part of the latter a shoot), with many rootlets attached. It develops a hollow, round, jointed, channeled, smooth, purplish stem, which is divided into numerous branches and grows to a height of 5 ft. or even higher. Greenish-white flowers are borne in compound umbels. The whole plant is aromatic.

The taproots are short and thick, 5 to 10 cm. long, and sometimes split. The numerous roots, frequently twisted or braided, possess a gray-brown, reddish, or purplish-brown color. They have a strong aromatic odor, and a warm, pungent, bitter-sweet taste. The seeds are oblong, round at the ends, and of whitish color. The fresh stems and leaf stalks serve as a garnish and for confectioneries. The flavor and perfume industries employ chiefly the root and seed, or their respective volatile oils, which can be recovered by steam distillation.

Habitat and Range.—Garden angelica thrives best on rich, alluvial soil, and in a temperate, rather cool climate. Wet cold over a continued period of time is not conducive to good growth. Europe's main angelica producing regions, where the bulk of root and seed originates, are located in Belgium, France (Clermont-Ferrand and Puy-de-Dôme), and Germany (Thuringia and Saxony). In Belgium and France angelica is cultivated for its root and seed; in Germany, primarily for its root. Prior to World War II Hungary, too, produced angelica root and seed, but the quantities were small.

Use of Root and Seed.—Use of angelica root and seed in pharmacy is probably a survival of those ancient beliefs which attributed medicinal properties to many aromatic herbs. The most important application of angelica root and seed is in French type alcoholic liqueurs, and especially in gin. In fact, next to juniper berries, angelica root is the main flavoring ingredient of gin. Instead of using root and seed, the flavor industry has recently shown preference for the essential oil, because it can be dosed more exactly.

BELGIAN ANGELICA ROOT AND SEED

Producing Regions.—Belgium's main producing regions are in the northern part of the province of Hainaut, particularly around Lessines.

Planting, Cultivating, and Harvesting.—Angelica is planted in September and October, before the winter cold sets in. In the following June and July the leaf stalks (which resemble common rhubarb) are harvested, largely for use in fruit preserves.

When cutting the leaf stalks, care must be taken to protect the principal central stalks, which will grow the following year, branch out, and produce the seeds. The plants reach a height of 6 to 7 ft. When the seed ripens in July, the umbels (seed clusters) are cut, gathered by the workers in their aprons, and emptied into sacks standing along the edges of the fields. The collecting is repeated several times, at intervals of a few days, as the seed ripens. The umbels are subsequently dried with warm air, by hanging either in garrets or in kilns. The dried umbels are beaten lightly, and the seed is sifted and winnowed.

No time must be lost in clearing the field for a new crop. The plants are pulled out, the roots collected and dried. If allowed to remain in the ground, the roots quickly rot.

Total Production of Root and Seed.—The total production of angelica seed in Belgium varies from 40 to 50 metric tons; that of roots averages from 15 to 20 tons—in other words about half, or less, of the seed production.

AMERICAN ANGELICA ROOT AND SEED

Planting, Cultivating, and Harvesting.—Stockberger[1] reported that angelica thrives best in a moderately cool climate, and may be grown in any good soil, although a deep, fairly rich, moist, but well-drained, loam gives best results. The soil should be deeply plowed and well prepared before planting. The plant is most readily propagated from divisions of old roots, which may be set out 18 in. apart in rows, either in the fall or in the spring. The seed germinates very poorly if more than one year old; therefore, it should be sown, as soon as ripe, in seed beds kept moist by watering at regular intervals. Early in the following spring, the seedlings are transplanted to their permanent location and set out 2 ft. apart in each direction. Plants may also be raised from seed sown during March in a spent hotbed or coldframe. To increase root development, the plants are sometimes transplanted a second time, after the first year's growth, and set 3 or 4 ft. apart. For the same reason, the tops are often cut back, to prevent formation of seed. Frequent cultivation during the growing seasons keeps the soil mellow and free from weeds.

The roots are usually dug up in fall of the second year, but occasionally roots of "first-year plants" are marketed. The harvested roots are washed and dried in the open air. To keep out insects and preserve the aroma, it is advisable to store the dried roots in tightly closed tin containers. It has also been suggested that the roots be preserved by the addition of a few drops of chloroform or carbon tetrachloride.

According to Willkie and Kolachov,[2] one acre of angelica requires 8 to 11 lb. of seed and yields 900 to 1,300 lb. of dried root.

Canadian Angelica Root Oil.—Bedoukian[3] reported on an angelica root oil distilled during 1943 from fresh root material grown around Montreal. The seed had been obtained from the Montreal Botanical Garden and had been verified as true *Angelica archangelica officinalis*.

The Canadian oil had the usual physicochemical properties of oils from other countries, except for the optical rotation, which was laevorotatory. Bedoukian attributes this factor to climatic conditions, but does not exclude the possibility that the plant may have developed a new strain because of unknown conditions.

Angelica Root Oil

Distillation.—Most of the aromatic plant material grown in Belgium is exported and processed in the essential oil factories of Southern France

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[1] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935).

[2] "Domestic Production of Essential Oils from Aromatic Plants," *Bull. Natl. Farm Chemurgic Council* (1940).

[3] *Am. Perfumer* 46 (August 1944), 54.

(Grasse), England, Germany, and the United States. Before shipping, the root must be dried thoroughly. When ordering roots for distillation purposes, material free from the lower woody stalk parts, which contain very little essential oil, should be specified. The slender rootlets are particularly rich in oil. Upon prolonged aging the roots lose part of their essential oil, the yield decreasing as the more volatile terpenes gradually evaporate. Fresher roots yield oils of lighter color and a more pronounced terpene note; whereas oils distilled from old roots are darker, of higher specific gravity, and of lower optical rotation. These oils possess a characteristic musk-like odor, which is caused by the preponderance of oxygenated compounds—particularly lactones.

According to Gildemeister and Hoffmann,[4] fresh angelica root, upon steam distillation, yields 0.10 to 0.37 per cent of essential oil, dried root 0.35 to 1.00 per cent.

In the author's experience, the yield of oil from normal, dried root ranges from 0.40 to 0.50 per cent; that from aged root is around 0.37 per cent.

Distillation of angelica root should last at least 10 hr. Prolonged distillation (up to 24 hr.) yields oils of superior quality: they contain a relatively large amount of high boiling compounds, particularly lactones, which are the most important and characteristic constituents, so far as odor and flavor are concerned. Such oils possess a higher specific gravity, a higher ester number, and a lower optical rotation than those described by Gildemeister and Hoffmann.[5] The somewhat elevated acid number can be reduced by proper chemical treatment of the oil (by shaking the oil with a dilute aqueous solution of sodium carbonate, for example).

Physicochemical Properties of Angelica Root Oil.—Gildemeister and Hoffmann[6] reported the following properties for angelica root oil:

Specific Gravity at 15°	0.859 to 0.918 (oils distilled from Thuringian roots often have a lower specific gravity, as low as 0.853)
Optical Rotation	+16° 0′ to +41° 0′ (French oils even when freshly distilled sometimes possess a considerably lower rotation)
Refractive Index at 20°	1.476 to 1.488
Acid Number	Up to 5.0
Ester Number	12.0 to 39.0
Ester Number after Acetylation	30.0 to 75.0
Solubility	Soluble in 0.5 to 6 vol. and more of 90% alcohol, sometimes with slight opalescence

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[4] "Die Ätherischen Öle," 3d Ed., Vol. III, 543.

[5] *Ibid.*

[6] *Ibid.*

Chiris[7] observed the following properties of angelica root oil:

Specific Gravity at 15°	0.863 to 0.875
Optical Rotation	+19° 0′ to +25° 0′
Refractive Index at 20°	1.479 to 1.482
Acid Number	Up to 2.4
Ester Number	11.0 to 19.0

Chiris also described oils distilled from root which had been stored for a long time. They had quite different properties, for instance:

Specific Gravity at 15°	0.938
Optical Rotation	+0° 26′
Refractive Index at 20°	1.4922
Acid Number	14.7
Ester Number	47.6
Solubility	Soluble in 1.5 vol. and more of 80% alcohol

Oils distilled from aged root material are by no means inferior; they are usually as good as, if not superior to, oils from newly harvested, dried roots, because of their very strong and characteristic odor. They possess less terpene character than oils from root of the latest harvest, the latter resembling the seed oils, so far as odor and flavor are concerned. Experts are of the opinion that a high content of oxygenated compounds in angelica root oil is preferable to a terpene character, because the latter can always be obtained by the use of angelica seed oil.

Three angelica root oils distilled by the author in France from root material that had been aged for some time, exhibited the following values:

	I	*II*	*III*
Specific Gravity at 15°	0.936	0.917	0.909
Optical Rotation	+3° 40′	+8° 32′	+2° 30′
Refractive Index at 20°	1.4870	1.4881	1.4813
Acid Number	16.4	15.4	12.6
Saponification Number	81.5	70.0	62.5
Solubility	Soluble in 0.5 vol. and more of 90% alcohol		

Angelica root oils distilled by Fritzsche Brothers, Inc., from European, mostly Belgian, root material had properties which varied within these limits:

Specific Gravity at 15°	0.907 to 0.936
Optical Rotation	+0° 50′ to +14° 26′
Refractive Index at 20°	1.4813 to 1.4870
Acid Number	7.3 to 16.4

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[7] *Parfums France* **12** (1934), 16.

Saponification Number. .	. 44.7 to 81.5
Solubility at 20°. .	. Soluble in 0.5 vol. and more of 90% alcohol

The physicochemical properties of angelica root oil change as the oil ages. Under the influence of light and air the color turns darker and the optical rotation decreases considerably. Gildemeister and Hoffmann,[8] for instance, reported that the rotation of an angelica root oil changed from +27° 0′ to +8° 0′ in the course of a six-year period. It is an interesting fact that the rotation of Manila elemi oil is affected similarly, and, since both oils contain phellandrene, the conclusion suggests itself that the change may be caused by phellandrene. Experience shows that the dextrorotation of elemi oil fractions which are particularly rich in phellandrene slowly decreases with age. (Cf. monograph on "Phellandrene," Vol. II of this work, p. 40 ff)

After the conclusion of World War II small quantities of angelica oil distilled in the producing regions of Belgium were offered to the trade. In regard to quality, however, few of the samples met the standards established years ago by the well-known distillers in Southern France, England, and Germany, probably for the reason that the new producers in Belgium had not yet acquired the necessary equipment and the experience for the proper preparation and distillation of the plant material. As Couvreur[9] pointed out, the Belgian essential oil industry is still in its infancy, and a great deal of knowledge will have to be gathered, under the guidance of experts, before the production of essential oils from locally grown plants, such as angelica, valerian, Roman chamomile, and hops will be successful.

Regarding the quality of the oils distilled from angelica root grown in the United States, it should be stated that they all possess a lovage-like odor and flavor, quite different from, and inferior to, that of the oils distilled from European grown root. Most likely, the American grown plant is of a different variety or even species, perhaps our masterwort (*Angelica atropurpurea* L.).

Adulteration of Angelica Root Oil.—The most common form of adulteration is the addition of phellandrene isolated from other, lower priced essential oils. Phellandrene being a natural constituent of angelica oil, it is difficult, if not impossible, to prove the addition of only moderate amounts. This is another reason why preference should be given to angelica root oils with a high content of oxygenated compounds and a low content of phellandrene.

Occasionally angelica root oil is adulterated with lovage root oil. In fact, the latter represents a common adulterant, because of a certain similarity between the two oils, which both contain high boiling lactones.

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[8] "Die Ätherischen Öle," 3d Ed., Vol. III, 543.

[9] *Ind. Parfum.* **1**, No. 8 (1946), 270.

Added lovage oil would increase the specific gravity and especially the refractive index of angelica root oil, but these deficiencies could be "remedied" by the addition of a corresponding amount of phellandrene. In other words, the skilled sophisticator has little difficulty in preparing lower priced oils which meet all the requirements of a routine analysis. In the evaluation of angelica root oils, therefore, it is advisable not to rely too much on analytical data, but to depend rather on careful odor and flavor tests.

Chemical Composition of Angelica Root Oil.—The lower boiling fractions of angelica root oil, which consist of terpenes, have been investigated by Beilstein and Wiegand,[10] by Naudin,[11] by the Schimmel chemists,[12] and by Haensel.[13] The higher boiling fractions, responsible for the musk-like odor of the oil and consisting mainly of lactones, have been studied by Ciamician and Silber,[14] by Böcker and Hahn,[15] by Kerschbaum,[16] and by Späth and Pesta.[17] The Schimmel chemists[18] also identified a few constituents which occur in the distillation waters.

The presence of the following compounds has been established:

d-α-Phellandrene. Quantitatively, this terpene is the chief constituent of angelica root oil. First identified by Haensel,[19] its presence in the oil was confirmed more recently by Dijkstra.[20]

α-Pinene. The same author also reported the occurrence of α-pinene in the oil.

A Terpene(?). Dijkstra observed a third terpene in the terpene fraction but could not identify it.

Borneol(?). According to Dijkstra the oil does not contain any *p*-cymene nor any primary alcohols. However, he isolated a secondary alcohol, probably borneol (m. 201°), but did not succeed in identifying it.

Sesquiterpenes(?). The fraction, from which the secondary alcohols were isolated, contained sesquiterpenes.

Osthenole. This parent phenol of osthole (see below) was isolated from angelica root oil by Späth and Bruck,[21] and named osthenole $C_{14}H_{14}O_3$, m. 124°–125°.

Osthole. The γ-lactone $C_{15}H_{16}O_3$ first observed in angelica root oil by Böcker and Hahn[22] was identified by Späth and Pesta[23] as osthole m. 82°–83° which occurs also in the oil derived from the roots of masterwort (*Imperatoria ostruthium*). According to the above named authors, dried angelica root contains about 0.2 per

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[10] *Ber.* **15** (1882), 1741.

[11] *Bull. soc. chim.* [2], **39** (1883), 407. *Compt. rend.* **96** (1883), 1153.

[12] *Ber. Schimmel & Co.,* April (1891), 3.

[13] *Chem. Zentr.* II (1907), 1620.

[14] *Ber.* **29** (1896), 1811.

[15] *J. prakt. Chem.* [2], **83** (1911), 243.

[16] *Ber.* **60** (1927), 902.

[17] *Ber.* **67** (1934), 853.

[18] *Ber. Schimmel & Co.,* April (1913), 20.

[19] *Chem. Zentr.* II (1907), 1620.

[20] *Pharm. Weekblad* **81** (1946), 387.

[21] *Ber.* **70** (1937), 1023.

[22] *J. prakt. Chem.* [2], **83** (1911), 243.

[23] *Ber.* **67** (1934), 853. See also Späth and Vierhapper, *Monatsh.* **72** (1938), 179.

cent of osthole. Späth and Holzen[24] succeeded in synthesizing this 7-methoxy-8-(γ,γ-dimethylallyl) coumarin.

Angelicin. Aside from osthole, Späth and Pesta[25] found other lactones in the same fraction of angelica root oil; one of these lactones was identified as $C_{11}H_6O_3$, m. 138°–139.5°, and named angelicin. Späth and Pailer[26] succeeded in synthesizing this furano-4′,5′,7,8-coumarin. Cf. monograph on "Osthole" and "Angelicin" in Vol. II of this work, p. 671 and p. 686, respectively.

The content of osthenole, osthole, and angelicin in the *volatile* oil of angelica root depends obviously upon the length of distillation and the steam pressure applied since the coumarin derivatives possess relatively high boiling points and are not readily volatilized by steam.

Lactone of 15-Hydroxypentadecanoic Acid. The most important constituent of angelica root oil, from the olfactory point of view, is the lactone of 15-hydroxypentadecanoic acid which was isolated from the oil by Ciamician and Silber,[27] and by Kerschbaum,[28] after saponification of the high boiling fractions with alcoholic potassium hydroxide. Most likely, 15-hydroxypentadecanoic acid $C_{15}H_{30}O_3$, as well as some lower and higher homologues, does not occur in the oil as a free acid, nor as an ether or ester, but as a lactone.[29] The work of Kerschbaum[30] has shown that the peculiar, characteristic, musk-like odor of angelica root and seed oil is probably due to the presence of lactones with more than twelve carbon atoms. Hydroxymyristic acid, the next lower homologue of 15-hydroxypentadecanoic acid, occurs in the oil derived from angelica seed.

Methyl Ethyl Acetic Acid (α-Methyl Butyric Acid). This acid accompanies 15-hydroxypentadecanoic acid in the high boiling fractions of angelica root oil and was identified in the course of the above-mentioned investigations by Ciamician and Silber, Kerschbaum, and Dijkstra.

Diacetyl, Methyl Alcohol, Ethyl Alcohol, Furfural, and a Base of Pyridine-like Odor. Occur in the distillation waters of angelica root oil, according to Schimmel & Co.[31]

Angelica Seed Oil

Yield of Oil and Physicochemical Properties.—According to Gildemeister and Hoffmann,[32] steam distillation of angelica seed yields 0.6 to 1.5 per cent of oil. Angelica seed, distilled in France by the author, gave yields ranging from 1.2 to 1.8 per cent.

Gildemeister and Hoffmann[33] reported the following properties for angelica seed oils:

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[24] *Ber.* **67** (1934), 264.

[25] *Ibid.*, 853. See also Späth and Vierhapper, *Monatsh.* **72** (1938), 179.

[26] *Ber.* **67** (1934), 1212; **68** (1935), 940.

[27] *Ber.* **29** (1896), 1811.

[28] *Ibid.* **60** (1927), 902.

[29] Cf. "Exaltolide," Vol. II of this work, p. 688.

[30] *Ber.* **60** (1927), 902.

[31] *Ber. Schimmel & Co.*, April (1913), 20.

[32] "Die Ätherischen Öle," 3d Ed., Vol. III, 546.

[33] *Ibid.*

Specific Gravity at 15°	0.851 to 0.890
Optical Rotation	+11° 0′ to +13° 30′
Refractive Index at 20°	1.484 to 1.491
Acid Number	Up to 2.2
Ester Number	15.0 to 30.0
Ester Number after Acetylation	27.0 to 49.0
Solubility	Soluble in 5 to 9 vol. of 90% alcohol, sometimes with opalescence or turbidity

A few lots of angelica seed oil distilled under the author's supervision in Seillans (Var), France had these properties:

	I	*II*	*III*	*IV*
Specific Gravity at 15°	0.855	0.862	0.856	0.860
Optical Rotation	+15° 0′	+14° 31′	+14° 50′	+14° 46′
Refractive Index at 20°	1.4847	1.4848	1.4840	1.4858
Acid Number	1.4	1.4	1.1	2.8
Saponification Number	14.0	23.8	14.8	21.5
Solubility	Slightly turbid in 10 vol. of 90% alcohol		Soluble in 4.5 to 5 vol. and more of 90% alcohol, with slight turbidity	

Angelica seed oils distilled by Fritzsche Brothers, Inc., had properties which ranged between the following limits:

Specific Gravity at 15°	0.855 to 0.881
Optical Rotation	+3° 44′ to +15° 0′
Refractive Index at 20°	1.4840 to 1.4898
Acid Number	1.1 to 2.8
Saponification Number	14.0 to 22.4
Solubility at 20°	Incompletely soluble in 10 vol. of 90% alcohol

Distilling superannuated Hungarian angelica seed, two to ten years old, Kopp[84] obtained oils (yield 0.62–0.93 per cent) which had a considerably higher specific gravity than the oils described above. The solubility in alcohol was poor, and the optical rotation ranged from −1° 24′ to −6° 12′, the latter for an oil distilled from ten-year old seed. In view of these properties, the quality of these oils must be considered as very inferior. As a matter of fact, the experiments of Kopp prove that only *fresh* angelica seed should be used for distillation purposes.

Adulteration of Angelica Seed Oil.—The most frequently encountered adulterant of angelica seed oil is phellandrene. Moderate additions are difficult to detect, because the oil contains phellandrene as a natural con-

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[84] *Pharm. Zentralhalle* **69** (1928), 353.

stituent. As with the root oil, it is advisable to rely upon a careful organoleptic examination.

Chemical Composition of Angelica Seed Oil.—The investigations on angelica seed oil carried out by Müller,[35] by Naudin,[36] and by the Schimmel chemists,[37] have shown that the seed oil and the root oil are similar in composition, but the seed oil contains more terpenes than the root oil, and the latter contains more of the oxygenated compounds, largely lactones.

The presence of the following constituents in angelica seed oil has been established:

β-Phellandrene. This is the only terpene so far identified, but may not be the only one occurring in the seed oil.

Methyl Ethyl Acetic Acid. Isolated after saponification of the oil with alcoholic potassium hydroxide solution.

Hydroxymyristic Acid. This acid $C_{14}H_{18}O_3$, m. 51°, was identified in the highest boiling fractions, also after saponification of the oil. Its next higher homologue, viz., 15-hydroxypentadecanoic acid $C_{15}H_{30}O_3$, occurs in the root oil, probably as γ-lactone.

The above listed compounds are the only ones which have been definitely identified in the volatile oil of angelica seed. More recently, Späth and Vierhapper[38] investigated the seed more thoroughly and identified in the *extract* a number of coumarin derivatives possessing relatively high melting points. Whether these lactones and coumarins occur also in the volatile oil of angelica seed depends obviously upon the length of distillation and the steam pressure applied when steam distilling the seed material. For completeness sake, however, we shall list the findings of Späth and Vierhapper who claim that angelica seed contains:

Imperatorin (0.50%). This xanthotoxolisoamylene ether $C_{16}H_{14}O_4$ melts at 102°.

Bergaptene (0.10%). This 5-methoxyfurano-2′,3′,6,7-coumarin $C_{12}H_8O_4$ melts at 224°.

Xanthotoxol (0.02%). This 8-hydroxyfurano-2′,3′,6,7-coumarin $C_{11}H_6O_4$ melts at 249°–251°.

Xanthotoxin (0.02%). This xanthotoxol methyl ether $C_{12}H_8O_4$ melts at 146°.

Umbelliprenin (0.04%). This umbelliferone farnesyl ether $C_{24}H_{30}O_3$ melts at 61°–63°.

A Phenol(?) (0.03%). The same authors also isolated a phenol $C_{12}H_8O_5$(?) from angelica seed.

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[35] *Ber.* **14** (1881), 2476.

[36] *Bull. soc. chim.* [2], **37** (1882), 107. *Compt. rend.* **93** (1881), 1146.

[37] *Ber. Schimmel & Co.,* April (1891), 3.

[38] *Ber.* **71** (1938), 1667. *Monatsh.* **72** (1938), 179, 185.

(In this connection see also the work of Noguti and Kawakami[39] on the chemical composition of an ether extract of the fruit of *Angelica glabra* Makino.)

The compounds listed above have been fully described in Vol. II of the present work.

Use of Angelica Root and Seed Oils.—Of the two, the root oil is more important because of its richer, more characteristic odor and flavor. Oil of angelica is employed chiefly in high grade liqueurs of the French type, such as Benedictine and Chartreuse blends, etc. Gin essences, too, contain a considerable portion of angelica oil.

The oil is also useful in high-grade perfumes, to which it imparts peculiar musk-like notes which are hard to identify.

SUGGESTED ADDITIONAL LITERATURE

K. Bournot, "Angelica and Lovage Oils," *Am. Perfumer* **36** (March 1938), 38.

T. F. West, "β-Phellandrene in Certain Essential Oils," *J. Soc. Chem. Ind.* **58** (1939), 124.

De Glazoff and Kolachov, "Comparison of Assays of Domestic and Imported Aromatic Plants and Essential Oils," *Trans. Kentucky Acad. Sci.* **10**, No. 1–2 (1942), 13.

H. Flück and W. F. Fehlmann, "The Drying of the Roots of the Official *Umbelliferae*," *Pharm. Acta Helv.* **22** (1947), 279, 489. *Chem. Abstracts* **43** (1949), 363.

OIL OF ANISE

Essence d'Anis *Aceite Esencial Anis* *Anisöl* *Oleum Anisi*

OIL OF ANISE SEED

Introduction.—There exist two plants, entirely different botanically, the fruits of which contain volatile oils of similar chemical composition and, therefore, of similar odor and flavor. The so-called star anise oil is distilled from *Illicium verum* Hooker f. (fam. *Magnoliaceae*) in Tonkin (French Indo-China), and in the adjacent province of Kwangsi (Southern China). It will be described in a separate monograph—in a later volume of this work.

The other oil, of finer and more delicate flavor, is that contained in the fruit of anise, *Pimpinella anisum* L. (fam. *Umbelliferae*).

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[39] *J. Pharm. Soc. Japan* **61** (1941), 77. *Chem. Abstracts* **36** (1942), 464.

Description.—Anise, *Pimpinella anisum* L., a native of the Orient, is a hapaxanthic annual herb, growing about 1 ft. high under cultivation. The greenish-gray, dried, ripe fruit, commercially called seed, tapers to a point, and varies in length from 2 to 5 mm.; it consists of two united mericarps. Anise seed is a popular flavoring agent, widely employed in baked goods, confectionery, and liqueurs. Some of the best-known French alcoholic beverages and *apéritifs* owe their flavor chiefly to anise seed. The volatile oil can be recovered from the fruit (seed) by steam distillation. In many instances the oil has now replaced the seed for flavoring purposes.

Range and Habitat.—*Pimpinella anisum* L., very likely a native of the Near East and Egypt, is widely cultivated in Central, Southern, and Southeastern Europe, in the southern part of the U.S.S.R., in Macedonia, Syria, Tunis, Morocco, India, China, Chile, and Mexico. To a limited extent the plant is now being grown also in various parts of the United States.[1] Depending on point of origin, the seed varies somewhat in appearance and volatile oil content; Spanish anise, for example, is smaller than the German or French, whereas Russian seed is very short. A deficient yield of oil may be caused also by adulteration of the seed with spurious seed or foreign matter.

Since the vegetative period of anise is long (130 to 140 days), it must be sown earlier than other plants; for the same reason, it requires a rather warm climate. According to Stockberger,[2] it has been found difficult to mature the crop in northerly locations, where the growing season is short, or in the south where the climate is hot and dry. Crooks and Sievers[3] claimed that there should be a frost-free season of at least 120 days from planting to harvest time. The plant requires uniform rainfalls during the growing season. Anise is very susceptible to sudden, extreme climatic changes from wet to dry periods. The temperature should be fairly uniform throughout the growing season, without excessive hot periods, particularly after rainfalls. Alternate rainy and dry periods, when the seed is near maturity, cause it to turn brown, thus greatly impairing the quality.

Soil.—A light, well drained, fertile or moderately rich, sandy loam is desirable for good growth of anise. The physical nature of the soil should be such that it lends itself well to pulverizing, yet retains moisture; then the small seed can be planted at a uniform depth, and cultivation of the small, young seedlings becomes feasible.

Planting and Cultivating.—According to Stockberger,[4] anise is grown from seed sown usually early in spring directly in the field, since the seedlings

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[1] See Willkie and Kolachov, "The Domestic Production of Essential Oils from Aromatic Plants," *Natl. Farm Chemurgic Council Bull.*, Columbus, Ohio (1940).

[2] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935).

[3] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941).

[4] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935).

are unfavorably affected by transplanting. The seeds, which should not be more than two years old, are sown thickly, about two to the inch, and covered ½ in. deep. As the plants develop very slowly, the seed should not be sown in weedy soil. When 2 to 3 in. high, the seedlings are thinned to stand 6 in. apart in the row. The rows may be 18 in. to 3 ft. apart, depending on the cultivation intended. An ounce of seed should sow a row 150 ft. long; about 5 lb. will plant an acre when the rows are 3 ft. apart. The plants must receive frequent and thorough cultivation throughout the growing season.

Crooks and Sievers[5] recommended planting the seed directly in the field in rows ranging from 18 to 30 in. apart, at the rate of about one to two seeds per inch. At this rate, approximately 5 to 10 lb. of seed would be required to plant one acre. In some European countries seed has been broadcast, but then weeds present a major difficulty in the harvest, and are likely to affect the market value of either seed or oil. When planting broadcast or with a small grain drill, where no cultivation is possible, the land must be fallowed and cleared of weeds.

Harvesting and Preparing for the Market.—The same authors[6] reported that in most anise producing countries the plants are pulled and stacked in the field to dry. In some cases the tops are cut off by hand, tied in bundles, and then stacked in conical piles with the fruiting heads toward the center, so that the seed continues to mature. The harvesting of anise presents quite a problem, due to progressive ripening of the umbels, as well as the uneven ripening of seed within each umbel. As a rule, the plant is either pulled or cut when all the seeds of the umbel are still green; then they may continue to mature after the bundles have been shocked with seed ends toward the center. In this way a considerable amount of seed continues to ripen, whereas those seeds that are mature do not discolor and shatter from the plant. In foreign countries threshing is accomplished usually by hand flailing, but there is no reason why this could not be done by machine.

Stockberger[7] stated that the plants will blossom about three months after planting, and a month later the seed should be sufficiently mature for harvesting. As soon as the tips of the seeds turn a grayish-green color they should be harvested; when left exposed to the weather, they quickly turn brown or black. The plants may be pulled by hand and piled, tops inward, in stacks about 6 ft. high, or they may be mowed and at once built up into cocks of the same height. After four or five days the seed will have

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[5] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941).

[6] *Ibid.*

[7] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935).

ripened; it should then be threshed out, thoroughly cleaned, and bagged for the market.

Yield of Seed per Acre.—Under favorable conditions, a yield of 400 to 600 lb. of seed per acre may be expected.

Consideration of Domestic Production.—Regarding the advisability of growing anise in the United States, Crooks and Sievers[8] arrived at certain conclusions, some of which apply not only to anise but to condiment plants in general. These authors believe that the Central and Eastern States offer good possibilities for anise production. Certain parts of California and western irrigated sections could probably be utilized, provided the amount of irrigation water is constant and the temperature not too high during the growing and maturing season.

Distillation.—Like most seed material, anise seed should be crushed prior to distillation. Chernukhin[9] found that ground anise seed yields 5 per cent more oil than whole seed does, and that with ground seed 10 to 15 per cent less steam and 25 per cent less time will be required for completion of the operation. The crushed seed must be distilled immediately to prevent any loss of oil by evaporation.

According to Gildemeister and Hoffmann,[10] the following yields of oil have been obtained from anise seed of various origin:

Origin of the Seed	*Yield of Oil* (%)
Bulgaria	2.4
Chile	1.9 to 2.6
Italy (Bologna)	3.5
Italy (Puglia)	2.7 to 3.0
Asia Minor	2.75
Macedonia	2.2
Moravia	2.4 to 3.2
Mexico	1.9 to 2.1
Eastern Prussia	2.4
U.S.S.R.	2.2 to 3.2
Spain	3.0
Syria	1.5 to 6.0
Thuringia	2.4

As has been mentioned before, origin is not wholly responsible for these differences in yield; they may be caused also by adulteration of the seed, or by impurities (spurious seed, earth, sand, and chaff) contained in the seed.

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[8] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941).

[9] *Masloboino Zhirovoe Delo* (1928), No. 5, 11. *Chem. Abstracts* **23** (1929), 3538.

[10] "Die Ätherischen Öle," 3d Ed., Vol. III, 502.

More recently, Fischer, Tornow and Proper,[11] using the Clevenger procedure, determined the volatile oil content in various types of anise seed of commercial origin and found that it varied from a minimum of 1.9 to a maximum of 3.1 per cent, the average being 2.29 per cent of oil.

Physicochemical Properties of Anise Seed Oil.—If solid material has separated, the oil must be warmed carefully at low temperature until completely liquefied; it must be thoroughly mixed before using. At a temperature above 20° C., anise oil is a colorless, strongly refractive liquid of characteristic, peculiar odor, and very sweet taste. According to Gildemeister and Hoffmann,[12] the oil congeals in the cold to a snow-white crystalline mass which begins to melt at 15° or higher and completely liquefies at 18° or 20°.

> "Under certain conditions the oil can be cooled considerably below its congealing point without solidifying, and can remain for a long time in this condition. However, a particle of dust, contact with an anethole crystal, a violent disturbance, or scratching of the inner surface of the vessel with a glass rod, causes sudden crystallization with an appreciable rise in temperature of the entire mass. The highest point on the thermometer immersed in the mass is known as the congealing point. Inasmuch as this is dependent on the anethole content of the oil, this congealing point is a valuable criterion in the evaluation of the oil. It lies between 15° and 19°, and in the case of good oils not below 18°."[13]

The other properties of anise oil vary within the following limits:

Specific Gravity at 20°	0.980 to 0.990
Optical Rotation	Slightly laevorotating up to −1° 50′
Refractive Index at 20°	1.552 to 1.559
Solubility	Soluble in 1.5 to 3 vol. of 90% alcohol

Since the congealing point of an anise oil gives a good indication of the anethole content, it may be used for a rapid estimation of the percentage of anethole contained in the oil. The following table was prepared by the laboratories of Fritzsche Brothers, Inc.,[14] New York, and is based on data obtained from known mixtures of purified anethole and purified limonene. The congealing point of the oil is determined in the usual manner (see Vol. I of this work, p. 253); the percentage of anethole is then computed from the table by interpolation.

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[11] *Bull. Natl. Form. Comm.* **13** (1945), 6.

[12] "The Volatile Oils," 2d Ed., trans. by E. Kremers, Longmans Green, London (1922), Vol. III, 343.

[13] *Ibid.*

[14] *Drug Cosmetic Ind.* **64** (1949), 620.

Congealing Point (°C.)	*Percentage of Anethole* (%)
+21.1	100
18.6	95
16.3	90
14.0	85
11.6	80
9.9	75
8.0	70
6.2	65
4.0	60
2.2	55

When exposed for long periods to the action of light or air, anise oil, especially in liquid form, slowly loses its capacity to crystallize, until finally it will no longer congeal. The specific gravity thereby increases, in some cases to above 1.0; the refractive index is reduced, and at the same time the oil becomes more readily soluble in 90 per cent alcohol.

When evaporating a sample of anise oil in a dish on a water bath, the oil will leave an evaporation residue amounting to several per cent. For an explanation, see the monograph on "Anethole" in Vol. II of this work, p. 508.

In the course of their above mentioned investigation of various anise seed oils, Fischer, Tornow and Proper[15] found the following properties:

	Specific Gravity at 25°/25°	*Refractive Index at 20°*	*Optical Rotation at 20°*
Minimum........	0.9827	1.5503	−0° 30′
Maximum........	0.9885	1.5560	+0° 30′
Average..........	0.9864	1.5539	0° 0′

Oil of anise seed contains from 80 to 90 per cent of anethole. For Spanish anise seed oil d'Argila[16] reported an anethole content ranging from 82 to 90 per cent.

Adulteration.—Anise oil is frequently adulterated with the lower priced star anise oil, which, according to the United States Pharmacopoeia, is also considered "anise oil." Yet, strictly from the flavoring viewpoint, anise oil (*Pimpinella anisum*) is undoubtedly superior to star anise oil (*Illicium verum*), the latter having a somewhat harsher odor.

Other adulterants are synthetic anethole (made from pine oil) and fennel oil. The latter can be detected by a change in the optical rotation, fennel oil being dextrorotatory.

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[15] *Bull. Natl. Form. Comm.* **13** (1945), 6.

[16] *El Monitor de la Farmacia* **54** (1948), 125. Through *Perfumery Essential Oil Record* **39** (1948), 244.

Chemical Composition.—The chemistry of anise oil is rather simple, the oil consisting mainly of two isomeric compounds of the empirical molecular formula $C_{10}H_{12}O$, namely anethole and methyl chavicol. They were identified by the Schimmel chemists,[17] and by Bouchardat and Tardy: [18]

Anethole. Eighty to 90 per cent of anise oil consists of this phenol ether which is solid at room temperature. Anethole is white, crystalline, of intensely sweet anise-like odor and flavor. At 22.5° it melts to a colorless, optically inactive, strongly refractive liquid.

Methyl Chavicol. This isomer of anethole has a slight anise-like odor but not the sweet flavor of anethole. Methyl chavicol is liquid at room temperature and, like anethole, optically inactive.

p-Methoxyphenylacetone (Anisketone). Bouchardat and Tardy,[19] and later Tardy [20] found in anise oil a ketone, the odor of which is somewhat reminiscent of bitter almond oil; they named it anisketone. Its formula and properties correspond to those of *p*-methoxyphenylacetone as obtained by Béhal and Tiffeneau.[21]

Anisketone is a liquid b. 263°, d_0 1.095, semicarbazone m. 182°.

The first fractions of anise oil contain acetaldehyde, some sulfur-containing compounds of disagreeable odor and perhaps very small quantities of terpenes. Thus, Rutovski and Leonov [22] reported about the presence of *d*-α-pinene, α-phellandrene, dipentene, camphene, and also of *d*-fenchone in Russian anise oil. However, their oils had quite abnormal physicochemical properties and were perhaps impure, or distilled from material other than seed of true *Pimpinella anisum* L. So far as fenchone is concerned, Tardy [23] and the Schimmel chemists [24] proved that pure Russian anise seed oil contains no fenchone.

Use.—Oil of anise is used widely in the flavoring of culinary preparations, beverages, confectioneries, pharmaceuticals, tooth pastes, and mouth washes.

Medicinally, the oil is occasionally employed to stimulate peristalsis in cases of colic.

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[17] *Ber. Schimmel & Co.*, October (1895), 6. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. I, 604.

[18] *Compt. rend.* **122** (1896), 624.

[19] *Ibid. Bull. soc. chim.* [3], **15** (1896), 612.

[20] Thèse, Université de Paris (1902), 11. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 506.

[21] *Bull. soc. chim.* [3], **25** (1901), 275. *Compt. rend.* **141** (1905), 597.

[22] *Trav. Sci. Inst. Chim. Pharm. Moscow* (1924), No. 10, 64. *Chem. Abstracts* **22** (1928), 2437. *Trav. Sci. Inst. Chim. Pharm. Moscow* (1928), No. 4, 16. *Chem. Abstracts* **23** (1929), 239.

[23] Thèse, Université de Paris (1902), 11. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 506.

[24] *Ber. Schimmel & Co.*, April (1896), 8.

Suggested Additional Literature

L. Rosenthaler, "Microchemical Characterization of Essential Oils," *Pharm. Acta Helv.* **1** (1926), 117.

N. Ivanov and V. F. Grigoreva, "Aromatic Oils of Germinating Anise Fruits which Undergo No Alteration," *Biochem. Z.* **202** (1928), 284.

T. G. Kovalev and V. V. Illarionov, "Dialectric Constants of Ethereal Oils in Relation to Their Constitution and Their Constituents," *J. prakt. Chem.* **135** (1932), 305.

B. Samdahl, "Toxicity of Old Samples of Anise Oil," *Norsk. Farm. Tids.* **40** (1932), 66. *Quart. J. Pharmacol.* **5** (1932), 588.

Wilson Baker and G. F. Flemons, "Dimerides of Anethole," *J. Chem. Soc.* (1948), 1984. *Chem. Abstracts* **43** (1949), 2180.

OIL OF ASAFOETIDA

Essence d'Ase Fétide *Aceite Esencial Asafetida* *Asantöl*
Oleum Asae Foetidae

Botany, Origin, and Description.—Asafoetida is the dried latex or gum oleoresin exuded from the rhizomes or taproots of several *Ferula* species, notably *F. asafoetida* L., *F. foetida* (Bunge) Regel, and *F. alliacea* Boiss. As Small[1] has pointed out, apart from *F. foetida*, the botanical sources of commercial asafoetida are still uncertain. The plants are native to western Afghanistan and eastern Iran (Persia) where, in early summer, they cover the otherwise arid and barren plains and high plateaus. The large cabbage-like tops of the plants are relished raw by the natives.

Collection of the gum lasts from the middle of April to the end of July. For this purpose the plants, prior to the flowering stage, are cut above the ground, the rhizomes or taproots thus being decapitated and laid bare. Every third day the white latex exuded from the rhizomes is collected. On exposure to air the soft white exudation turns brown, hard, and somewhat brittle. After three months the rhizomes lose their vitality and no longer yield any latex.

According to Igolen,[2] asafoetida is gathered by laying bare a part of the taproot, and by making successive incisions at the junction of the stalk and the taproot. This causes the flow of a milky sap which rapidly

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[1] *Food* **12** (1943), 125, 154.

[2] *Parfums France* **14** (1936), 267.

thickens. With three incisions certain plants will furnish as much as 1 kg. of asafoetida.

The commercial drug reaches Europe and America via Persian Gulf ports and Bombay. There exist at least two distinct types, one turning red and brownish on exposure of the fresh surface to the air, and the other type remaining white or pale buff. Asafoetida possesses a most powerful, pungent, and obnoxious alliaceous odor; hence its common name "devil's dung." The drug contains from 3 to 20 per cent of volatile oil which can be recovered by steam distillation, about 25 per cent of gum and 40 to 64 per cent of resin. The latter appears to consist of asaresinotannol both free and combined with ferulic acid. Umbelliferone seems to be present in combined state.

Physicochemical Properties of Asafoetida Oil.—Harrison and Self[3] suggested the following properties for oil of asafoetida:

Specific Gravity at 15.5°	0.915 to 0.993
Optical Rotation	+10° 58′ to −17° 3′
Refractive Index at 20°	1.4942 to 1.5259
Sulfur Content	8.9 to 31.4%

Examining 41 lots of asafoetida, Clevenger[4] obtained yields of volatile oil ranging from 7.5 cc. to 12 cc. per 100 g. of oleoresin. The physicochemical properties of the volatile oils (from Bombay asafoetida) were:

Specific Gravity at 20°/20°	0.906 to 0.973
Optical Rotation at 20°	−9° 0′ to +9° 18′
Refractive Index at 20°	1.493 to 1.518
Sulfur Content	15.3 to 29.0%

The sulfur content was determined by Clevenger:[5]

Place approximately 0.5 g. of the volatile oil, weighed accurately, into a 150 cc. acetylization flask. Through the condensing tube add 5 cc. of water, then 5 cc. of concentrated nitric acid. Heat gently on the steam bath until the reaction is started, then set aside under a hood until the reaction has practically subsided. Add 3 g. of powdered potassium bromide through the condenser tube, then heat on the steam bath for 20 min. and cool. Add 10 cc. of 50 per cent sodium hydroxide solution through the condensing tube. Disconnect the condenser from the flask, transfer the contents to a nickel crucible, carefully evaporate to dryness and ignite. Dissolve the residue in water, remove nitrous and nitric acids by evaporation with hydrochloric acid and determine the sulfur as barium sulfate.

The sulfur-containing constituents of asafoetida are primarily responsible for the disagreeable garlic-like odor of the drug and its volatile oil.

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[3] *Pharm. J.* **88** (1912), 205; **89** (1912), 139. *Chemist Druggist* **80** (1912), 269; **81** (1912), 202. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 550.

[4] *J. Am. Pharm. Assocn.* **21** (1932), 668.

[5] *Ibid.*

Chemical Composition of Asafoetida Oil.—The chemical composition of asafoetida oil was investigated by Semmler,[6] later by Mannich and Fresenius.[7]

The presence of the following constituents has been reported:

Pinene(?). d_{10} 0.8602, α_D +32° 30′. The terpene yielded a liquid dibromide $C_{10}H_{16}Br_2$.

Another Terpene(?). This terpene was present only in small quantities and gave a solid tetrabromide $C_{10}H_{16}Br_4$.

The higher boiling fractions contained mainly organic disulfides.

Secondary Butylpropenyl Disulfide. Semmler[8] reported that the crude oil contains 45 per cent of a disulfide b_9 83°–84°, d_{15} 0.9721, α_D −12° 30′.

Years later Mannich and Fresenius[9] investigated a corresponding fraction of asafoetida oil and obtained 40 per cent of a fraction b_{10} 82°–84°. They confirmed the empirical molecular formula $C_7H_{14}O_2$ suggested by Semmler and proved that this compound, the main constituent of asafoetida oil, is secondary butylpropenyl disulfide.

A Disulfide(?) $C_8H_{16}S_2$. b_9 92°–96°.

A Disulfide(?) $C_{10}H_{18}S_2$. b_9 112°–115°.

A Disulfide $C_{11}H_{20}S_2$. b_9 126°–127°, d_{14} 1.0121, α_D −18° 30′.

Semmler[10] reported that the oil contains 20 per cent of this disulfide which is mainly responsible for the disagreeable odor of asafoetida oil.

A Trisulfide(?) $C_6H_{10}S_3$. This compound b_{16} 112°–122°, d_{15} 1.0845 is probably diallyl trisulfide.

A Compound(?) $(C_{10}H_{16}O)_n$. b_9 133°–145°, d_{22} 0.9639, α_D −16° 0′.

Crude asafoetida oil contains about 20 per cent of this compound which yields cadinene when treated with sodium.

Use.—Oil of asafoetida may be used most sparingly for the flavoring of all kinds of food products, particularly table sauces, to which it lends distinct effects in conjunction with onion and garlic. In India gum asafoetida, as such, is widely employed as a condiment; in Iran (Persia) the natives rub asafoetida on warmed plates prior to placing meat on them.

The drug has also been recommended in pharmaceutical preparations as a local stimulant to the mucous membranes—for example, of the alimentary tract.

The volatile oil has not attained any commercial importance because the flavoring and pharmaceutical industries employ chiefly alcoholic tinctures of the gum, or the alcohol soluble oleoresin.

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[6] *Arch. Pharm.* **229** (1891), 1. *Ber.* **23** (1890), 3530; **24** (1891), 78.

[7] *Arch. Pharm.* **274** (1936), 461.

[8] *Ibid.* **229** (1891), 1. *Ber.* **23** (1890), 3530; **24** (1891), 78.

[9] *Arch. Pharm.* **274** (1936), 461.

[10] *Ibid.* **229** (1891), 1. *Ber.* **23** (1890), 3530; **24** (1891), 78.

OIL OF CARAWAY

Essence de Carvi *Aceite Esencial Alcaravea* *Kümmelöl*
Oleum Carvi

Botany.—*Carum carvi* L. is a hapaxanthic or biennial herb. During the second year it develops a slender stem bearing alternate, pinnate, or bipinnate leaves with narrow, pointed terminal segments.

The infloresecence consists of a long stalked, compound umbel, with small white flowers appearing in May and June. The fruits, commercially called seeds, are oblong, laterally compressed, dark brown cremocarps, which ripen in August during the second year of growth. They possess a characteristic, aromatic odor, and a warm, sweetish, spicy taste. For this reason, the dried seed is widely employed for flavoring bread, cakes, confectionery, cheeses, and all kinds of food products. Odor and flavor of the seed are due to the essential oil, which can be isolated by steam distillation.

Habitat and Range.—*Carum carvi* L. is a native of Europe and Asia, where it grows wild in meadows and pastures; it has also become naturalized in the North and Northwest of the United States. The fruit of wild caraway, although inferior in appearance, is said to yield more essential oil than that of the cultivated plant. Since available quantities of wild seed are not nearly sufficient for market demands, caraway is widely cultivated in many parts of the temperate zones—in Holland, the U.S.S.R., Hungary, Poland, Denmark, Germany, Norway, and lately also in the United States. For many years Holland has been the world's principal source of caraway seed and oil. This type of seed is the best in regard to quality; the African and Near East varieties have a somewhat inferior aroma. About 10 per cent of Holland's total caraway seed production is used for distillation.

DUTCH CARAWAY SEED OIL

Holland, with its proximity to the sea and fertile soil, is eminently suited for the production of caraway seed. On rich soil caraway grows even in northern countries like Norway, but the more temperate and humid climate of Holland seems to be more favorable, especially during winter. First cultivated in Holland around 1850, caraway has grown from a humble beginning into Holland's second important crop, flax being the leading one.

Caraway seed has become a speculative article, undergoing considerable price variations, which depend upon the acreage planted, yield per hectare, weather conditions, appearance of the seed and yield of oil. It is traded as a regular commodity on the Amsterdam Produce Exchange and other exchanges of the world's capitals, according to the so-called "Amsterdam conditions," which specify prime seed free from impurities and containing a certain percentage of essential oil.

The average yearly crop of Dutch caraway seed amounts to approximately 130,000 bags of 1 cwt. each (1 cwt. = about 50 kg.). Total production in Holland has ranged from only 4,500 bags in 1919 to almost 290,000 bags in 1924. About 6,500 hectares were under cultivation in 1935. In years of abundant caraway production, such as 1924, 32 bags per hectare were harvested; but as few as 16 bags may be harvested in years of abnormal weather conditions or when insect pests and ergot (*Secale cornutum*) do great damage, as happened in 1923 and 1927.

Toward the end of World War II and during the retreat of the German armies, wide sections of Holland's caraway "belt" were flooded with water from the North Sea and rendered useless for years to come. However, great efforts have been made to reclaim this land, and to re-establish the valuable caraway crop for export.

Years ago the Dutch farmers cultivated caraway most unscientifically, a high yield of seed per acre being considered of paramount importance. The harvest, however, was often considerably reduced by the caterpillar of the caraway moth (*Depressaria nervosa*), by the presence of weeds (ergot), and, most of all, by seed shattering caused by premature double-splitting. This last feature, particularly, caused tremendous losses during spells of hot weather: in the course of bundling and transporting the cut herb to the barns for threshing, a great amount of seed would drop to the ground and be lost. Thanks to the work of R. J. Mansholt and that of K. Zijlstra [1] on plant selection, a caraway variety was developed possessing these advantages:

1. Uniform seed ripening at about the same period.
2. The seed does not easily drop from the stalks, which feature permits harvest of the plant even on hot days and during noon hours.
3. A high content of volatile oil particularly rich in carvone.

Producing Sections in Holland.—The most important areas of caraway cultivation in Holland are in the provinces of Groningen, Noord Holland, Zeeland, Zuid Holland and Noord Brabant. There, *Carum carvi* exclusively is cultivated; the wild growing *Carum verticillatum* and *Carum bulbocastanum* are found but rarely in the provinces of Limburg and Noord Brabant.

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[1] *Ber. Schimmel & Co.*, October (1915), 20; (1927), 59.

Planting and Cultivating.—Sown at the end of March or beginning of April, the plant germinates within one to two weeks, and matures in about fifteen months. Caraway being a biennial, the seed ripens only in the second year after planting. Peas, mustard, beans, white clover, and flax serve as cover crops. Caraway fits well into the rotation of crops and into the agricultural program of the Dutch farmers.

Fertile, well-tilled soil is favorable for growing caraway. The rows are 12 to 16 in. apart; 5 to 8 lb. of seed will plant one acre. The plantation must be weeded thoroughly, as the tender young plants are easily suffocated and crowded out. At the beginning of winter some farmers cover their plantings slightly; although this is not absolutely necessary, it does protect the young plants against frost damage. With the arrival of spring the soil is loosened and carefully weeded. The plants develop rapidly, blossom in May, and ripen early in July. The seed must be harvested when its color changes to a dark brown; otherwise it will drop off the stalks, since fully matured seed splits into two mericarps. It is advisable, therefore, to harvest a little early rather than too late.

Harvesting.—In the old days the plants were cut with sickles, then bundled to be dried and transported to the barns for flailing. This caused a great amount of seed shattering. Today the harvesting is done almost entirely with modern machines, preferably in the early morning when the dew is still fresh on the plants and when there is less danger of seed loss. Sunny days are chosen for harvesting because the seed then contains more oil.

After being cut the plants are shocked up and left in the fields for a week or ten days until dried. Threshing is now done in the fields. The plant cocks are carefully hauled to the threshing machines on triangular planks and thrown into the threshers. Any shattered seed is collected on large tarpaulins spread around the machines. The threshing machines separate the seed automatically into four bags, containing:

1. Large sized fruit.
2. Small sized fruit.
3. Chaff.
4. *Secale cornutum* and other impurities.

The threshing machine is usually combined with an automatic bale-presser. The hay bales are left in the field until the whole harvest is finished. Immediately after cropping the land is plowed and prepared for the sowing of wheat or other crops.

Seed Trade.—The Dutch growers sell their seed through grain merchants to local distillers or to exporters who supply the world's most important caraway users, viz., the United States, Great Britain, and continental

Europe. Frequently, the prosperous and independent Dutch farmers prefer to hold their seed, sometimes for several years, until prices are sufficiently attractive. In the meantime, they grow other crops such as wheat, barley, peas, etc., thus causing a considerable diminution of caraway production. This feature, together with weather conditions, insect pests, etc., makes the trade in caraway seed a quite speculative one.

Yield of Oil.—The essential oil content of Dutch caraway seed ranges from 3 to 6 per cent, averaging 4 per cent. It is said that sunny, dry weather during seed maturation diminishes the content of oil, but the oil is then high in carvone and correspondingly low in terpenes. On the other hand, cool, damp weather increases the oil content, but the oil is low in carvone and other oxygenated compounds. This variation might be caused by photochemical forces which transform terpenes into oxygenated compounds. It is also possible that during sunny, hot weather, some of the more volatile oil constituents, and particularly the terpenes, evaporate, so that the content of the less volatile, oxygenated compounds increases.

Kofler[2] reported that the volatile oil content of caraway seed increases during storage, but Kofler's contention could not be confirmed by Biele,[3] or by Sandermann.[4] Such an increase is only apparent, and caused exclusively by evaporation of moisture and loss of weight during drying and storing of the seed.

Distillation of Caraway Seed.—To attain a good yield and a high quality of oil, only well matured seed must be employed. The seed is crushed between rotating cylinders and immediately charged into the still to avoid any evaporation of oil. The stills should be equipped with perforated grids, on which the crushed seed material is spread evenly to permit complete penetration by live steam. Distillation of one charge lasts from 6 to 8 hr. In past years it was customary to distill the uncrushed seed, although the yield of oil is somewhat inferior to that from crushed seed. The exhausted seed was then dried and sold to the Far East for use in temple incense or as an adulterant of regular seed. Exhausted seed can be identified under the microscope by its shriveled appearance and by the presence of ruptured cells on the surface.

Exhausted dried seed contains 20 to 23 per cent of crude proteins and 14 to 16 per cent of fat; thus, it may serve as cattle feed.

HUNGARIAN CARAWAY SEED OIL

Although the bulk of caraway originates from Holland and the U.S.S.R., limited quantities are produced also in Hungary and other Central Euro-

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[2] *Pharm. Ztg.* **81** (1936), 931. *Ber. Schimmel & Co.* (1937), 122.

[3] *Acta Pol. Pharm.* No. 1, Pt. II (1938). *Ber. Schimmel & Co.* (1939), 42.

[4] *J. prakt. Chem.* [2], **151** (1938), 160.

pean countries. There caraway grows wild in localities with a humid climate, particularly along the Austrian-Hungarian frontier. Considerable quantities occur in meadows, where the plant is collected by the peasant population for use as a condiment.

After World War I, caraway cultivation in Hungary was greatly increased, until 200 to 350 hectares were planted yearly. In 1937, however, only about 50 hectares were under cultivation. Caraway can be grown in almost every part of Hungary on loam soil, but best results are obtained in a humid climate. Hungarian producers claim that their plants can withstand winter frosts without damage.

Seed imported from Holland is used for planting, but the resulting seed remains relatively small and the yield of oil is inferior. Seed grown in Hungary from Dutch seed, on large-scale distillation, yields from 3.30 to 4.60 per cent of essential oil, whereas wild growing seed from Western Hungary, half the size of the Dutch seed, gives from 5.00 to 5.30 per cent of oil. An attempt was made, in Hungary, to cultivate wild caraway in the hope of obtaining seed of larger size without losing the higher oil content of the wild growing type; the result, however, was neither a decrease in the yield of oil nor an increase in the size of the seed.

Hungarian caraway oil from cultivated seed possesses normal physicochemical properties very similar to those of the Dutch product. The carvone content of the oil from wild seed is about 56 per cent.

To summarize, caraway is now cultivated in Hungary on a very limited scale only, but an increase of the acreage has been planned.

Caraway also grows wild in a section of the Carpathian Mountains called the "Wooded Carpathians." This territory, much disputed over by Hungary and Czechoslovakia, was finally annexed by the U.S.S.R. at the end of World War II. On distillation, the seed of this wild growing caraway yielded from 4 to 8.67 per cent of oil, whereas seed of wild caraway from Transylvania yielded 3.92 to 5 per cent of oil. The quality of these oils was entirely satisfactory.[5]

NEAR EAST AND NORTH AFRICAN CARAWAY SEED OILS

The author carried out distillation experiments with North African and Near East caraway seed and obtained oils of low carvone content (15 to 37 per cent). In regard to flavor, they did not compare with Dutch caraway seed oils.

The yield varied from 0.4 to 1.0 per cent, which would make commercial production of these oils relatively too costly, especially in view of their inferior quality.

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[5] Private communication of Dr. Jules de Bittera, Budapest.

American Caraway Seed Oil

Climatic and Soil Conditions.—According to Crooks and Sievers,[6] caraway grows in a wide variety of soils, but probably best on an upland, fertile clay. The cultivated plant is usually a hardy biennial. It will withstand quite a severe continental climate, and mature seed even in a rather short growing season. The plant is particularly adapted to the cool climate of temperate regions; it does not appear so well suited to the warm climate of the South. The most critical climatic factor occurs during the harvest period, when rainfall or wind may result in complete loss of the crop.

In irrigated regions of the western and southwestern United States, the possibility of making late summer or fall plantings should be considered. Then it might be possible to harvest about eleven months after planting, instead of waiting fourteen months, as is required when caraway is planted at the usual time (early spring).

Planting, Cultivating and Harvesting.—According to Stockberger,[7] soil of a somewhat clayey nature, containing a fair proportion of humus and valuable plant food, is particularly suited to caraway; but the plant generally grows well in any good upland soil which will produce fair crops of corn or potatoes.

Early in spring the seed should be sowed in drills about 16 in. apart, from 6 to 8 lb. of seed being required per acre. Frequent shallow cultivation throughout both growing seasons keeps the soil mellow and free of weeds; a weedy crop, at harvest time, usually means a product of inferior quality.

The moment the first seeds ripen (usually in June of the second year), the crop is ready for harvesting. The plants are cut with a mower and left in the swath until almost dry; they may subsequently be built up into small cocks or brought in from the field for the curing to be finished in a barn loft. If the seeds shatter extensively on handling in the field, the crop should be hauled in tight wagons. Drying completed, the seeds are threshed out, cleaned, and stored in bags of about 100 lb. capacity.

Crooks and Sievers[8] recommend drilling the seeds about ½ in. deep in rows 16 in. apart. Weedy soil requires hand weeding. Sowing broadcast or in rows too close for cultivation would prevent the adequate control of weeds.

Caraway is usually grown as a biennial, by planting in early spring and harvesting in June of the second year. As the seed attains final maturity in the curing process, there is hazard of an excessive amount of shattering

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[6] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.,* July (1941), 9.

[7] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No 663 (1935), 16.

[8] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.,* July (1941).

caused by handling of the plants. For this reason, they should be cured in barns or open sheds where the shattered seed can be collected. Seed that does not shatter from the plant after the drying process can easily be flailed by hand or threshed in an ordinary grain thresher.

Yield of Seed per Acre.—A yield of 800 to 1,200 lb. of seed may be expected under favorable conditions. However, this does not represent an annual yield, because a planting made in early spring does not yield a crop until the second June.

Consideration of Domestic Production.—Large areas in the North Central States, the Northeastern States, and the Pacific Northwest seem well suited for this crop. Since the harvest takes place usually in June, it is important to have a good curing season, with a minimum of rainfall. For this reason, the Pacific Northwest has possibilities, particularly in dry, irrigated regions. For the same reason, it would be hazardous to attempt cultivation in the Atlantic Coast States and in the Central States. Certain limited regions of the Mountain States, now under irrigation, probably offer the best possibilities.

Crooks and Sievers[9] enumerate some factors in favor of, and others against, domestic production of caraway seed.

GENERAL

Physicochemical Properties of Caraway Seed Oil.—According to Gildemeister and Hoffmann,[10] the physicochemical properties of caraway seed oil vary within the following limits:

Specific Gravity at 15°	0.907 to 0.919
Optical Rotation	+70° 0′ to +81° 0′
Refractive Index at 20°	1.484 to 1.488
Carvone Content (Neutral Sulfite Method)	50.0 to 60.0%
Solubility	Seldom soluble in 70% alcohol; soluble in 2 to 10 vol. of 80% alcohol, sometimes with faint opalescence; clearly soluble in equal volumes of 90% alcohol

Genuine oils imported from Holland and the U.S.S.R., and analyzed in the laboratories of Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 25°/25°	0.904 to 0.909
Optical Rotation at 25°	+74° 20′ to +78° 15′
Refractive Index at 20°	1.4858 to 1.4879

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[9] *Ibid.*

[10] "Die Ätherischen Öle," 3d Ed., Vol. III, 487.

Carvone Content (Neutral Sulfite Method)	51 to 57.6%
Solubility at 25°	Soluble in 2 to 4 vol. of 80% alcohol; clearly soluble in more alcohol

Oils distilled from imported Dutch caraway seed by Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 25°/25°	0.905 to 0.911
Optical Rotation at 25°	+74° 10′ to +76° 48′
Refractive Index at 20°	1.4868 to 1.4878
Carvone Content (Neutral Sulfite Method)	53 to 59%
Solubility at 25°	Soluble in 1.5 to 3.5 vol. of 80% alcohol; clearly soluble in more alcohol

The specific gravity and the refractive index stand in direct relation to the carvone content, the optical rotation in inverse relation to the carvone content. A normal caraway seed oil should contain not less than 50 per cent, by volume, of carvone.

When exposed to light and air for a certain length of time, oil of caraway seed, like carvone, assumes a yellowish tint. The oil becomes more viscous and the specific gravity increases.

Distilling caraway seed grown during the summer of 1943 by A. E. Slessman in Fremont, Ohio, Fritzsche Brothers, Inc., obtained 4.0 per cent of a normal oil which had these properties:

Specific Gravity at 25°/25°	0.910
Optical Rotation at 25°	+75° 24′
Refractive Index at 20°	1.4873
Carvone Content	59.7%
Solubility at 25°	Soluble in 1 to 1.5 vol. and more of 80% alcohol

The oil possessed a clean, full caraway odor.

Analysis of Caraway Oil.—Most important in evaluating caraway oil is the determination of the carvone content, by volume, according to the neutral sulfite method, which gives very satisfactory results. Details will be found in Vol. I of this work, p. 283.

This method is generally preferred over the hydroxylamine hydrochloride method. The latter requires 24 hr. for completion, using a 0.5 g. sample, and should be employed only if a small quantity of oil is available, insufficient to carry out the neutral sulfite method.

Determination of the specific gravity, solubility in 80 per cent alcohol, optical rotation, and refractive index, in addition to the carvone content, usually suffices for evaluating a caraway oil.

According to Gildemeister and Hoffmann,[11] the percentage of carvone in oil of caraway seed can be calculated quite easily through a simple equation by figuring 0.964 for the specific gravity of carvone and 0.850 for the specific gravity of limonene (more exactly, for all the constituents besides carvone). The equation reads as follows:

$$x = \frac{(a - b) \cdot 100}{c}$$

wherein a = specific gravity of oil to be analyzed;
b = specific gravity of limonene (0.850);
c = difference in specific gravity of carvone (0.964) and limonene (0.850);
x = percentage of carvone.

However, determination of the carvone content by the sulfite method is more exact.

Adulteration.—Additions of terpenes (chiefly *d*-limonene), obtained as by-products from the extraction of carvone, or from orange oil, are sometimes encountered. Foreign constituents should be looked for, particularly in the noncarvone portion of the oil obtained in the neutral sulfite assay. However, the minimum requirement of 50 per cent of carvone in normal oils prevents substantial additions of such material. In order to compensate for the deficiency of carvone and for the lowered specific gravity of adulterated oils, other ketones, such as piperitone, or certain aromatics, benzyl alcohol, for example, are sometimes employed. They can be identified by their odor, or by fractionating the carvone portion of the oil isolated in the sulfite assay.

Oil of Cohobation.—When cohobating the distillation waters of caraway seed, an oil with a specific gravity of 0.935 to 0.945 is obtained. It contains a high percentage of water soluble, oxygenated compounds, particularly carvone (75 to 80 per cent). This so-called "water-oil" has a poor odor and flavor and should not be mixed with normal seed oil. It may, however, be used for the extraction of carvone, which can be isolated easily.

Caraway Oil from Immature Seed.—Sandermann[12] obtained from flowering plants an oil with these properties:

Specific Gravity at 20°	0.863
Specific Optical Rotation	+78° 0′
Carvone Content	7.0%
Limonene Content	About 75%

This oil contained azulene and cadinene in the fraction b_6 130°–135°. Cadinene, according to Sandermann, is not present in caraway seed oil; it

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[11] *Ibid.*, 493.

[12] *J. prakt. Chem.* [2], **151** (1938), 160.

occurs only in the stalks and leaves and amounts to about 50 per cent of the oil distilled from those plant parts.

According to Sandermann, oil of caraway is formed in the seed quite some time before the harvest and does not undergo marked changes thereafter. This is especially true in regard to the carvone content, which reaches its maximum before full seed maturity.

Distilling green fruit, shortly after the flowering stage, Sandermann[13] obtained an oil with the following properties:

Specific Gravity at 20°	0.896
Specific Optical Rotation	+71° 0′
Carvone Content	47.0%
Limonene Content	Much less than in the oil from the flowering plants (see above)

The same author contended that oxidation in the caraway plant converts more than 50 per cent of limonene into carvone, within two weeks, and that reducing forces, simultaneously at work, are responsible for the presence of dihydrocarveol and dihydrocarvone.

The findings of Sandermann are partly in contradiction to those of Schimmel & Co.,[14] who years ago proved by large-scale distillation tests that the carvone content of caraway seed oil depends upon the state of plant maturity, and that it is highest in oils distilled from fully matured seed.

Caraway Chaff Oil.—Occasionally the chaff resulting as by-product in the threshing and winnowing of the seed is submitted to steam distillation. The oil resulting should not be added to regular caraway seed oil, because it has a harsh and, therefore, inferior odor and flavor. It can, however, be employed as a lower grade oil for technical purposes, such as the scenting of soaps.

Chemical Composition of Caraway Seed Oil.—The first investigations of the chemistry of caraway seed oil date back more than a century, when Voelckel[15] found that it contains an oxygenated compound (then called carvol) and an oxygen-free compound (then called carvene). Their actual nature was recognized much later by Wallach[16] who identified:

Carvone. A good oil contains from 50 to 60 per cent of carvone, which is the most important constituent and the principal carrier of the characteristic odor of caraway oil.

d-Limonene. The other main constituent of caraway seed oil is a terpene b. 175° which was originally named carvene, but later identified as *d*-limonene. Tetrabromide m. 104°–105°.

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[13] *Ibid.*

[14] *Ber. Schimmel & Co.*, October (1896), 47.

[15] *Liebigs Ann.* **35** (1840), 308.

[16] *Ibid.* **277** (1893), 107.

According to Gildemeister and Hoffmann,[17] the odor of this terpene fraction differs from that of a *d*-limonene derived from citrus oils, because of the presence of small quantities of carvone in "carvene." Such carvone can be removed with hydrazine in acetic acid solution and by shaking the terpene subsequently with a dilute solution of potassium permanganate.

Aside from the above two main constituents, oil of caraway seed, according to the Schimmel chemists,[18] contains small quantities (1 to 2 per cent) of other compounds:

A Base of Narcotic Odor. Its nature has not yet been established. Present only in traces. Oil of anise seed (*Pimpinella anisum*) contains similar bases.

Dihydrocarvone. $b_{735.5}$ 221°, d_{15} 0.9297, α_D $-16°\ 18'$, n_D^{20} 1.47107.
Identified as dibromide $C_{10}H_{15}BrO \cdot HBr$, m. 69.5°-70.5°, and as oxime m. 89°.

Dihydrocarveol. Present in the fraction b_6 94°-97.5°. After purification through the benzoyl compound, the alcohol had these properties: b_{7-8} 100°-102°, d_{15} 0.9368, α_D $-6°\ 14'$, n_D^{20} 1.48364.

Carveol. Also occurs in caraway seed oil, according to Blumann and Zeitschel.[19]

Acetaldehyde, Methyl Alcohol, Furfural, and Diacetyl. Their presence in the distillation waters was proved by the Schimmel chemists.[20]

In the high-boiling fractions of caraway oil Schmidt [21] recently identified:

d-Dihydrocarveol. d_4^{15} 0.924, $[\alpha]_D$ $+33°\ 30'$, n_D^{20} 1.4780; dinitrobenzoate m. 123°, $[\alpha]_D$ $+54°\ 30'$.

l-Dihydrocarveol. The *l*-dihydrocarveol identified years ago by Schimmel & Co. was shown to be a mixture of three stereoisomers, the preparation of which in pure form afforded an excellent clue to the structural relationship of the various members of the dihydrocarveol series.

l-Neodihydrocarveol. d_4^{15} 0.930, $[\alpha]_D$ $-32°\ 30'$, n_D^{20} 1.4802; *p*-nitrobenzoate m. 107°, $[\alpha]_D$ $+15°\ 0'$; dinitrobenzoate m. 138°, $[\alpha]_D$ $+7°\ 0'$.

l-Isodihydrocarveol. m. 38°-39°, d_{15} 0.942 (superfused), $[\alpha]_D$ $-28°\ 0'$ (in alcohol), n_D^{20} 1.4816 (superfused); phthalate m. 104°-105°, $[\alpha]_D$ $-16°\ 36'$ (in alcohol); *p*-nitrobenzoate m. 45°-46°, $[\alpha]_D$ $-19°\ 0'$ (in chloroform).

d-Perillyl Alcohol. Characterized by oxidation to *d*-perillaldehyde, which yielded a semicarbazone m. 198°-200°.

d-Dihydropinol. b_{750} 186°-188°, d_{15} 0.9284, α_D $+104°\ 0'$, n_D^{20} 1.4621.

Use.—Caraway seed oil is used in oral preparations to overcome an unpleasant odor or taste. When employed for the scenting of soaps, the oil gives characteristic, full notes.

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[17] "Die Ätherischen Öle," 3d Ed., Vol. III, 489.
[18] *Ber. Schimmel & Co.*, April (1905), 50.
[19] *Ber.* **47** (1914), 2628.
[20] *Ber. Schimmel & Co.*, October (1899), 32.
[21] *Chem. Ber.* **83** (1950), 193.

The main use of caraway seed oil, however, is in the flavoring of all kinds of food products, e.g., meats, sausages, canned goods; it is employed in pickle compounds, confectionery; and in liqueurs of the kümmel type.

Oil of caraway seed is considered a mild stomachic and carminative.

SUGGESTED ADDITIONAL LITERATURE

E. Kopp, "Roumanian Caraway Oil," *Pharm. Zentralhalle* **68** (1927), 212. *Chem. Abstracts* **21** (1927), 1890.

A. Jermstad and O. Ostby, "Norwegian Caraway Oil," *Pharm. Zentralhalle* **75** (1934), 33. *Chem. Abstracts* **28** (1934), 5925.

M. Janicsek, "Some Hungarian Essential Oils," *Kiserletügyi Közlemenyek* **37** (1934), 147. *Chem. Abstracts* **29** (1935), 1938.

L. Kofler and G. V. Herrensschwand, "Estimation of Essential Oils in Drugs, and the Oil Content of Peppermint, Sage, Fennel and Caraway," *Arch. Pharm.* **273** (1935), 388. *Chem. Abstracts* **30** (1936), 568.

A. Bänninger, "Investigation of the Influence of Mountain Climates on the Content of Active Components of Pharmaceutical Plants," *Ber. schweiz. botan. Ges.* **49** (1939), 239. *Chem. Abstracts* **35** (1941), 6735.

L. Wilson Greene, "Chemical Microscopy of Essential Oils," *Perfumery Essential Oil Record* **30** (1939), 309.

"Volatile Oils of Anise, Caraway, Celery Fruit, Coriander, Cubebs and Fennel," Report of the American Pharmaceutical Association Laboratory, *Natl. Form. Comm. Bull.* **7** (1939), 231.

J. F. Clevenger, "Volatile Oils of Anise, Caraway, Celery Fruit, Coriander, Cubeb and Fennel," *Natl. Form. Comm. Bull.* **7** (1939), 293.

S. Sabetay, "Procedure for the Determination of Essential Oil in Drugs and Spices, by Codistillation *in Vacuo* with Ethylene Glycol," *Ann. chim. anal. chim. appl.* **22** (1940), 217. *Chem. Abstracts* **35** (1941), 4547.

K. H. Bauer et al., "Cultivation Relations of Some Drug and Aromatic Plant Species with Special Reference to the Content of Valuable Constituents. An Experiment Comparing the Growth Relationships on the Basis of Three Year Studies Carried out in the Different Regions of the Altreich," *Landw. Jahresber.* **92** (1942), 1. *Chem. Abstracts* **38** (1944), 6490.

H. Flück, "Influence of Altitude on the Active Principle Content of Wild Growing Medicinal Plants," *Hundert Jahre Schweiz. Apoth.-Ver.* 1843–1943 (1943), 426. *Chem. Abstracts* **38** (1944), 1842.

L. Fischer, Pa. A. Tornow and B. L. Proper, "Content and Physical Properties of Certain Volatile Oils," *Natl. Form. Comm. Bull.* **13** (1945), 6.

OIL OF CARROT

Essence de Carotte *Aceite Esencial Zanahoria* *Möhrenöl*

Introduction.—*Daucus carota* L., the common carrot, is cultivated in many countries for culinary purposes. The seed contains an essential oil which can be isolated by steam distillation.

In France, the principal producer of this oil, there exist two types of carrot: one is the well known, long, cylindrical root, sweet and of reddish color, which serves for human consumption. The other is the larger, coarser root used as cattle feed. The latter is usually of whitish or yellowish color and contains less sugar than the first type.

Literature differentiates between the oils distilled from the seed of the two types of carrot, but growers in the important center of St. Rémy-en-Provence in Southern France informed the author that both qualities of seed are employed for distilling purposes, and that no differentiation is made in France when supplying the distilleries with seed.

Producing Regions.—The centers of the carrot seed industry in France are in the Département Seine et Loire and in the south of France. The quantity of seed produced yearly varies between 200,000 and 300,000 kg., sometimes reaching a maximum of 500,000 kg. It depends entirely upon demand and upon orders given by the dealers and exporters of seed. The region of St. Rémy-en-Provence alone produces normally about 100,000 kg.

During World War II large quantities of carrot seed oil were distilled in Southern France, the oil being used for the flavoring of all kinds of food substitutes.

Planting, Cultivating, and Harvesting.—In France the growing and cultivation of *Daucus carota* and the cleaning of the seed closely resemble those of celery and parsley seed.

Like celery and parsley, carrots are grown in St. Rémy-en-Provence exclusively for the seed, which is sold to truck farmers cultivating carrots for culinary purposes near the large cities in France or abroad. One hectare yields 800 to 1,000 kg. of seed.

There exists a considerable difference in the price of seed from the latest harvest and of old, superannuated seed, which has lost its germinating power. Since the cheaper superannuated seed gives almost as good an oil as new seed it is preferred for the purpose of distillation.

Distillation.—Distillation of carrot seed must be carried out according to the general principles applying to all seed material, i.e., it is first crushed, and then distilled with direct steam, care being taken that the steam does not form channels through the seed material in the still, which would result in a subnormal yield of oil.

The author obtained yields varying from 0.4 to 0.8 per cent of oil from French carrot seed.

Physicochemical Properties of Carrot Seed Oil.—According to Gildemeister and Hoffmann,[1] oils distilled from German carrot seed possess the following properties:

Specific Gravity at 15°	0.870 to 0.944
Optical Rotation	−8° 25′ to −37° 0′
Refractive Index at 20°	1.482 to 1.491
Acid Number	1.0 to 5.0
Ester Number	17.0 to 52.0
Ester Number after Acetylation	77.5 to 95.7
Solubility	Soluble in 0.5 vol. and more of 90% alcohol; some oils are soluble in 2 to 5 vol. of 80% alcohol

Oils distilled by the author in France from seed of carrots used for edible purposes and for cattle feed had these properties:

	Seed from Edible Carrots	*Seed from Carrots Used as Cattle Feed*	
Specific Gravity at 15°	0.928	0.906	0.917
Optical Rotation	−12° 15′	−22° 18′	−18° 25′
Refractive Index at 20°	1.4882	1.4799	1.4821
Acid Number	1.4	1.4	2.8
Saponification Number	10.3	42.0	40.1
Ester Number after Acetylation	47.6	79.3	93.3
Solubility at 20°	Not clearly soluble in 80% alcohol up to 10 vol. Soluble in 0.5 vol. and more of 90% alcohol	Same solubility	Same solubility

Genuine carrot seed oils produced in France and analyzed by Fritzsche Brothers, Inc., had properties varying within the following limits:

Specific Gravity at 15°	0.906 to 0.930
Optical Rotation	−11° 54′ to −22° 18′
Refractive Index at 20°	1.4799 to 1.4888
Acid Number	1.4 to 2.8
Saponification Number	10.3 to 40.1
Ester Number after Acetylation	47.6 to 93.3
Solubility	Soluble in 0.5 vol. of 90% alcohol, clear to slightly opalescent up to 10 vol.

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[1] "Die Ätherischen Öle," 3d Ed., Vol. III, 568.

Two samples of Hungarian carrot seed oil, distilled probably from wild growing plants (yield 0.135 to 0.240 per cent), were analyzed by Fritzsche Brothers, Inc., New York, in 1947:

	I	*II*
Specific Gravity at 15°.....	0.939	0.941
Optical Rotation..........	−4° 24′	−6° 42′
Refractive Index at 20°....	1.4900	1.4909
Acid Number.............	5.2	2.4
Saponification Number.....	32.1	15.0
Solubility at 20°...........	Soluble in 0.5 vol. and more of 90% alcohol	

The odor of these two oils was normal.

Three oils distilled during 1943–1944 from carrot seed grown in Stockton, California (near San Francisco), and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

	I	*II*	*III*
Specific Gravity at 15°/15°...	0.928	0.928	0.927
Optical Rotation............	−4° 50′	−4° 45′	−4° 18′
Refractive Index at 20°......	1.4899	1.4884	1.4890
Acid Number...............	4.7	5.6	4.7
Saponification Number.......	26.1	20.5	18.8
Solubility..................	Soluble in 0.5 vol. of 90% alcohol and more		

The odor and flavor of these oils were not quite as characteristic as those of the French oils.

It appears that considerable quantities of carrot seed oil could be produced in that section of California, provided the demand warrants an extension of the present plantings.

Asahina and Tsukamoto [2] distilled the oils from the seed of two varieties of carrots, one with long cylindrical root and the other with cone-shaped root. The oils had these properties:

	Cylindrical Root	*Cone-shaped Root*
Yield................	1.6%	0.6%
Specific Gravity......	0.8944	0.9364
Optical Rotation......	−20° 31′	−1° 27′
Refractive Index......	1.4917	1.4859
Methoxy Content....	2.67%	Traces

Chiris,[3] experimentally distilling the chaff of carrot seed, obtained oils with properties quite different from those of pure seed oils:

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[2] *J. Pharm. Soc. Japan* No. 538 (1926), 97. *Ber. Schimmel & Co.* (1927), 70.

[3] *Parfums France* **14** (1936), 49.

Specific Gravity at 15°	0.932 to 0.941
Optical Rotation	−1° 0′ to +4° 10′
Refractive Index at 20°	1.4909 to 1.4931
Acid Number	1.8 to 3.5
Ester Number	11.2 to 16.4
Ester Number after Cold Formylation	54.1 to 59.7
Carotol Content	14 to 18%

Oil of Carrot Herb.—In order to investigate the oil of carrot seed and oil of carrot stalks of the short conical variety, Asahina and Tsukamoto[4] distilled oil exclusively from seed, oil exclusively from stalks, and oil from stalks plus seed. The oils had these properties:

	Oil from Seed	*Oil from Stalks*	*Oil from Stalks Plus Seed*
Specific Gravity at 22°	0.9088	0.9584	0.9270
Specific Optical Rotation at 22°	−5° 59′	+5° 4′	+1° 2′
Acid Number	0	24.91	2.86
Saponification Number	74.08	65.97	69.59

The above-ground parts of *wild* growing carrot plants were distilled by A. F. Slessman of Fremont, Ohio, in the summer of 1943. The oils examined in the laboratories of Fritzsche Brothers, Inc., had properties varying within the following limits:

Specific Gravity at 15°/15°	0.868 to 0.881
Optical Rotation	−28° 24′ to −31° 46′
Refractive Index at 20°	1.4727 to 1.4771
Acid Number	0.8 to 1.3
Saponification Number	23.3 to 29.5
Solubility	Not clearly soluble in 10 vol. of 90% alcohol

This type of oil has an odor and flavor differing from that of carrot seed oil, yet it shows good possibilities for use in flavor work where it could produce new and attractive notes.

Distilling the fresh umbels of carrots, harvested at the moment when the flowers began to develop seed (first week of August), Chiris[5] obtained, with a yield of 1.65 per cent, a mobile, colorless, volatile oil of penetrating odor which had these properties:

Specific Gravity at 15°	0.8804
Optical Rotation at 15°	−35° 09′
Refractive Index at 20°	1.4727
Acid Number	0.28

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[4] *J. Pharm. Soc. Japan* No. 525 (1925). *Ber. Schimmel & Co.* (1927), 70.

[5] *Parfums France* **14** (1936), 127.

Ester Number	60.32
Ester Number after Cold Formylation	126.25
Carotol Content	35.4%
Solubility	Soluble in 1.5 vol. of 90% alcohol, with turbidity

Chemical Composition.—

I. Seed Oil of Carrots with Cylindrical Roots.—The chemistry of carrot seed oil (from cylindrical roots) has been investigated by Richter,[6] and by Asahina and Tsukamoto.[7] The presence of the following constituents has been established:

Formic Acid(?). Presence possible, according to Richter.[8]

Acetic Acid. In ester form.

Butyric Acid (Probably Isobutyric Acid). In free form.

Palmitic Acid. Also in free form.

l-α-Pinene. In the laevorotatory fractions b. 158°–166°, of the saponified oil, Richter identified pinene as nitrosochloride and nitrolbenzylamine.

l-Limonene. In the fraction b. 168°–176°. Identified as nitrosochloride and nitrolpiperidine m. 103°–106°.

Daucol. Richter found in the high boiling fraction a crystalline compound, $C_{15}H_{26}O_2$ which he believed to be a dihydroxysesquiterpene alcohol, assigning to it the name daucol. When purified through its xanthogenate the alcohol had these properties:
M. 115°–116°, $[\alpha]^{14}_{D}$ $-17°\ 9'$ to $-17°\ 28'$.

The presence of two atoms of oxygen points toward two hydroxyl groups but only one group can be acetylized. The alcohol does not add bromine.

Asarone. This phenol ether m. 59° was identified by Asahina and Tsukamoto.[9] Oxidation to asaryl aldehyde m. 115°; semicarbazone m. 208°.

Carotol. Oxidation to dihydroxycarotol m. 142°. (See chemical composition of "Seed and Stalk Oil of Carrots with Conical Roots.")

Bisabolene. Identified as trihydrochloride m. 79.5°.

II. Seed and Stalk Oil of Carrots with Conical Roots.—Asahina and Tsukamoto[10] also investigated the chemical composition of an oil distilled from the seeds and stems of carrots with conical roots and established the presence of:

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[6] *Arch. Pharm.* **247** (1909), 391, 401. See also Deussen and Hahn, *Ber.* **43** (1910), 523. *Ber. Schimmel & Co.*, April (1910), 73.

[7] *J. Pharm. Soc. Japan* No. 538 (1926), 97. *Ber. Schimmel & Co.* (1927), 70.

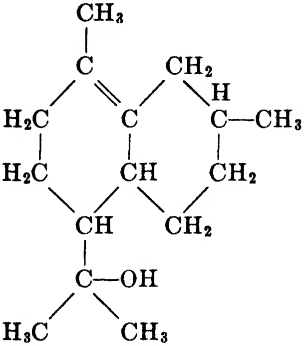
[8] *Arch. Pharm.* **247** (1909), 391, 401. See also Deussen and Hahn, *Ber.* **43** (1910), 523. *Ber. Schimmel & Co.*, April (1910), 73.

[9] *J. Pharm. Soc. Japan* No. 538 (1926), 97. *Ber. Schimmel & Co.* (1927), 70.

[10] *J. Pharm. Soc. Japan* No. 525 (1925). *Ber. Schimmel & Co.* (1927), 70.

Carotol. A sesquiterpene alcohol, $C_{15}H_{26}O$, of mobile consistency, which they named carotol. (Cf. Vol. II of this work, p. 763).

More recently Sorm and Urbánek[11] investigated the constitution of carotol, d_4^{20} 0.9702, $[\alpha]_D^{18} + 6° 54'$, n_D^{20} 1.4997, and concluded that it has the following structural formula:



Carotol

III. Oil of Carrot Herb.—Investigating an oil distilled from the whole overground plant (*Daucus carota* L.) cultivated in Southern France (Département Vaucluse), Palfray and Lepesqueur[12] reported on the presence of the following compounds: aliphatic aldehydes(?), formic acid, acetic acid, *l*-*α*-pinene, and carotol.

Use.—In France carrot seed has been used for many years for the preparation of alcoholic tinctures which find application in certain alcoholic liqueurs. These tinctures impart to the liqueur a smooth and full character which rounds out and conceals harsher notes.

Oil of carrot is very useful also in modern perfume compositions. It blends well with many types of scents, particularly orris, and produces notes which are hard to identify.

SUGGESTED ADDITIONAL LITERATURE

G. Igolen, "Essential Oils of Carrot," *Parfums France* 14 (1936), 177.

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[11] *Coll. Czech. Chem. Communications* **13** (1948), 49, 177. *Chem. Abstracts* **42** (1948), 7283; **43** (1949), 3808.

[12] *Compt. rend.* **198** (1934), 1365.

OIL OF CELERY

Essence de Céleri *Aceite Esencial Apio* *Sellerieöl*
Oleum Apii Graveolentis

A. Oil of Celery Seed

Botany.—*Apium graveolens* L., the common celery, is a hapaxanthic herb, grown as a biennial and, under certain conditions, as an annual. It is a native of Eurasia; as a *wild* plant it prefers soils containing sodium chloride and, therefore, grows in coastal regions. Celery is today widely cultivated in the temperate zones as an important garden crop, the bleached leaf stalks being relished as a popular vegetable. From the beet-like taproot (the uppermost part being a shoot) with its fibrous sideroots rises an aerial stem, 2 to 3 ft. high, branched and leafy, which bears compound umbels of small, white flowers. The small fruit (or seed, as it is called commercially) consists of an ovate, dark brown cremocarp. Possessing a characteristic, agreeable odor and a warm, aromatic, somewhat pungent taste, it is employed as condiment in the flavoring of food products. The seed serves also as birds' food. The volatile or essential oil distilled from celery seed is used extensively for flavoring purposes.

Producing Regions.—The main producing regions, where celery is raised for its seed, are located in Southern France (Département Bouches du Rhône), in India, and lately also in California (Sacramento and Santa Clara valleys).

FRENCH CELERY SEED OIL

Producing Regions.—For culinary purposes celery is grown almost everywhere in France, the main producing section of the seed being in the south of France, with St. Rémy-en-Provence, not very far from Avignon and Marseille, as the center. In fact, the little town of St. Rémy owes its reputation largely to the cultivation and export of celery seed, large quantities of which are shipped to horticulturists, truck farmers, and flavor manufacturers in every country, and particularly the United States. Numerous farmers around St. Rémy grow celery and then separate, purify, and store the seed until it is sold to brokers or exporters located in St. Rémy or in Marseille. The trade in celery seed has greatly increased in the past years, the highly speculative commodity being quoted on the produce exchanges of Marseille, Paris, London, and New York.

Prior to 1940, a few large brokers in Marseille obtained almost complete control over the French celery seed market and, therefore, over the prices. This fact, and the tendency of the growers in St. Rémy to hold their crop for several years until prices are sufficiently high, accounts for the occasionally high prices of the French seed. Indeed, the growing of this seed has usually been quite profitable; and growers in St. Rémy have been able to retain their monopoly, the competing production in the Départements of Drôme and Vaucluse being rather unimportant.

Before the last war, celery seed was not distilled in St. Rémy, but chiefly in Marseille and in Grasse. The St. Rémy growers raise celery principally for the seed; they do not sell the stalk and leaf material because in dried form it can be used as fertilizer.

The total harvest of celery seed in Southern France in normal years prior to World War II amounted to about 2,000,000 kg.; in abnormal years it fell as low as 200,000 or 300,000 kg.

Planting, Cultivating, and Harvesting.—Celery is planted by seed in nurseries during July and August. Late in the fall, before cold weather sets in, the young plants are transplanted into open fields. The harvest takes place the following August and lasts about eight days. The plants are collected in the early morning; after several hours of drying, the material is ready for threshing.

The crude seed, after threshing, is submitted to winnowing and finally sifted into various sizes. The whole procedure results in a number of products:

1. Large, selected seed.
2. Small seed.
3. Wastage (chaff, winnowings) of seed.
4. Dried umbels and leaves, after seed has been removed.
5. Stalks and leaves from the whole herb.

A few distillers use the stalk and leaf material (No. 5) for distillation. The yield of oil, however, is very small, and the quality different. Distilling experiments carried out by the author with broken material (No. 4) gave a low yield (about 0.5 per cent) and an oil of poor quality, which was not characteristic of celery seed. Yet, this refuse is occasionally purchased by distillers, which partly explains the inferior qualities of some oils offered on the market.

The crude seed is marketed in France and other countries. Some buyers accept the product as it comes from the farmers, i.e., including a small percentage of impurities. In some cases, however, customs regulations or buyers demand a prime quality. For this purpose, the dealers in France submit the crude seed to further purification whereby about 1.5 to 3.0 per cent of seed chaff or seed winnowings (No. 3) are obtained. This is second quality distillation material; to a certain degree it possesses the flavor of seed, because this type of chaff consists mostly of crushed and broken seed, and not of leaf chaff. However, the quantity available on the market is much too limited for the production of large quantities of oil. Therefore, it cannot be depended upon as a regularly available raw material. Certain countries and buyers insist upon large size seed and refuse any admixture of small seed. To comply with these requirements, the French brokers and exporters again clean the seed, eliminating all small seed (No. 2) which consequently can be sold at somewhat lower prices. This presents excellent material for distillation. The large seed (No. 1) may be used for distilling only when the prices of celery seed in general are sufficiently low, i.e., in years of abundant crop.

One hectare produces normally about 800 kg. of seed per year; during years of unfavorable weather conditions the yield may fall to 400–500 kg.

Indian Celery Seed Oil

India produces considerable quantities of celery seed, much of which is exported to Europe and the United States for oil distillation. (See below.)

American Celery Seed Oil

Prior to World War II, imports of celery seed to the United States amounted to about one and one-quarter million pounds, in addition to that imported in the form of essential oil. It is not known how much of the imported seed was employed for planting and how much for seasoning or other purposes. America's domestic production serves principally for the vegetable-seed trade.

Planting, Cultivating, and Harvesting.—According to Crooks and Sievers,[1] celery may be grown for seed in several ways, depending on climatic conditions. In the Sacramento and Santa Clara valleys, where most of the seed is produced for planting purposes, the usual practice is to start the seedlings in the summer, and in the fall to transplant them to the field in check rows about 3 ft. apart. Freezing temperatures, which sometimes occur in this region, apparently do not damage the plants. In the following spring, the plants grow rapidly, and by midsummer they produce many flower heads, which mature in August. In the Eastern States the plants are often grown as annuals by chilling the seedlings in the seed bed early in spring; this causes the plants to produce seed stalks that season. Another

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[1] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941).

practice is to carry the plants through the winter, with heavy mulching to protect them from severe frost.

These methods are used in raising celery for the vegetable-seed trade which offers higher prices than could be expected, under normal conditions, for condiment, and particularly for distillers', seed.

The harvesting of celery seed may be accomplished by much the same methods as are used for harvesting the seed of other umbelliferous plants. In California the plants are cut and laid on long strips of cloth on the ground. After thorough curing, a roller is hauled back and forth over the material to separate the seed. Threshing can also be done with modified grain threshers. In regions where good drying weather cannot be expected at all times, the crop would have to be stacked in the field and so handled that damage from rain would be reduced to a minimum; or it could be cured under cover. The thoroughly dried seed may be cleaned with a fanning mill, packed, and stored in a dry place.

Yield of Seed per Acre.—The yield of celery seed is apparently not very large, and varies considerably. From 300 to 600 lb. per acre have been reported.

Consideration of Domestic Production.—Crooks and Sievers[2] expressed the opinion that the growing of celery seed for the condiment and essential oil trade seems most feasible in those regions where the seed is already being produced for the vegetable-seed trade, particularly in California. This seed must necessarily be of the very best quality. Poorer grades and old seed are now being used as birds' food. Perhaps the growing of this crop can be so increased that the entire domestic market will be supplied.

GENERAL

Distillation of Celery Seed.—The volatile or essential oil contained in the seed is isolated by steam distillation. For this purpose, the seed should be crushed and, to avoid loss of oil by evaporation, immediately charged into the still. It is important that the seed be spread evenly on the perforated grids with which a still serving for seed distillation should be equipped. The possibility of steam channeling must be prevented, for if this occurs only a part of the seed will be attacked by steam, and a poor yield of oil will result.

Distillation of one batch lasts from 10 to 12 hr. The distillation waters are usually redistilled (cohobated).

Yield of Oil.—According to the author's experience, the yield of oil varies from 1.90 to 2.45 per cent for French seed, and from 2.14 to 2.50 per cent

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[2] *Ibid.*

for Indian seed. Figures on the oil yield from American grown seed are not readily available, because the American seed is too high priced for distilling purposes.

Investigating the volatile oil content of commercial celery seed of various origin, Fischer, Tornow and Proper [3] found that the yield of oil ranged from 1.3 to 2.5 per cent, the average being 1.78 per cent.

Old, superannuated seed yields less oil than ripe, sound seed of the latest harvest. Chaff, too, gives an inferior yield, as a considerable portion of the oil, and particularly the more volatile terpenes, has evaporated on the large surface of the broken chaff particles. For the same reason, chaff oils show physicochemical properties quite different from those of oils distilled from normal seed.

Physicochemical Properties.—Gildemeister and Hoffmann [4] reported the following properties for oil of celery seed:

Specific Gravity at 15°	0.866 to 0.898; mostly above 0.872
Optical Rotation	+51° 0′ to +82° 0′
Refractive Index at 20°	1.478 to 1.486
Acid Number	Up to 4.0
Ester Number	16.0 to 55.0
Ester Number after Acetylation	43.0 to 67.0
Solubility	Soluble in 6 to 8 vol. of 90% alcohol, mostly with turbidity. Soluble in 1 to 1.5 vol. of 95% alcohol; sometimes opalescent with more

According to the same authors,[5] high specific gravity and a rotation below +60° indicate that the oil was distilled from material containing chaff.

Celery seed oils distilled during recent years in the factories of Fritzsche Brothers, Inc., from French seed grown in St. Rémy-en-Provence, had properties which varied within the following limits:

Specific Gravity at 15°	0.873 to 0.914
Optical Rotation at 20°	+46° 30′ to +75° 45′
Refractive Index at 20°	1.4800 to 1.4880
Saponification Number	30.0 to 74.0
Solubility	In many cases not clearly soluble in 90% alcohol, up to 10 vol. and more; often with haziness or turbidity, and sometimes with slight precipitation

Although these limits exceeded in some respects those given by Gildemeister and Hoffmann, the oils were of excellent quality and possessed the

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[3] *Bull. Natl. Form. Comm.* **13** (1945), 6.

[4] "Die Ätherischen Öle," 3d Ed., Vol. III, 472.

[5] *Ibid.*

characteristic odor and flavor of celery seed. In the author's opinion, a high gravity, high refractive index, and high ester number after acetylation indicate a large percentage of oxygenated compounds, which incidentally are the most valuable constituents of celery seed oil.

There are, however, genuine celery seed oils of low specific gravity. The latter should then be accompanied by a low refractive index, low saponification number and high optical rotation.

The laboratories of Chiris[6] reported that they examined pure oils of celery seed, the properties of which differed from those suggested by Gildemeister and Hoffmann (see above):

Specific Gravity at 15°	0.878 to 0.902
Optical Rotation	+56° 0′ to +75° 0′
Refractive Index	1.479 to 1.487
Acid Number	1.5 to 3.5
Ester Number	40 to 65
Ester Number after Acetylation	50 to 72
Solubility	Soluble in 0.5 to 2 vol. of 90% alcohol, turbid on further dilution

These oils had a higher specific gravity, a lower optical rotation, and a higher ester number, than the oils described by Gildemeister and Hoffmann. In the opinion of Gildemeister and Hoffmann, a high ester number would indicate an admixture of chaff oil; yet the Chiris laboratories claim that their oils possessed a strong and lasting odor, due probably to a high content of sedanolide and other oxygenated constituents.

When evaluating a celery seed oil, special attention should be given to its odor and flavor rather than to physicochemical properties which vary considerably even in pure oils. Oils distilled by the author also had properties beyond the limits of Gildemeister and Hoffmann, but possessed an exceptionally good and strong odor and flavor. The physicochemical properties of celery oil can easily be "arranged" and brought within desired limits; therefore properties alone are not conclusive when attempting to detect adulteration in a celery seed oil.

Four genuine celery seed oils of excellent quality (I to IV), distilled by the author in France, had properties shown in the table below:

	I	*II*	*III*	*IV*
Specific Gravity at 15°	0.885	0.903	0.909	0.912
Optical Rotation	+66° 36′	+54° 30′	+51° 15′	+49° 40′
Refractive Index at 20°	1.4823	1.4859	1.4875	1.4879
Saponification Number	43.9	65.3	70.9	73.7
Solubility	All four oils were turbid in 90% alcohol			

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[6] *Parfums France* **7** (1929), 206. Louveau, *Rev. des Marques* **15** (1937), 37.

	IV *Original Oil*	*IV-a* *Rectified Oil*	*IV-b* *Rectification Residue*
Specific Gravity at 15°	0.912	0.867	1.067
Optical Rotation	+49° 40′	+77° 0′	Too dark
Refractive Index at 20°	1.4879	1.4803	1.5148
Acid Number	2.2	2.8	11.2
Ester Number	71.5	9.3	214.7
Ester Number after Acetylation	79.3	17.7	226.0
Solubility	Turbid in 90% alcohol	Soluble in 6 vol. and more of 90% alcohol	Not soluble in 90% alcohol

Oil No. IV appears abnormal according to the limits suggested by Gildemeister and Hoffmann; yet it had a very good and strong flavor.

Rectification of this oil with live steam yielded 75 per cent of rectified oil and about 25 per cent of residue. The rectified oil (No. IV-a) had properties very similar to those given by Gildemeister and Hoffmann; yet it had lost the characteristic flavor of true celery seed, because the important high boiling constituents had remained in the rectification residue (No. IV-b).

Rectification of celery seed oil is therefore of more theoretical interest than practical value. It merely proves that odor and flavor of this oil are influenced largely by the high boiling oxygenated constituents. An oil containing a high percentage of these compounds is likely to have constants exceeding the upper limits suggested by Gildemeister and Hoffmann.

If rectification of celery seed oil is carried out with slightly superheated steam under atmospheric pressure, a note reminiscent of burning rubber originates. Distillation with superheated live steam *in vacuo* gives better results but demands more complicated apparatus.

Oil of celery seed consists, roughly speaking, of a lighter and a heavier portion, the former being composed mostly of terpenes, the latter of oxygenated compounds. Occasionally it happens that during celery seed distillation the lighter and the heavier fractions of the oil separate in the Florentine flask.

Genuine celery seed oils distilled by Fritzsche Brothers, Inc., New York, during recent years from imported Indian celery seed had the following properties:

Specific Gravity at 15°	0.872 to 0.891
Optical Rotation at 20°	+65° 53′ to +76° 51′
Refractive Index at 20°	1.4803 to 1.4841
Saponification Number	25.1 to 47.6
Solubility at 20°	Similar to that of oils distilled from French seed (see above)

An oil obtained by distilling the distillation waters (cohobation) had these properties:

Specific Gravity at 15°	0.929
Optical Rotation at 20°	+39° 0′
Refractive Index at 20°	1.4961
Saponification Number	56.0
Solubility	Turbid in 6.0 vol. of 90% alcohol and more

The odor and flavor of the Indian oils are normal, but usually not quite as fine as those of oils distilled from French seed.

In the course of their above-mentioned work on commercial celery seed of various origin (including probably European and East Indian seed), Fischer, Tornow and Proper[7] found that the volatile oils distilled from this material have physicochemical properties ranging within these limits:

	Specific Gravity 25°/25°	*Refractive Index 20°*	*Optical Rotation 25°*	*Acid Number*	*Ester Number*
Minimum	0.8623	1.4787	+54° 4′	1.61	26.00
Maximum	0.9064	1.4882	+78° 30′	2.95	74.91
Average	0.8822	1.4835	+65° 46′	2.47	43.08

Celery Chaff Oil.—Gildemeister and Hoffmann[8] also reported the properties of two oils distilled entirely from chaff.

	I	*II*
Specific Gravity at 15°	0.9220	0.9241
Optical Rotation	+43° 13′	+33° 30′
Refractive Index	1.48982	1.48963
Acid Number	1.8	3.4
Ester Number	33.0	85.9
Ester Number after Acetylation	63.5	...
Solubility	Soluble in 2.8 vol. of 90% alcohol	Soluble in 0.4 vol. of 90% alcohol

The high specific gravity and low optical rotation of these chaff oils result from evaporation of low boiling terpenes, especially limonene, on the large surface of the broken chaff material. The odor and flavor of the chaff oil are harsher and coarser than those of the true seed oil.

Adulteration of Celery Seed Oil.—Oil of celery seed is frequently adulterated with chaff oil, or with terpenes (chiefly *d*-limonene) resulting from the concentration of sweet orange oil. Since *d*-limonene is a natural constituent of celery seed oil, such additions are difficult to detect. They

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[7] *Bull. Natl. Form. Comm.* **13** (1945), 6.

[8] "Die Ätherischen Öle," 3d Ed., Vol. III, 472.

manifest themselves by a corresponding lowering of the specific gravity, and slight increase in the dextrorotation of the oil. Oil of celery seed should, therefore, always be submitted to a very careful organoleptic examination.

Chemical Composition of Celery Seed Oil.—The presence of the following compounds has been established in celery seed oil:

d-Limonene. Identified by the Schimmel chemists[9] as bromide m. 105° in the fraction b. 176°–177°, α_D +107°.

The oil contains about 60 per cent of *d*-limonene. Other terpenes are apparently not present. The oil is free from pinene since fractional distillation yields no fraction boiling below 170°.

Selinene. Ciamician and Silber[10] found in celery seed oil a sesquiterpene $C_{15}H_{24}$ which was later investigated by the Schimmel chemists.[11] They freed the corresponding fractions from phenols by repeated shaking with a 5 per cent solution of sodium hydroxide and by distilling the separated hydrocarbon over metallic sodium. B. 265°–273°. Dihydrochloride m. 72°–74°. Redistillation of the hydrocarbon *in vacuo* gave two fractions.

According to Semmler and Risse,[12] selinene, as it occurs in celery seed oil, consists of a mixture of α- and β-isomers, the latter largely predominating.

From 10 to 15 per cent of selinene is present in celery seed oil.

Aside from limonene and selinene which amount to about 70 per cent of the oil, celery seed oil also contains some oxygenated compounds. Although present only in small quantities, they are, nevertheless, very important and mainly responsible for the characteristic odor and flavor of the oil.

Sesquiterpene Alcohols $C_{15}H_{26}O$. The Schimmel chemists[13] had already noticed the presence of 2.5 to 3.0 per cent of alcohols in celery seed oil but left them unidentified. Ruzicka and Stoll,[14] investigating the highest boiling fractions, found them to contain at the most 1 per cent of mainly bicyclic sesquiterpene alcohols $C_{15}H_{26}O$. Later Ruzicka, Wind and Koolhaas came to the conclusion that the "selinenol" $C_{15}H_{26}O$ obtained from selinene $C_{15}H_{24}$ consists of mainly α-eudesmol and some β-eudesmol.

Sedanolide. The highest boiling fractions of celery seed oil contain 2.5 to 3.0 per cent of this lactone b_{17} 185°. Its corresponding hydroxy acid, the sedanolic acid $C_{12}H_{20}O_3$, m. 88°–89°, is easily reconverted into sedanolide.

Sedanonic Anhydride. The same high boiling fractions also contain about 0.5 per cent of sedanonic anhydride which is tetrahydro-*n*-butylidene phthalide. See in this connection "Sedanonic Acid," in Vol. II of this work, p. 609. The other constituents of celery seed oil are also described in detail in Vol. II.

Sedanolide and sedanonic acid anhydride are the two constituents chiefly responsible for the characteristic odor of celery seed oil.

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[9] *Ber. Schimmel & Co.*, April (1892), 35; April (1910), 96.
[10] *Ber.* **30** (1897), 492, 501, 1419, 1424, 1427.
[11] *Ber. Schimmel & Co.*, April (1910), 96.
[12] *Ber.* **45** (1912), 3301, 3725; **46** (1913), 599.
[13] *Ber. Schimmel & Co.*, April (1910), 96.
[14] *Helv. Chim. Acta* **6** (1923), 852.

Aside from the compounds described above, the oil furthermore contains:

A Phenol, Probably Guaiacol. According to Ciamician and Silber.[15]

Another Phenol or Phenol Ether $C_{16}H_{20}O_3$. It forms white needles m. 66°-67°.

Palmitic Acid.

On fractionation of the oil, about 10 per cent remained as residue in the still (Schimmel & Co.).

Louveau [16] reported that aside from the above described constituents, oil of celery seed contains also 2 to 3 per cent of an unidentified terpene alcohol (terpineol?).

Use of Celery Seed Oil.—Celery seed is said to have a sedative and tonic effect upon the central nervous system, whence the use of celery seed oil in nerve tonics.

The principal use of this oil, however, is in the flavoring of all kinds of food products—canned soups and meats, sausages, and particularly in the flavoring of the popular celery salts, celery tonics, and culinary sauces. Celery seed oil is one of the most valuable flavoring agents, imparting warm, aromatic, and pleasing notes to food products.

Oleoresin Celery.—The so-called oleoresins of celery have in late years attained ever-increasing popularity among food producers.

These oleoresins are prepared by extracting celery seed with volatile solvents (particularly alcohol), filtering and freezing the solutions, and driving off the alcohol *in vacuo*. Depending upon the solvent used, the consistency, appearance and flavor of the resulting oleoresins will vary.

Oleoresins possess not only the volatile top note of the essential oil, although in a much more dilute form, but also the "body," i.e., the fixed extractive matter of the celery seed. In other words, the oleoresins combine all flavor principles of the seed in the form of standardized and soluble products, which are easy to handle, and thus save the labor of preparing tinctures and extracts.

B. Oil of Celery Herb

The volatile oil of celery is contained not only in the seed but also in other overground parts of the plant, e.g., in the leaves; but the content of oil in the parts other than seed is so small that the cost of distillation is almost prohibitive. In order to obtain a more normal yield, the overground parts of the plant would have to be distilled just before seed ripening, as is done with dill herb and parsley herb.

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[15] *Ber.* **30** (1897), 492, 501, 1419, 1424, 1427.

[16] *Rev. des Marques* **15** (1937), 37.

Two oils distilled from celery herb, including the immature seed, and analyzed by Fritzsche Brothers, Inc., had the following properties:

	French Oil	*Hungarian Oil*
Specific Gravity at 15°	0.862	0.878
Optical Rotation	+72° 15′	+62° 34′
Refractive Index at 20°	1.4771	1.4810
Saponification Number	25.2	44.8
Solubility at 20°	Hazy in 6 vol. of 90% alcohol. Slightly hazy in 10 vol.	Hazy in 10 vol. of 90% alcohol

Obviously, the odor of the herb oil is entirely different from that of the seed oil, the former being more representative of the plant as such. Doubtless this new type of oil could be introduced to great advantage in many products of our food industry. So far, however, celery herb oil has not yet attained any commercial importance.

Experimenting along the same lines the laboratories of Antoine Chiris[17] reported about two oils which they distilled in 1937 from the overground parts of celery at different stages of maturity:

	Fresh Plants in Full Flowering (June 20th)	*Fresh Plants with Ripe Seed (August 8th)*
Specific Gravity at 15°	0.9052	0.9210
Optical Rotation at 25°–27°	+35° 5′	+41° 21′
Refractive Index at 20°	1.4877	1.4881
Acid Number	4.20	5.60
Ester Number	68.03	85.57

The odor of these oils was excellent and typical of celery.

Distilling the whole overground part of celery plants, Sorgonà Luisi[18] obtained an oil possessing these properties:

Specific Gravity at 20°	0.8918
Optical Rotation at 21°	+46° 0′
Refractive Index at 21°	1.4865
Acid Number	3.41
Ester Number	47.18
Ester Content, Calculated as Linalyl Acetate	16.50%
Ester Number after Acetylation	57.30
Total Alcohol Content, Calculated as $C_{10}H_{18}O$	16.48%
Solubility	Soluble in 9 vol. of 90% alcohol

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[17] *Parfums France* **15** (1937), 225.

[18] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi, Reggio Calabria* **15** (1940), 38. *Chem. Abstracts* **37** (1943), 3561.

SUGGESTED ADDITIONAL LITERATURE

"Volatile Oils of Anise, Caraway, Celery Fruit, Coriander, Cubebs and Fennel," Report of the American Pharmaceutical Association Laboratory, *Bull. Natl. Form. Comm.* 7 (1939), 231.

J. F. Clevenger, "Volatile Oils of Anise, Caraway, Celery Fruit, Coriander, Cubeb and Fennel," *Bull. Natl. Form. Comm.* 7 (1939), 293.

OIL OF CORIANDER

Essence de Coriandre *Aceite Esencial Coriandro* *Corianderöl*
Oleum Coriandri

A. Coriander Seed Oil

Botany.—*Coriandrum sativum* L. is an annual hapaxanthic herb with an erect, branching stem, growing to a height of about 2 ft. and carrying compound leaves. The small flowers, which appear in June, are white or rose colored; the fruit is globular and composed of two concavo-convex mericarps. The fruit, or, as it is commercially called, the seed, ripens in August. The overground parts of the green plant, particularly the leaves, possess a peculiar, rather disagreeable odor. However, the mature dried seed is distinguished by a pleasant, warm, somewhat spicy aroma and is, therefore, employed for flavoring all kinds of food products, sauces, soups, baked goods, and confectionery, as well as alcoholic liqueurs (chiefly gin). The volatile or essential oil, to which the odor of coriander seed is due, may be isolated from the seed by steam distillation.

Habitat and Range.—*Coriandrum sativum* L., a native of Southern Europe, Asia Minor and the Caucasus, where it has been known for a very long time, not only grows wild, but is cultivated extensively in many countries favored by a suitable climate. The principal producers of coriander seed are the U.S.S.R., Hungary, Poland, Roumania, Czechoslovakia, Morocco, and lately also Guatemala, Mexico, and the United States. The bulk of coriander seed oil offered on the world market originates from the U.S.S.R. Prior to World War II, coriander was grown in Hungary on about 500 hectares belonging to a few landed proprietors. After World War II, Hungary's large estates were broken up with the result that in 1947 coriander was grown on about 150 hectares only, which are worked by small land holders.

Althausen, Boruff, Gamlin, Koenig, and Landes[1] made a comprehensive study of the physicochemical properties of various types of coriander seed. These workers established definite standards, among them ultraviolet absorption spectra of the essential oils and emission spectra of the seed ashes, by which it is possible to approximate or define the geographical origin of a sample of coriander seed subject to inspection.

EUROPEAN CORIANDER SEED OIL

Planting and Cultivating.—In Hungary, *Coriandrum sativum* L., an annual umbelliferous plant, attains a height of 30 to 70 cm. according to conditions of soil and locality. The umbels are white; the fruit is globular and 5 to 7 mm. in diameter. If harvested at the proper state of maturity the fruit has a light brown color. The plant is not sensitive to cold and is quite resistant to heat and drought. Coriander adapts itself easily to any kind of soil, but the best yield is obtained in light and fertile ground. The plant grows well after any other crop and, hence, offers no difficulty in the rotation of crops; it forms a very suitable green crop before wheat.

According to de Bittera,[2] coriander must be planted in soil free from weeds. Deep plowing in the fall is essential, the ground, free of clods, thereby becoming smooth and light for the following spring. The soil is prepared for sowing either with a disk harrow or through repeated harrowing with the common harrow. If the structure of the soil is too light, a roller should be passed before the drill plow (sowing machine) in order to render the soil firmer. Immediate manuring must be avoided, however, as this would cause much weed development.

The best time for sowing is in March, when barley and oats are sown. Benefiting from the winter humidity of the soil, the seeds germinate well and evenly within eight to ten days. The distance between the rows is 35 cm., but in soil absolutely free of weeds the seeds may be sown in a row distance of 11 to 13 cm. In the latter case, however, the ground cannot be hoed. The drill plow is followed by a harrow, which covers the seeds with earth, but only slightly. From 8 to 10 kg. of seed sow one "kataster joch" (1.422 acres or 0.575 hectares).

The cultural care begins right after sprouting of the seed. At first the young plants develop very slowly but as soon as they have taken root they grow almost visibly. After the plants have reached a height of about one span (5 to 7 in.) they are hoed for the second time. From then on the

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[1] *Spice Mill* **63**, August, September and October (1940).

[2] Private communication by Dr. Jules de Bittera, Budapest, to whom the author is greatly indebted for much of the information pertaining to Hungarian coriander seed oil.

plants grow rapidly, the leaves protecting the ground around the plants so well that further care is not necessary. If the seed is sown at a greater row distance, e.g., 36 to 37 cm., a cultivator can be used instead of a hoe. When not yet matured, coriander has a strong, peculiar, and disagreeable odor.

Harvesting.—By the end of July or the beginning of August the seeds reach maturity, and as soon as the color of most of them has changed from green to rust-brown, harvesting commences. The progress of ripening has to be watched carefully; the change of color into reddish-brown or yellowish-brown is quite a reliable indication that cutting should be delayed no longer. Cutting is usually done with scythes or with sickles, in case the seeds are already too ripe. The cut plants are left on the field, gathered into swaths, to be piled up into larger heaps on the following day, after the dew has dried off. Two or three days later the plants are loaded upon carts lined with big cloth or canvas sheets, transported to the threshing machines, or put up in small ricks. Regular threshing machines adjusted for the threshing of rapeseed may be used. If the weather is sunny and dry, the seeds are spread out on sheets near the threshing machine, where they are turned over repeatedly with a shovel so that they dry more quickly. After 1 to 2 hr. they can be transported to the granary for final drying. They are spread out, four to five fingers high in an airy space, and turned over several times to prevent formation of heat, sweat, or mold. When finally air dry, the seed is stored in big heaps.

One "kataster joch" (1.422 acres or 0.575 hectares) yields from 500 to 1,200 kg. of coriander seed and, in addition, 2,000 to 2,500 kg. of straw which may be used as sheep feed.

According to Ramstad,[3] coriander test plots planted in Norway yielded 1,500 kg. of seed per hectare, in spite of the cold. Analysis of the seed showed 1.4 to 1.7 per cent of volatile oil, and 12.0 to 12.4 per cent of fatty oil. Central Europe, according to the same author, averages 1,000 kg. of seed per hectare, yielding only 0.5 per cent of volatile oil.

Bauer and collaborators[4] found that coriander attains its greatest yield of volatile oil (0.91 per cent) with a growing period of 110–122 days in cool, somewhat damp weather.

AMERICAN CORIANDER SEED OIL

Soil and Climatic Conditions.—According to Crooks and Sievers,[5] coriander may be grown in a wide range of soils but thrives best in a deep and

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[3] *Medd. Norsk Farm. Selsk.* **4** (1942), 77. *Chem. Abstracts* **38** (1944), 218.

[4] *Landw. Jahresber.* **92** (1942), 1. *Chem. Abstracts* **38** (1944), 6490.

[5] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.,* July (1941).

fertile garden loam of limestone origin. An excessive amount of water or conditions responsible for acid soil are unfavorable. Too much nitrogen may cause delayed ripening, or prolong the progressive ripening period and reduce the yield.

Coriander matures within ninety days and should have a continuous, uniform supply of moisture and a fairly even temperature throughout the growing season. The plant requires a sunny location. Rain or wind, during the harvest period, may be very damaging to the seed, which shatters easily.

Planting, Cultivating, and Harvesting.[6]—Stockberger[7] recommended that the soil be well prepared before planting. For field cultivation, the seed is sown in rows 3 ft. apart; but, if the cultivating is done by hand, the distance between the rows may be reduced to 18 in. The seed should be sown thickly in order to insure a good stand. When well up, the plants are thinned to stand 4 to 5 in. apart in the rows. Cultivation must continue until the plants flower, about two months after planting.

When most of the seeds have ripened, the plants are cut with scythes or a mower, preferably in the early morning while still moist with dew, in order to prevent seed shattering. The plants must be partially cured in small cocks in the field, the drying being finished in a barn loft or under any suitable shelter. Finally, the seeds are threshed out and cleaned.

According to Crooks and Sievers,[8] the seed should be planted in early May, or as soon as there is sufficient moisture and warmth in the soil for germination, but after the danger of frost has passed. Seed should be planted about 1 in. deep at the rate of 10 to 15 lb. per acre, in rows 15 to 30 in. apart. The seed might be planted broadcast, but for the difficulty encountered with weeds. Cultivation is much the same as for any truck crop requiring frequent and light cultivation to keep out weeds, some hand weeding also being required. Coriander does not compete successfully with weeds; besides, the final product must contain no foreign matter, the presence of which may add an undesirable flavor. Plantings made early in May usually bloom in about nine weeks and mature seed in the latter part of July.

The same authors reported that the ripening of coriander fruit is progressive, which characteristic causes some difficulty in the harvest. The harvest may start when approximately one-half of the total fruits formed on the plant have turned gray. Harvest at a later stage risks excessive shattering of the mature seeds; whereas an earlier harvest leads to consid-

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[6] In this connection, see also Willkie and Kolachov, "The Domestic Production of Essential Oils from Aromatic Plants," *Natl. Farm. Chemurgic Bull.* (1940), 12.

[7] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935), 20.

[8] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.,* July (1941).

erable loss from immature seed and brings about an undesirable aroma of the volatile oil. A high yield could very likely be obtained by pulling the plant and stacking it in a drying barn or in the field, with umbels turned toward the center of the stack. By this method many of the seeds will continue to mature from food reserves in the stalk, and the mature seed will drop to the center of the stack where it can be collected. Such a method of curing produces a superior quality, as well as maximum yield, but involves more hand labor than mechanical methods. Harvesting by machinery may be done with a field mower or binder. According to various reports, grain combines have been used with some success in the U.S.S.R. Because of the loss from shattering and the hazard of unfavorable weather, it is doubtful that a combine could be used advantageously in any part of the United States, except possibly in some favorably irrigated sections where no rain occurs during the harvest season. The dried fruits are stored or marketed in bags. In case of storage, fumigation would probably be necessary to prevent insect damage.

Yield of Seed per Acre.—From experimental plantings it is estimated that the yield of coriander seed ranges from 500 to 800 lb. per acre. Yields as high as 1,100 lb. have been reported in the United States, and some reports of yields of over 2,000 lb. have come from foreign countries. These maximum yields could hardly be expected for our country, except where ideal conditions for growth exist, and with every effort being made, by the use of hand labor, to prevent any loss through seed shattering.

Lowman, Gilbert and Kelly [9] recently studied the adaptation of coriander varieties to domestic culture. Seeds from seventeen different sources, representing six countries of origin, and grown at Beltsville, Md., as summer crops, were compared for plant growth, yield and quality of seed. Twelve of these were grown for similar comparisons at Bard, Imperial County, Cal., as winter crops. Two distinct types of plants were observed, one early and the other late maturing; both of these exhibited several varietal characteristics. The early maturing type was found to be best suited to growing conditions in California, while either type produced normal growth under conditions in the east, when grown as summer crops. Yields of seed at Beltsville varied between seasons and varieties from about 200 lb. to over 1,000 lb. per acre, and at Bard from only a few pounds per acre for the least adapted varieties to over 3,000 lb. for those most suited to conditions in California. Date of planting, and application of nitrogen in the form of ammonium nitrate gave significant differences in seed yields at Bard, Cal. Seed produced by the late maturing type was highest in essential oil, but the early maturing type seed, because of its more uniform color and size, appears to be better suited to the spice trade.

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[9] *Am. Perfumer* **54** (1949), 209, 300.

Consideration of Domestic Production.—Crooks and Sievers[10] discussed the reasons for and against the production of coriander seed in the United States, some factors offering favorable aspects, others limiting the prospect.

Scofield[11] rates the oil distilled from Kentucky-grown coriander seed higher than that from Russian or Hungarian seed.

De Glazoff and Kolachov[12] found that the seeds of Russian and Moroccan coriander planted in the United States have a higher content of essential oil than the original seeds, and that the flavor of the domestically grown seed equals that of the imported product.

GENERAL

Distillation and Yield of Coriander Seed Oil.—Chernukhin[13] realized the importance of grinding the seed prior to distillation when he increased the yield of oil by 17 per cent, saving at the same time 10 to 15 per cent of steam. Tanasienko and Mezinova[14] arrived at similar conclusions; with crushed seed they could complete distillation in 3 to 4 hr. instead of the usual 12 to 15 hr. required for whole seed. Distilling crushed seed, these authors obtained 21 per cent more essential oil than when distilling whole seed.

After grinding the seed has to be distilled immediately; otherwise a considerable part of the oil will be lost by evaporation.

Leikin[15] studied the distillation of coriander seed with slightly superheated steam and found that thereby he could reduce the length of distillation from 9 to 6 hr.

J. de Bittera[16] carried out comparative, large-scale distillation experiments in Hungary and proved that crushed coriander seed after 9½ hr. of steam distillation yielded 0.92 per cent of oil, whereas uncrushed seed of the same lot, distilled in the same still and with steam of the same pressure, yielded only 0.88 per cent of oil, after 12¾ hr.

Stills of several thousand liters capacity are employed. The oil yield ranges from 0.4 to 1.1 per cent for crushed Hungarian coriander seed; on the average it runs from 0.5 to 0.6 per cent. Inferior qualities contain less oil. The oil content depends primarily upon weather conditions prevailing during the year of planting rather than upon the quality of the soil. It is influenced also by the state of ripeness, unripe or half-ripe seeds giving not

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[10] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941).

[11] *Natl. Farm Chemurgic Council Bull.*, August (1940), 55.

[12] *Trans. Kentucky Acad. Sci.* **10,** No. 1–2 (1942), 13.

[13] *Masloboino Zhirovoe Delo* (1928), No. 5, 11. *Chem. Abstracts* **23** (1929), 3538.

[14] *Masloboino Zhirovoe Delo* **15** (1939), No. 6, 25. *Chem. Abstracts* **34** (1940), 3438.

[15] *Masloboino Zhirovoe Delo* (1933), No. 1, 37. *Chem. Abstracts* **27** (1933), 5889.

[16] Private communication of Dr. Jules de Bittera, Budapest.

only abnormally low yields but oils of inferior and disagreeable odor. (In this connection see "Coriander Herb Oils.")

The yield of oil from Hungarian seed compares not unfavorably with that from Russian seed which, like the German and Czechoslovakian kind, averages 0.8 to 1.0 per cent. Roumanian seed, according to Gildemeister and Hoffmann,[17] yields 0.34 to 0.81 per cent of oil; French seed, 0.4 per cent; Dutch seed, 0.6 per cent; Italian seed, 0.35 to 0.5 per cent; the large sized seed from Morocco, only 0.2 to 0.3 per cent; and East Indian seed, 0.15 to 0.25 per cent. Varentzov [18] found that in general smaller coriander seed contains more essential oil than larger sized seed does.

The exhausted seed material may be dried and employed as cattle feed; it contains 11 to 17 per cent of proteins and 11 to 21 per cent of fatty matter.

Physicochemical Properties of Coriander Seed Oil.—Althausen, Boruff, et al.,[19] reported for authentic oils distilled from coriander seed of various origin, the properties given in Table 5.1 below.

According to Gildemeister and Hoffmann,[20] the properties of coriander seed oil vary within the following limits:

Specific Gravity at 15°......	0.870 to 0.885; usually not higher than 0.878
Optical Rotation...........	+8° 0′ to +13° 0′
Refractive Index at 20°. ...	1.463 to 1.471
Acid Number..............	Up to 5.0
Ester Number...	3.0 to 22.7
Solubility at 20°...........	Solúble in 2 to 3 vol. of 70% alcohol

Genuine coriander seed oils imported by Fritzsche Brothers, Inc., from the U.S.S.R. and Hungary during past years had properties varying within these limits:

	Russian Oils	*Hungarian Oils*
Specific Gravity at 25°/25°....	0.863 to 0.875	0.864 to 0.865
Optical Rotation.............	+9° 30′ to +11° 6′	+10° 15′ to +11° 30′
Refractive Index at 20°.......	1.4630 to 1.4661	1.4636 to 1.4645
Saponification Number........	2.8 to 7.5	10.3 to 12.1
Solubility at 25°..............	Soluble in 1.5 to 2.5 and more volumes of 70% alcohol	Soluble in 2 to 3 and more volumes of 70% alcohol

The odor and flavor of these oils were excellent and characteristic.

The linaloöl content, as determined on some lots, varied from 64.0 to 72.4 per cent.

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[17] "Die Ätherischen Öle," 3d Ed., Vol. III, 455.

[18] *Trans. Sci. Chem.-Pharm. Inst. Moscow* (1927), No. 17, 183. *Chem. Abstracts* **23** (1929), 1722.

[19] *Spice Mill* **63**, September (1940), 40.

[20] "Die Ätherischen Öle," 3d Ed., Vol. III, 455.

TABLE 5.1. COUNTRY OF ORIGIN OF THE CORIANDER SEEDS FROM WHICH OILS WERE DERIVED

Physicochemical Properties Determined	England	Czecho-slovakia (Moravia)	Morocco (Unbleached)	Morocco (Bleached)	Hungary	Poland	Roumania
Refractive Index at 20°	1.4641	1.4644	1.4658	1.4689	1.4644	1.4643	1.4648
Specific Gravity at 20°/20°	0.872	0.871	...	...	0.871	0.871	0.871
Specific Gravity at 20°/4°	0.871	0.870	0.873	0.879	0.869	0.869	0.869
Optical Rotation at 32°	+10° 48′	+10° 36′	+9° 30′	+4° 0′	+10° 36′	+10° 24′	+9° 36′
Acid Number	0.82	1.81	1.63	9.65	0.86	2.10	1.47
Ester Number	12.20	16.40	19.70	19.30	13.00	11.50	6.10
Acetyl Number	65.30	46.60	34.30	36.70	41.00	42.00	45.20
Solubility in 70% Alcohol	Cloudy below 2 vol. Clear in 2 vol. or more	Cloudy below 2.5 vol. Clear in 2.5 vol. or more	Same as English	...	Same as English	Same as English	Same as English
Color	Colorless	Colorless	Colorless	Brownish-yellow	Colorless	Colorless	Colorless
Bouquet	Characteristic residue-like oleates and high molecular weight fatty acids	Characteristic residue "sweet" like orange terpenes	Characteristic decidedly humic undertone	Characteristic residue has turpentine character	Characteristic residue-like oleates and high molecular weight fatty acids	Characteristic residue "sweet" like orange terpenes	Characteristic residue has a ginger note. RCHO high

Two oils distilled by the author in Southern France from imported Moroccan and Yugoslavian seed had the following properties:

	Moroccan Seed	*Yugoslavian Seed*
Specific Gravity at 25°	0.868	0.866
Optical Rotation	+8° 48′	+10° 15′
Refractive Index at 20°	1.4632	1.4637
Saponification Number	29.3	18.6
Solubility at 25°	Soluble in 2 to 2.5 vol. and more of 70% alcohol	Soluble in 2.5 vol. and more of 70% alcohol

The oils had normal properties. Odor and flavor of the oil distilled from the Yugoslavian seed were excellent and better than those of the Moroccan oil.

Oils distilled in Fremont, Ohio, and in the Clifton, N. J., factory of Fritzsche Brothers, Inc., from domestic seed material had the following properties:

Specific Gravity at 25°	0.863 to 0.866
Optical Rotation	+9° 40′ to +10° 20′
Refractive Index at 20°	1.4634 to 1.4638
Saponification Number	6.4 to 19.6
Solubility at 25°	Soluble in 2 to 2.5 vol. and more of 70% alcohol

The oils had normal properties. Their odor and flavor, however, were not quite as pronounced and fine as those of Russian or Hungarian oils.

An oil of coriander seed distilled in Guatemala and analyzed by Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 25°	0.870
Optical Rotation	+9° 40′
Refractive Index at 20°	1.4640
Saponification Number	17.9
Solubility at 25°	Soluble in 1.5 vol. of 70% alcohol, opalescent in 10 vol.

The properties of this oil were normal; the odor, however, was not quite as strong as that of the Russian or Hungarian oils.

Chemical Composition of Coriander Seed Oil.—The first investigations of coriander seed oil date back to the middle of the last century when Kawalier[21] isolated the main constituent, a compound of the empirical molecular formula $C_{10}H_{18}O$. Grosser[22] identified it as an alcohol. Semmler[23] found that the compound consisted of an olefinic chain and named it

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[21] *Liebigs Ann.* **84** (1852), 351. *J. prakt. Chem.* **58** (1853), 226.

[22] *Ber.* **14** (1881), 2485.

[23] *Ibid.* **24** (1891), 206.

coriandrol. Barbier[24] showed that coriandrol and linaloöl were identical chemically as well as physically, except for the opposite optical rotation. Coriandrol is, therefore, nothing else but *d*-linaloöl.

Walbaum and Müller[25] submitted coriander seed oil to a closer investigation and proved that it contained from 60 to 70 per cent of linaloöl and about 20 per cent of hydrocarbons. The same authors[26] established the presence of the following constituents in coriander seed oil:

d-α-Pinene. Oxidation with potassium permanganate gave *d*-pinonic acid m. 68.5°–70°.

dl-α-Pinene. Oxidation to *dl*-pinonic acid m. 104°–105°. Identified also by means of the nitrolbenzylamine m. 123°–124°.

β-Pinene. Oxidation with potassium permanganate to nopinic acid m. 125°–127°.

Dipentene. Very small quantities; tetrabromide m. 123°–124°.

p-Cymene. Optically inactive, d_{15} 0.8601, n_D^{20} 1.48565. Oxidation with potassium permanganate gave hydroxyisopropylbenzoic acid m. 155°–156°.

α-Terpinene and γ-Terpinene. These two terpenes form a large part of the hydrocarbons present in oil of coriander seed. The fraction b. 179°–180° yielded a nitrosite m. 154°–155°; a dihydrochloride m. 51°–52°, and a dihydrobromide m. 58.5°–59.5°. Oxidation with dilute potassium permanganate solution gave optically inactive α,α′-dihydroxy-α,α′-methyl isopropyl adipic acid m. 189° (from α-terpinene), and the erythritol $C_{10}H_{16}(OH)_4$, m. 235°–236° (from γ-terpinene).

Thus, the two isomers of terpinene occur in coriander seed oil. Formerly "terpinene" had been considered homogenous.

Terpinolene(?) and Phellandrene(?). Their presence is possible but has not been definitely established.

Aside from these hydrocarbons which amount to about 20 per cent of the oil, coriander seed oil contains the following oxygenated compounds:

d-Linaloöl. The main constituent. About 60 to 70 per cent of coriander seed oil consists of the alcohol $C_{10}H_{18}O$ which was originally called coriandrol by Semmler.[27] Later Barbier[28] identified it as the optical antipode of *l*-linaloöl. Both antipodes upon oxidation yield citral and may be transformed into geraniol. Walbaum and Müller[29] calculated that the oil contains about 50 per cent of linaloöl when acetylizing in the regular way, but 67.5 per cent when acetylizing according to Boulez.[30] Large-scale fractionation yielded about 70 per cent of

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[24] *Compt. rend.* **116** (1893), 1460.

[25] "Festschrift Otto Wallach," Göttingen (1909), 654.

[26] *Ibid.*

[27] *Ber.* **24** (1891), 206.

[28] *Compt. rend.* **116** (1893), 1460.

[29] "Festschrift Otto Wallach," Göttingen (1909), 654.

[30] *Ber. Schimmel & Co.*, April (1907), 127.

linaloöl. By cold formylation[31] Chiris[32] found between 65 and 90 per cent of linaloöl.

n-Decylaldehyde (*n*-Decanal). Semicarbazone m. 102°. Oxidation of the aldehyde gave decylic acid.

Other Aldehydes(?). Several other aldehydes of rather unstable character also seem to be present in the oil.

Geraniol. Isolated and purified by means of its calcium chloride compound: b. 231°–232°, d_{15} 0.881, α_D ±0°; diphenylurethane m. 80°–81°.

l-Borneol. Slightly laevorotatory; hexagonal plates m. 204° crystallized from petroleum ether solutions.

Oxidation yielded camphor. Oxime m. 118°.

Acetic Acid and Traces of Decylic Acid. These acids were isolated from the saponification lye of the ester fractions.

Use of Coriander Seed Oil.—Like the seed, the oil is used widely in gin essences and for the flavoring of canned soups and foods, spicy sauces, baked goods and confectionery; it is used also in pharmaceutical and other preparations for covering disagreeable odor and taste.

Oil of coriander seed is a valuable ingredient in perfumes; its soft, pleasant, slightly spicy note blends into scents of oriental character. It harmonizes well with jasmine, imparting life and lift to otherwise dull or too synthetic compositions.

B. Coriander Herb Oil

There appears to be considerable confusion and contradiction in literature, especially in Russian publications of the last twenty years, regarding the content and the composition of the volatile oil of coriander during various stages of plant development. Thus, Ivanov, Grigor'eva and Ermakon[33] reported that quantity and properties of coriander oil do not vary at different stages of plant maturity. Spiridonova[34] found that the physicochemical properties of coriander oil undergo considerable changes during the successive stages of growth from flowering to full maturity but that the entire plant can be used for distillation since stalks and leaves yield considerable oil (0.95 per cent). Distilling coriander at different stages of maturity, Schimmel & Co.[35] years ago had come to the following conclusions:

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[31] *Parfums France* (1924), 320.

[32] *Ibid.*

[33] *Bull. Applied Botany, Genetics, Plant Breeding U.S.S.R.* **21** (1929), No. 4, 321. *Chem. Abstracts* **26** (1932), 5605.

[34] *J. Gen. Chem. U.S.S.R.* **6** (1936), 1536. *Chem. Abstracts* **31** (1940), 1949.

[35] *Ber. Schimmel & Co.*, October (1895), 12.

1. Fresh, flowering, whole plants yielded 0.12 per cent of oil: d_{15}^{15} 0.853 (after 2½ months, 0.856), α_D^{18} + 1° 2′.
2. Fresh, semimatured herb, with seed yielded 0.17 per cent of oil: d_{15}^{15} 0.866 (after 1 month, 0.869), α_D^{18} + 7° 10′.
3. Mature seed, distilled immediately after the harvest yielded 0.83 per cent of oil: d_{15}^{15} 0.876, α_D^{16} + 10° 48′.

On these findings the author would like to comment that, from his own experience, oils distilled from the overground parts of coriander, including unripened seed, have a very peculiar, quite disagreeable odor, totally different from that of seed oil. It is absolutely impossible to use leaf oil instead of seed oil in any flavor, perfume, or pharmaceutical formula. The leaf or herb oil has a pronounced odor of decylaldehyde or other higher fatty aldehydes; in fact, the leaf oil contains so large an amount of higher aliphatic aldehydes that it might almost be considered as a source of these compounds, should price of the oil permit. Two oils, distilled from leaf and stalk material including unripe seed in Fremont, Ohio, and Geneva, Indiana, during 1942, and analyzed in the laboratories of Fritzsche Brothers, Inc., had these properties:

	Ohio Oil	*Indiana Oil*
Specific Gravity at 25°/25°	0.849	0.849
Optical Rotation	+3° 25′	+2° 1′
Refractive Index at 20°	1.4540	1.4548
Saponification Number	22.8	50.1
Aldehyde Content, Calculated as Decylaldehyde (Hydroxylamine Hydrochloride Method)	65.5%	72.0%
Solubility at 25°	Soluble in 3.5 vol. of 70% alcohol, opalescent in 10 vol.	Soluble in 1 to 1.5 vol. and more of 80% alcohol

Chemical Composition of Coriander Herb Oil.—The chemical composition of coriander herb oil differs from that of the seed oil. Carlblom[36] distilled the green herb of blooming coriander (*Coriandrum sativum* L.) in the district of Saratow (U.S.S.R.) and obtained 0.1 per cent of an oil which consisted almost entirely of aldehydes. The oil had these properties:

d_{20}^{20}	0.8524
α_D	+2° 33′
n_D^{20}	1.4555
Acid Number	1.85
Aldehyde Content (Hydroxylamine Method)	95.0%

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[36] *J. prakt. Chem.* [2], **144** (1936), 225.

Solubility	Insoluble in 70% alcohol

The oil consisted mainly of a mixture of aldehydes:

n-Decanal. About 10 per cent.

n-2-Decen-1-al and 8-Methyl-2-nonen-1-al. These two aldehydes represent isomers of decylenaldehyde.

The oil also contained:

Myrcene. Carlblom [37] suggested that myrcene plays an important part in the formation of linaloöl as the plant matures from the blooming to the seeding stage. He disclaims any genetic relationship between the aldehydes, as present in the blooming herb, and linaloöl, the main constituent of the seed oil.

According to Bryusova, Shagalova, and Novikova,[38] the oil from the green parts of coriander contains up to 95 per cent of aldehydes, 10 per cent of which is decylaldehyde.

SUGGESTED ADDITIONAL LITERATURE

M. Janicsek, "Hungarian Essential Oils," *Mezögasdasagi Kutatasok* **2** (1929), 153. *Chem. Abstracts* **25** (1931), 2810.

E. Kopp, "Roumanian Coriander Oil," *Pharm. Zentralhalle* **70** (1929), 789.

I. I. Vanin and A. A. Chernoyarova, "Linaloöl from Coriander Oil," *J. Russ. Phys. Chem. Soc.* **62** (1930), 2013. *Chem. Abstracts* **25** (1931), 4251.

I. I. Vanin and A. A. Chernoyarova, "Fatty and Essential Oils from *Coriandrum sativum* Grown in the Northern Caucasus," *J. Applied Chem. U.S.S.R.* **6** (1933), 922. *Chem. Abstracts* **28** (1934), 3833.

V. Isagulyantz and E. Smolyaninova, "Coriander Oil and Its Utilization. Preparation of Linalyl Acetate. (A New Method for the Acetylization of Linaloöl.)," *Riechstoff Ind.* **8** (1933), 194.

M. L. Mezinova, "Methods of Collecting Ethereal Coriander Oil at the Alekseevskii Works," *Masloboino Zhirovoe Delo* **14** (1938), No. 3, 22. *Chem. Abstracts* **32** (1938), 8071.

"Volatile Oils of Anise, Caraway, Celery Fruit, Coriander, Cubebs and Fennel," Report of the American Pharmaceutical Association Laboratory, *Bull. Natl. Form. Comm.* **7** (1939), 231.

J. F. Clevenger, "Volatile Oils of Anise, Caraway, Celery Fruit, Coriander, Cubeb and Fennel," *Bull. Natl. Form. Comm.* **7** (1939), 293.

P. Rovesti and F. Veneziani, "Investigation of Some Medicinal Drugs of the Empire. The Coriander Oil of the A.O.I.," *Rivista ital. essenze profumi* **21** (1939), 535. *Chem. Zentr.* I (1940), 2825. *Chem. Abstracts* **36** (1942), 2684.

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[37] *Ibid.*

[38] *Sintezy Dushistykh Veshchestv, Sbornik Statei* (1939), 247. *Khim. Referat. Zhur.* (1940), No. 4, 117. *Chem. Abstracts* **36** (1942), 3781.

F. Tanasienko, "Obtaining Essential Oil from the Coriander Plant, and Problems of Production Control," *Masloboino Zhirovaya Prom.* **16** (1940), No. 5–6, 54. *Chem. Abstracts* **35** (1941), 6737.

L. Fischer, P. A. Tornow and B. L. Proper, "Content and Physical Properties of Certain Volatile Oils," *Bull. Natl. Form. Comm.* **13** (1945), 6.

OIL OF CUMIN

Essence de Cumin *Aceite Esencial Comino* *Cuminöl* *Oleum Cumini*

Botany.—*Cuminum cyminum* L. is a slender, rather pretty annual growing to a height of 1 ft. or less and bearing very finely divided leaves. The aromatic, dried ripe fruits (seeds) are of elongated, oval shape, about 5 to 6 mm. long, and light brown in color. Their odor is peculiar, strong, and heavy; the flavor warm, slightly bitter, and somewhat disagreeable. They contain about 2.5 per cent of an essential oil, which can be isolated by steam distillation.

The dried fruit is widely used as a condiment; it forms one of the most important flavoring constituents in East Indian curries. It is also employed in native dishes of Central and South America, and for the flavoring of certain types of sausage and cheese.

Habitat and Range.—Probably a native of Turkestan or upper Egypt, cumin has been grown in Mediterranean countries for so long that its origin is difficult to trace. The seed was known in biblical times; it is mentioned in the Ebers Papyrus (1550 B.C.). Today cumin is cultivated in East India, in southern Russia (Ukraine), and along the southern and eastern shores of the Mediterranean (in Morocco, Algeria, Syria, and on the islands of Malta and Cyprus). It is not raised commercially in the United States, but hundreds of tons of the dried seed are imported annually. The natives of Central America (e.g., Mexico and Guatemala) grow it on a small scale.

Planting and Cultivating.—Crooks and Sievers[1] reported that the cumin plant thrives best on a well-drained, rich, sandy loam in regions where temperatures are mild and equable during the growing season of three or four months. The crop can be grown from seed. In the Mediterranean region the seed is frequently broadcast after winter crops of cereal, potatoes, or cabbage. Complete control of weeds is necessary, because the plant

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[1] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941), 17.

is small and tender. For that reason, planting of the seed in rows spaced to permit a maximum use of cultivators would seem preferable in regions where hand labor is costly.

Harvesting and Preparing for the Market.—The crop is ready for harvest when the plants wither and the seed loses its dark green color. In the Mediterranean region the plants are cut by hand, allowed to dry, and the seed beaten out with sticks, after which it is further dried and then cleaned of earth and other extraneous matter. If grown on a large scale in this country, it would have to be harvested in a more economical way. Drying in shocks and threshing with a modified grain thresher would probably be feasible. In general, the harvesting of cumin involves the same problems as the harvesting of the other aromatic seed crops.

The yield of cumin seed is reported to range from 100 to 1,000 lb. per acre, with 500 lb. a fair average production under reasonably good conditions.

Crooks and Sievers[2] suggested the Gulf Coast and the Pacific Coast states for the cultivation of cumin. These authors also advised that the harvesting would be less of a problem if the crop were grown under irrigation in the dry regions of our West and Southwest The tender nature of the plant plus the necessity for complete control of weeds calls for much hand labor; this seems to recommend the crop for Central and South American countries.

Distillation.—The dried fruit is crushed and, immediately after crushing, distilled with steam. Distillation lasts about 12 hr. It is advisable to redistill (cohobate) the distillation water.

According to Gildemeister and Hoffmann,[3] seeds of different origin give the following yields of oil:

	Per Cent
Malta	3.5 to 5.0
Morocco	3.0
East India	2.3 to 3.5
Syria	2.5 to 4.0

Fritzsche Brothers, Inc., New York, obtained yields of oil varying from 2.4 to 3.6 per cent. The yield depends greatly upon the age of the seed, the older seed containing less oil.

Physicochemical Properties.—Oils distilled by Fritzsche Brothers, Inc., from Mediterranean seed had properties varying within the following limits:

Specific Gravity at 15°	0.917 to 0.924
Optical Rotation	+4° 22′ to +5° 6′
Refractive Index at 20°	1.5011 to 1.5038

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[2] *Ibid.*

[3] "Die Ätherischen Öle," 3d Ed., Vol. III, 467.

Aldehyde Content, Calculated as Cuminaldehyde (Hydroxylamine Hydrochloride Method)	47.4 to 51.5%
Solubility in 80% Alcohol	Soluble in 5 vol. and more; occasionally hazy to turbid in 10 vol.

An oil distilled from Mexican cumin seed had these properties:

Specific Gravity at 15°	0.936
Optical Rotation	+2° 55′
Refractive Index at 20°	1.5070
Aldehyde Content, Calculated as Cuminaldehyde (Hydroxylamine Hydrochloride Method)	62.7%
Solubility in 80% Alcohol	Soluble in 2 vol. and more

The odor of this oil was soft, despite its high aldehyde content—an oil of very good quality.

Gildemeister and Hoffmann[4] reported the following properties for oil of cumin seed:

Specific Gravity at 15°/15°	0.900 to 0.930
Optical Rotation	+3° 20′ to +8° 0′
Refractive Index at 20°	1.494 to 1.507
Aldehyde Content, Calculated as Cuminaldehyde (Phenylhydrazine Method)	35 to 42%
Solubility	Soluble in 3 to 10 vol. of 80% alcohol. Oils with a high specific gravity are the more soluble ones

The same authors recommend the hydroxylamine hydrochloride method as giving the best results in the assay of the aldehyde content. The neutral sulfite, as well as the bisulfite method, give too low values in the determination of the cuminaldehyde content.

Fischer, Tornow and Proper[5] assayed the content of volatile oil and its physicochemical properties in various types of commercial cumin seed and arrived at these figures:

	Yield of Oil v/w (%)	*Spec. Grav. 25°/25°*	*Opt. Rot. 25°*	*Refr. Ind. 20°*	*Aldehyde Content*[6] *(%)*
Minimum	3.1	0.8923	+3° 0′	1.4945	32.0
Maximum	4.5	0.9246	+6° 30′	1.5060	42.0
Average	3.53	0.8969	+3° 56′	1.4968	36.5

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[4] *Ibid.*

[5] *Bull. Natl. Form. Comm.* **13** (1945), 6.

[6] Procedure of the Association of Official Agricultural Chemists ["Official and Tentative Methods of Analysis," 6th ed. (1945), 542]. This procedure is a modification of the well-known Sodium Sulfite Method.

On these results the author would like to comment that the figures for the aldehyde content appear rather low; according to his own experience oils distilled from seed soon after the harvest usually have a higher content of cuminaldehyde. Moreover, the method of assaying the aldehydes employed by Fischer, Tornow and Proper, gives too low values in the case of cuminaldehyde.

Chemical Composition.—The first investigations of cumin seed oil date back to the middle of the last century when Bertagnini[7] found that the main constituent of the oil consisted of an aldehyde. Isolating it as bisulfite compound, Kraut[8] prepared cuminaldehyde in its pure form.

The most thorough investigation of cumin seed oil was undertaken by the Schimmel chemists[9] who identified the following constituents:

dl-Pinene and *d*-α-Pinene. Only very small quantities of these terpenes occur in the oil. B. 158°–168°. Benzylamine compound m. 120°–123°. Oxidation of pinene to optically active *d*-pinonic acid m. 68°–69°

p-Cymene. Oxidation to hydroxyisopropylbenzoic acid m. 155°–156°.

β-Pinene. Oxidation of the *p*-cymene fraction gave small quantities of *l*-rotatory nopinic acid m. 125°–126°; oxidation of the nopinic acid with potassium permanganate yielded nopinone; nopinone semicarbazone m. 187°–188°.

Dipentene. The fraction b. 178°, α_D +0° 35′, absorbed about 10 per cent of bromine; by the action of gaseous hydrogen chloride, a dihydrochloride m. 48° was obtained. The small yield of nitrosochloride and the slowness by which it formed pointed toward dipentene.

β-Phellandrene(?). Nitrite reaction negative, but presence of phellandrene indicated by the nature of the products of oxidative degradation.

Cuminaldehyde. The main constituent, 35 to 62 per cent of which is contained in the oil. Isolated and purified through the bisulfite compound.
B_7 97°–99°, d_{15} 0.9731, α_D +0° 3′. Semicarbazone m. 210°–211°; oxime m. 55°–57°. Oxidation with chromic acid to cuminic acid m. 113°–114°.

Dihydrocuminaldehyde (Perillaldehyde). Only small quantities are present in cumin oil. It occurs in the first fractions of the aldehydes. Isolated by fractional crystallization of the semicarbazone m. 200°–201°.
That the hydrogenated cuminaldehyde found by the Schimmel chemists[10] consists actually of perillaldehyde was confirmed later by Berenguer.[11]

Cuminyl Alcohol. In the higher boiling fractions b_7 100°–115°, which do not react with bisulfite but still possess an odor of cuminaldehyde. The ester number (211) after acetylation pointed toward alcohols, although characteristic derivatives could not be obtained. Oxidation with potassium permanganate gave cuminic acid m. 112°–113°.

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[7] *Liebigs Ann.* **85** (1853), 275.
[8] *Ibid.* **92** (1854), 66.
[9] *Ber. Schimmel & Co.*, October (1909), 34.
[10] *Ibid.*
[11] *Anales soc. españ. fís. quím.* **31** (1933), 189. *Chem. Zentr.* I (1933), 3375.

A Compound(?). Traces of a compound b_3 90°–107° occur in the oil but its nature has not been established.

Adulteration.—The most annoying adulterant of cumin oil is synthetic cuminaldehyde, the presence of which cannot be detected analytically, except that the addition of an excess of synthetic aldehyde would affect the optical rotation of the oil.

Use.—Cumin seed oil is employed advantageously instead of the seed in many types of flavoring compounds, especially in curries and culinary preparations of oriental character. Because of its powerful odor and flavor, the oil must be used sparingly and most carefully.

SUGGESTED ADDITIONAL LITERATURE

L. W. Greene, "Chemical Microscopy of Essential Oils," *Perfumery Essential Oil Record* **30** (1939), 309.

OIL OF DILL

Essence d'Aneth *Aceite Esencial Eneldo* *Dillöl* *Oleum Anethi*

Introduction.—Common garden dill, *Anethum graveolens* L., resembles the fennel plant (*Foeniculum vulgare* Mill.) but is smaller. A hapaxanthic annual plant, it grows to a height of 3 or 4 ft. The flowers are yellow. The entire plant is aromatic, but most of the volatile oil is contained in the seed (fruit). Dill leaves are used as a seasoning for soups, sauces, and particularly pickles; the seed is employed as a condiment.

The essential oil can be extracted, by steam distillation, from the herb, including the immature fruit, and from the mature and separated fruit. The two oils, however, differ in composition, and hence in odor and flavor. The so-called herb or "weed" oil (isolated from the overground parts, including the unripe seed) is preferred today by the food industry because of its more characteristic dill herb character. The seed oil, with its high carvone content, resembles oil of caraway. During the last years, dill herb oil has largely replaced the whole herb for flavoring and seasoning purposes.

Anethum graveolens is a native of the Orient and Mediterranean countries, growing wild in various parts of Europe, including Southern Russia, and in Africa and Asia. It is cultivated in the United States, Hungary, Germany, and England.

North American Dill Oil

Habitat and Range.—Although the herb was introduced into gardens of North America many years ago, commercial planting was not started until about 1930. Today the United States is totally independent of its former European sources of supply.

The herb, as well as the oil, is produced in Ohio, Idaho, and Oregon, hundreds of acres being under cultivation. The dill oil industry has set a fine example of what can be accomplished in the United States toward the production of aromatic herbs and essential oils formerly monopolized by Europe.

According to Crooks and Sievers,[1] dill can be grown in the North Central States, and possibly in some of the cooler irrigated valleys in the West, where drying of the crop presents less of a problem than in more humid regions. Dill culture on a commercial scale exclusively for the production of seed for the condiment trade does not appear to offer much opportunity. That it can be grown as an annual and requires no seedbed propagation are favorable factors, but the market outlet is limited and the gross returns are not large. Loss of seed by shattering, and the fact that harvesting must be done at just the right stage, may make it difficult to fit the crop into general farming operations.

The present production of dill oil in the United States is entirely sufficient to cover domestic requirements, and any large scale extension is only likely to lower the prices to uneconomical levels.

Planting and Cultivating.[2]—Dill grows well in any good garden soil, a fertile, prepared, sandy loam being most suitable. Light sand or heavy clay should be avoided. Although a native of Mediterranean countries, dill is quite a hardy plant and may thrive in much cooler climates, provided it finds a warm situation and well-drained soil.

Dill is best grown as an annual crop. The land should be plowed in the fall, or as early in the spring as the weather permits. The usual procedure is to sow the seed, very early in spring, about ½ in. deep, with specially constructed drills. The rows are spaced at 14 to 18 in., the drills 1 ft. apart. Depending on the method of cultivation for the control of weeds, the rows are sometimes spaced as far as 3 ft. apart. It has been claimed that the seed crop is better when the plants are not crowded too much. For the same reason, the plants should be thinned at the proper time, so that their distance in the rows is not less than 6 to 15 in.

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[1] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.,* July (1941).

[2] See also Stockberger, "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935).

Experienced growers try to plant dill herb over a three-week period, so that it will mature during three weeks. By staggering the time of planting, the growers can harvest the herb while it is in prime condition, without getting much overmature herb. This feature has a great influence upon the quality of oil distilled. Unfortunately, it is not always possible to plant in this way, as the seed must be drilled when the weather permits.

One-half ounce of seed suffices for 150 ft. of drill; at this rate, 1 lb. should sow one acre.

Good results have been obtained by sowing late in the fall; the seed then germinates in the spring as soon as conditions become favorable. This is often much earlier than the ground can be prepared and the seed planted, in the case of spring sowing.

When planted early in spring, the herb produces seed the same year. However, if conditions do not favor prompt germination and rapid early growth, the plants may not reach full development, and the seed crop will be small.

Frequent cultivation and freedom from weeds are essential to good crops. Hence dill is cultivated by hand as soon as the young shoots break through the ground. Hand weeding follows, and then cultivation three or four times with power cultivators. The hand weeding is often done by school boys working in groups of fifteen, each group guided by an older supervisor.

Dill herb seems to be more susceptible to weather hazards than most crops. If heavy hail hits the plants during the flowering period, they may be injured so much that the yield of oil is practically nil The same might happen through damage by strong winds or driving rains. Extreme heat during the critical period of maturity is apt to blight the herb, with similar results in regard to yield of oil.

Harvesting.—Proper timing of the harvest is very important, the quality of oil depending mainly upon the state of maturity of herb and seed. The harvest takes place in early fall.

If the crop is grown for the production of herb oil, it should be cut when the most advanced seed is turning brown Since herb oil is used mainly as a substitute for the herb in pickling, the crop must be harvested at exactly the stage when the flavor of the oil is identical to that of the herb as it is generally employed. By staggering the planting time, large areas can be harvested at the proper stage of maturity. Specially built binders are used to mow the herb. It is advisable to harvest only as much as can be processed in the distillery during one day After very short drying in the fields, the herb is hauled to the distillery. Drying for many hours in the field would result in considerable loss of oil by evaporation, especially of the more volatile terpenes. Consequently, the oil distilled from dried herb would be relatively high in carvone, a feature not desirable in herb oils.

When, on the other hand, the crop is grown for seed, a different harvesting procedure must be followed. Crooks and Sievers[3] point out that the progressive ripening of the seed and the tendency of fully ripe seed to shatter involves the same difficulties in the harvesting of dill seed that are encountered in the case of the other aromatic seed crops. The best practice seems to be to mow the plants when the earliest seed is ripe. In very dry weather this is preferably done early in the morning when the plants are damp with dew. The harvested material may be placed in small cocks in the field until dry, when the seed can be easily threshed out. In the case of small plots, the upper parts of the plants may be cut by hand and the material deposited on canvas sheets in which it is taken from the field when dry, thus avoiding loss from shattering; or in case of bad weather, it can be taken directly to a barn or outbuilding and dried under cover. This procedure, however, is impractical for even small acreages of the crop. The threshed seed should be spread in a thin layer and turned over frequently until thoroughly dry. The yield of seed per acre ranges from 500–700 lb.

Courtesy of Fritzsche Brothers, Inc., New York.

FIG. 37. Production of dill herb oil in Fremont, Ohio. Charging of a still with herb material.

Distillation of Dill Herb.—A well-known producer[4] in the mid-west operates six large and modern stills, each holding about 2,000 lb. of green herb. Steam generated in a separate steam boiler is blown through each tank for

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[3] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.,* July (1941).

[4] Courtesy Mr. A. F. Slessman, Fremont, Ohio.

1½ hr., the oil separating in a Florentine flask. Other producers extend the time of distillation to 4 hr.

The yield of oil varies from 20 to 30 lb. per acre; it may be higher or lower in exceptional years.

The quality of the oil runs about uniform, provided the herb is harvested at the proper moment. The herb should be distilled when rather fresh; otherwise, the seed attached to the stacked plant material continues to ripen, and the oil thus obtained approaches the seed character. The more mature the herb, the more hours will be required to complete distillation. Yield of oil increases with the state of dryness, but only to a certain point, because the dried herb containing an abundance of fully ripened seed is very difficult to distill. In fact, it is sometimes impossible to exhaust such plant material, the uncrushed seed yielding its oil only partially and slowly. Distillation of such mature herb is a lengthy process, lasting sometimes 8 or 9 hr.; in this case the oil will be very high in carvone, resembling dill seed oil in that respect.

More exact data on the changes that occur in the chemical composition of dill oil during the various stages of plant growth will be found under Hungarian Dill Oil.

Physicochemical Properties of American Dill Herb Oil.—Numerous samples and shipments of genuine American dill herb oils analyzed by Fritzsche Brothers, Inc., during the past had properties varying within the following limits:

Specific Gravity at 15°	0.880 to 0.910
Optical Rotation	+86° 0′ to +105° 0′
Refractive Index at 20°	1.4770 to 1.4840
Carvone Content (Neutral Sodium Sulfite Method)	12.0 to 40.0%
Solubility	Soluble in 0.5 to 1.5 vol. and more of 90% alcohol; usually clear but occasionally with opalescence

Occasionally pure oils have been examined, the properties of which fell outside the limits described above.

The wide variance in these data is due to the fact that, in actual distillation, the ratio between seed and herb varies considerably. The more seed the distillation material contains and the riper this seed, the higher will be the carvone content of the oil, the higher the gravity, and the lower the optical rotation. The properties of a dill oil depend upon the ratio between the content of phellandrene and carvone, which in turn depends upon the ratio of herb to seed in the distillation material; in other words, upon the state of maturity of the plant.

For flavoring purposes, oils with a low ketone (chiefly carvone) content are generally preferred to those with a high ketone content.

The laboratories of Fritzsche Brothers, Inc., have also examined oils distilled from Indian seed and herb (*Anethum sowa* D.C.); these oils show a higher gravity and lower rotation in relation to the carvone content than the American or European oils. This condition is caused, most likely, by the presence of a larger amount of dillapiole in the Indian oils.

American Dill Seed Oil.—So far, the United States has produced only small quantities of dill seed oil, our food and pickle industries definitely preferring the herb oil. Dill seed oil, with its content of approximately 50 to 60 per cent of carvone, resembles oil of caraway seed in odor and flavor and could be employed as a substitute for that oil, should caraway seed become unavailable. American and European dill seed oil might also serve for the isolation of carvone. (Oil of Indian dill seed, *Anethum sowa* D.C., contains dillapiole and much less carvone than European dill oils.)

Distillation of dill seed oil, like that of any seed material, offers some difficulties of operation. (See chapter on Distillation, in Vol. I of this work, pp. 104, 162.) One acre produces 500 to 700 lb. of dill seed; the yield of oil from the seed is 2.5 to 3.5 per cent.

(For further details on dill seed oil see "Hungarian Dill Oil.")

European Dill Oil

Introduction.—In central Europe *Anethum graveolens* L. is grown in almost every kitchen garden, and in many localities it grows wild. The wild dill propagates itself from the fallen seed.

The herb is widely employed for flavoring meats and vegetable dishes, particularly cucumbers and pickles. The seed is rarely used as such, but considerable quantities are exported to other parts of Europe. In Hungary the essential oils of both the seed and the herb have been produced for some years. In 1947 the dill plantations in that country serving for the distillation of herb oil covered an area of about 70 acres, with a substantial increase planned for the coming years. A much larger acreage has always been devoted to the production of seed.

Planting and Cultivating.—Dill thrives best in a deep soil and can be cultivated where clover and alfalfa grow wild. The plant is not selective; hence it fits well into the rotation of green crops. The soil should be deeply plowed during the fall and extirpated and harrowed in spring. Because of the small size of the seed, the soil must be smooth and free of clods. Care should be taken not to fertilize directly beneath dill, because this would favor uneven ripening and development of weeds. Sowing takes place during the second half of March or the first half of April, when the soil is still sufficiently damp to assure germination. The seed is sown in rows usually

30 cm. apart; but, if the soil is free of weeds, the rows may be only 11 to 13 cm. apart. When planting for seed production the rows are usually kept 35 to 40 cm. apart. The planted seed needs but a thin covering of soil. One Hungarian "kataster joch" (1.422 acres) requires 8 to 10 kg. of seed. The planting must be hoed twice, care being taken to eliminate all weeds. The period of harvest varies and depends upon the weather.

A. Hungarian Dill Herb Oil

Harvesting.—For the production of dill herb oil, the plant should be harvested immediately after the blooming period, when the seed has just started to ripen but is not yet fully developed. This period is very short, lasts not longer than two weeks, and usually falls sometime between the 20th of June and the end of July. To obtain a good, typical herb oil, distillation has to be speeded up and a great amount of plant material must be distilled within a short period of time. If the plants grow too high, they have to be cut off correspondingly higher above the ground to avoid useless stalk material, which contains no oil, and would only fill up the stills with inert matter. The herb should be distilled as fresh as possible; otherwise the seed attached to the stacked up plant material continues to ripen, and the oil thus obtained approaches the undesired seed oil character. One Hungarian "kataster joch" (1.422 acres) produces 1,000 to 2,000 kg. of green dill herb.

Distillation.—Distillation is carried out in stills of 2,000 to 3,000 liter capacity, with direct steam of 5 to 7 atmospheres boiler pressure. Complete distillation of one charge requires from 3 to 4 hr. The yield of oil ranges from 0.29 to 1.50 per cent, depending upon the condition of the plant material, its maturity, height, and state of dryness. The drier and more mature the herb, the more time is required for distillation. However, the yield of oil increases with the state of dryness, but only up to a certain point, because dry herb material containing an abundance of fully ripened seed is very difficult to distill.

Physicochemical Properties of Hungarian Dill Herb Oil.—Samples of genuine Hungarian dill herb oil analyzed in the laboratories of Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 15°	*Optical Rotation*	*Refractive Index at 20°*	*Carvone Content (%)*	*Solubility*
0.897	+88° 10′	1.4829	34.5	In some cases clearly soluble in 80% alcohol; in other cases with haziness or cloudiness
0.908	+81° 10′	1.4855	42.0	
0.898	+90° 12′	1.4832	42.5	
0.878	+101° 4′	1.4800	25.6	
0.903	+85° 5′	1.4849	39.0	
0.900	+82° 30′	1.4841	37.0	

Shipments of pure Hungarian dill herb oils examined by Fritzsche Brothers, Inc., had properties which varied within these limits:

Specific Gravity at 15°	0.878 to 0.900
Optical Rotation	+82° 30′ to +101° 4′
Refractive Index at 20°	1.4789 to 1.4841
Carvone Content (Neutral Sodium Sulfite Method)	22.5 to 37.0%
Solubility	Soluble in 0.5 vol. and more of 90% alcohol. Occasionally oils are soluble in 1 to 10 vol. of 80% alcohol. Solubility improves with increased carvone content

A lower content of carvone is associated with a lower specific gravity and a higher optical rotation.

Changes in the Properties of the Oil During Plant Growth.—Dill herb oil contains two main constituents, i.e., phellandrene and carvone. The more mature and drier the herb material used for distillation, the higher is the carvone content of the oil, and the lower is its content of terpenes (chiefly phellandrene and *d*-limonene). Such an oil, on the basis of odor, properties, and composition, closely resembles seed oil. The typical odor and flavor of herb oil are due mainly to its content of *d*-phellandrene; the higher the content of phellandrene, the more the oil resembles the fresh herb. The herb character predominates as long as the oil contains less than 35 per cent of carvone; in fact, oils of only 20 per cent and less carvone content have the finest and most pronounced herb character. Oils with more carvone exhibit a lower content of phellandrene, usually in favor of more limonene. Such oils resemble seed oils more than herb oils. One Hungarian "kataster joch" (1.422 acres) produces about 8 to 18 kg. of dill herb oil.

A few data[5] may illustrate the changes in the composition of dill herb oils caused by the state of ripeness of the herb material:

1. An oil distilled from partly seeding, partly flowering herb material contained 13.0 per cent of carvone. Optical rotation +106° 0′. The odor possessed a fine dill herb character.

2. An oil distilled from similar material contained 15.6 per cent of carvone. Optical rotation +100° 30′. It had a fine dill herb character.

3. An oil distilled from herb material cut right after the flowering period contained 21.8 per cent of carvone. The odor was similar to the first two oils.

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[5] Private communication from Dr. Jules de Bittera, Budapest.

4. An oil distilled from green herb material cut at the proper moment of maturity, but partly dried before distillation, had a specific gravity at 15° of 0.8929, a carvone content of 34.6 per cent, and an optical rotation of +74° 0′.

5. An oil distilled from half-matured and half-dried herb material had a carvone content of 45.8 per cent.

6. An oil distilled from plant material cut when half-matured, but completely dried after cutting had a carvone content of 52.0 per cent and an optical rotation of +67° 45′.

7. An oil distilled from similar plant material had a carvone content of 58.0 per cent and a specific gravity at 15° of 0.920. It gave a strong phellandrene reaction. The oil was soluble in 0.9 parts of 80 per cent alcohol.

8. An oil distilled from dill seed and chaff had a carvone content of 64.4 per cent.

Adulteration of Dill Herb Oil.—Commercial dill herb oil is frequently adulterated with all kinds of terpenes, e.g., limonene, and the terpenes resulting from the preparation of sweet orange oil concentrates. The most common adulterants, however, are the terpenes obtained in the extraction of carvone from caraway seed oil. It is almost impossible to detect sophistication of that sort in the course of ordinary routine analysis. The oil must, therefore, be submitted to very careful organoleptic tests.

B. Hungarian Dill Seed Oil

Harvesting.—The seed usually ripens from the end of July to the beginning of August. The plants must be harvested when the seeds have lost their green color. The cutting is done with scythes. For further ripening, the plants are stacked up in shocks, four to six sheaves to each pile. The material is then threshed out in regular threshers, such as are used for rapeseed. Subsequently the threshed seed is dried in barns in order to prevent the formation of mold. One Hungarian "kataster joch" (1.422 acres) produces about 300 to 700 kg. of dill seed.

Before distillation the seed must be crushed between heavy cylinders. Hungarian dill seed yields from 2.30 to 3.50 per cent of oil.

Physicochemical Properties of Hungarian Dill Seed Oil.—The physicochemical properties of commercial Hungarian dill seed oil usually correspond with those given by Gildemeister and Hoffmann[6] for European oils in general:

Specific Gravity at 15°	0.895 to 0.915, usually above 0.900; in exceptional cases up to 0.917

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[6] "Die Ätherischen Öle," 3d Ed., Vol. III, 528.

Optical Rotation	+70° 0′ to +82° 0′
Refractive Index at 20°	1.484 to 1.491
Carvone Content (Neutral Sodium Sulfite Method)	40.0 to 60.0%, usually 40.0 to 55.0%
Solubility	Soluble in 4 to 9 vol. of 80% alcohol; exceptionally in 1.5 to 2.0 vol.

These figures should be slightly modified. Some lots of Hungarian seed oil have a carvone content exceeding 60.0 per cent: their specific gravity is correspondingly higher (around 0.926), their optical rotation correspondingly lower (around +67° 0′).

Two genuine European dill seed oils examined by Fritzsche Brothers, Inc., had these properties:

	Hungarian Oil	*Russian Oil*
Specific Gravity at 15°	0.919	0.918
Optical Rotation	+76° 25′	+71° 10′
Refractive Index at 20°	1.4881	1.4882
Carvone Content (Neutral Sodium Sulfite Method)	53.0%	53.6%
Solubility	Soluble in 1 to 1.5 vol. and more of 80% alcohol	

One exceptional lot of Hungarian dill seed oil had these properties:

Specific Gravity at 15°	0.940
Optical Rotation	+58° 30′
Refractive Index at 20°	1.4919
Carvone Content	68.0%
Solubility	Soluble in 4 vol. of 70% alcohol

The quite unusual properties of this lot suggest the conclusion that the oil was distilled partly, if not entirely, from chaff. Nevertheless, the odor and flavor of this oil were normal.

ENGLISH DILL SEED OIL

In England dill is grown in Suffolk, Bedfordshire, and Lincolnshire.

The plant, an annual, requires a well-drained soil of medium to light texture. For planting the seed is sown during March or early April, in drills 12 in. apart, on the basis of 10 to 12 lb. per acre. The plantings must be kept free from weeds. The crop matures about the middle or end of August. Good judgment is required to recognize the proper state of plant maturity for harvesting. At this time as many seeds as possible should be nearly ripe, before having reached the stage where they drop off. Not all the seed in a single planting ripen at the same time. The whole plant is then mown, the sheaves are stocked in the field and left for complete ripening of the seed, after which the crop can be threshed. One acre yields about 700 lb. of dill seed.

Prior to distillation the seed is crushed between heavy rollers, then mixed with water and distilled in stills fitted with a steam jacket (water distillation—see Vol. I of this work, pp. 112, 120 and 142), the aqueous phase of the distillate being returned to the still for cohobation. If, on the other hand, the spent seed is to serve as cattle feed, the crushed seed is placed in steam stills and distilled with live steam as in the case of lavender or peppermint. The exhausted seed will then be relatively dry.

The yield of oil from crushed seed ranges from 3 to 4 per cent.

Physicochemical Properties of English Dill Seed Oils.—English dill seed oils examined in the laboratories of Stafford Allen and Sons, Ltd., London,[7] had properties which varied within these limits:

Specific Gravity at 15.5°	0.898 to 0.915
Optical Rotation at 20°	+74° 0′ to +82° 0′
Refractive Index at 20°	1.4830 to 1.4880
Ketone Content, Calculated as Carvone	48% to 57%
Solubility at 15.5°	Soluble in 7 to 10 vol. of 80% alcohol; soluble in 0.2 to 0.5 vol. of 90% alcohol

CULTIVATION OF DILL IN GERMANY

Germany's main producing areas were located in the provinces of Saxony (Aschersleben and environs), Thuringia (Erfurt and environs) and Silesia (Liegnitz and environs). Years ago, dill was cultivated quite extensively in Germany; but the much cheaper seed from Poland, Holland, and Central European countries brought about a gradual reduction in the dill acreage of Germany. Thuringia and Saxony, because of their suitable soil, still produce some dill.

In Germany, the entire plant is used for the flavoring of dill pickles, sometimes in conjunction with the seed. There exists an occasional demand for distillers' seed but, so far, herb containing the seed is not distilled in Thuringia or in the province of Saxony. Pickle manufacturers purchase the entire plant when it is green-yellow because in this state it has the desired and characteristic odor and flavor.

The soil should be light; medium soil, too, will do, unless it is clayey or sandy. For cultivation purposes, the seeds are machine drilled directly in the fields, between March and May. The rows are spaced 20 to 22 cm.

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[7] Private communication.

apart, but the plants in each row are kept quite close. Dill, an annual crop, must be sown every year. The herb commences to grow at the end of May or the beginning of June. When the flowers turn yellow the plants are cut for use in pickles. If not cut, the flowers shortly thereafter turn to a deep yellow. In this state, too, the plants may be used for pickling purposes; in fact, this period (end of June) is the principal cutting season. During August the seeds develop and turn brown, the plants then becoming unsuitable for the flavoring of pickles. From the middle of August to mid-September the seeds mature fully and must be harvested very carefully. For this purpose the plants are cut with scythes or machines, then bundled and stacked up in the fields until all seeds become fully ripe and dry. Subsequently the material is transported into barns and threshed in machines. Finally the seed is winnowed.

SPANISH DILL HERB (WEED) OIL

Spain used to produce small quantities of dill herb oil, distilled from the overground parts of plants containing the green, unripe seed. These plants grow wild in the provinces of Huelva and Extremadura. The harvest takes place in June and July. Distillation of one charge lasts from 5 to 8 hr., 150 kg. of herb material yielding about 1 kg. of oil. Production of this type of oil could be stepped up to about 4,000 lb. per year, provided a sufficiently attractive price was paid for these oils. However, the odor and flavor of this type of oil is inferior to that of the Hungarian or American oils which are distilled from cultivated herb. The Spanish oils, distilled from wild growing plants, contain only a small percentage of carvone; they exhibit a strong phellandrene reaction.

CHEMICAL COMPOSITION OF DILL SEED OIL

Carvone. The main constituent, amounting to 40 to 60 per cent of the oil, was identified by Gladstone[8] and by Beyer.[9] It is identical with the carvone occurring in caraway seed oil.

d-Limonene. Found by Wallach[10] as the principal terpene. It is present in the fraction b. 175°–180° and was identified as tetrabromide m. 104°–105°.

Phellandrene. The Schimmel chemists[11] obtained a positive reaction with sodium nitrite and glacial acetic acid in an English oil, also in Spanish oils, i.e., in those dill oils which are distilled from the seed *and* herb. German oils, distilled exclusively from seed, gave a positive phellandrene reaction only if the first fraction was tested.

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[8] *J. Chem. Soc.* (London) **25** (1872), 1–25. *Jahresber. Chem.* (1872), 816.

[9] *Arch. Pharm.* **221** (1883), 283.

[10] *Liebigs Ann.* **227** (1885), 292.

[11] *Ber. Schimmel & Co.,* April (1897), 16; October (1898), 20.

Paraffins. Occur in the fractions boiling above carvone. Crystallized from petroleum ether, they melt at 64°.

Dillapiole b. 285°, which occurs in Indian seed oil (*Anethum sowa* D.C.), has not been found in European oils distilled exclusively from seed.[12]

The above mentioned constituents were identified years ago in dill seed oils of European origin. More recently, Branigan[13] reported that dill seed oil contains also

α-Pinene. Traces only; nitrolbenzylamine m. 123.1°.

Dipentene. Tetrabromide m. 125°.

Dihydrocarvone. Identified as dibromide m. 70.4° and as oxime m. 89° in a small fraction of dill oil produced from American seed.

According to the same worker,[14] small quantities of α-pinene, dipentene, and dihydrocarvone occur in both European and American dill seed oils.

CHEMICAL COMPOSITION OF DILL HERB OIL

The Schimmel chemists[15] identified the following compounds in oil distilled from dill herb:

d-α-Phellandrene. The main constituent, α_D +88° 22′, d_{15} 0.8494. Nitrite m. 109°–113°.

Terpinene. Identified as nitrite m. 155°–156°, dihydrochloride m. 51°–52°, and as terpinene terpin m. 136°–137°.

Limonene or Dipentene. *Cis*-terpin hydrate m. 116°–117°.

Carvone. Present in much smaller quantities than in the seed oil.

Dillapiole. Conversion into dillisoapiole m. 44°–45°, also dillapiolic acid m. 150°–151°.

Isomyristicin. Originally mistaken for dillisoapiole, this compound m. 44° finally proved to be isomyristicin $C_{11}H_{12}O_3$ which also occurs in mace oil; confirmation by mixed melting point.

Oxidation with ozone and reductive splitting of the ozonide easily gave myristicinaldehyde m. 131°.

Myristicin. The same investigators[16] identified myristicin $C_{11}H_{12}O_3$ in the fraction b_4 126°, d_{20} 1.1442, n_D^{20} 1.5407; confirmed by combustion analysis and preparation of dibromomyristicin dibromide m. 130°.

In the high boiling fractions a bluish compound and waxes, both not yet identified, were noticed.

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[12] *Ibid.*, April (1897), 16.

[13] *Am. Perfumer* **48** (Feb. 1946), 69.

[14] Private communication by Mr. G. V. Branigan, New York.

[15] *Ber. Schimmel & Co.*, April (1903), 24; October (1908), 38; (1927), 25.

[16] *Ibid.*

In a more recent publication, Branigan[17] lists *α-pinene* and *camphene* as constituents of dill herb oil, but does not indicate how he identified these terpenes.

Steam distilling a concentrated extract of dried dill herb, Elze[18] obtained a volatile oil, d_{15} 0.903, α_D +68°, which contained *n-octyl alcohol* b. 190°–192.5°, d_{15} 0.830.

Use of Dill Herb Oil

The employment of dill herb oil produced from the whole overground part of the plant has become increasingly extensive in the United States and Canada. At first, it was used primarily to flavor processed dills produced from salt stock, and in many cases it completely replaced the dill herb itself for that application. The lack of uniformity of flavor, obtained from the use of dill herb in so-called genuine dills, later prompted many manufacturers to supplant the herb with the corresponding oil, to accentuate and standardize the flavor. This now constitutes a very regular practice, with an increasing tendency to depend more and more on the oil and less on the herb itself.

Fabian,[19] in the course of investigations on the conservation of spices in food manufacture, found that dill herb actually absorbs some of the essential oils from some of the other spices (pimenta, cassia, bay leaves, mustard, celery seed, chili, peppers, cardamom, and ginger root) employed for making dill pickles. The same author demonstrated the great waste of essential oils when whole spices are used.

Since oil of dill herb is not particularly soluble in the acid brine used for dill pickles, it is very important for its successful employment that due steps be taken to insure as complete a solution as possible.

This involves first cutting or dissolving the oil with some neutral solvent, followed by the addition of this oil solution to the brine during vigorous and fairly prolonged agitation of the latter. Such agitation is frequently accomplished by means of a high-speed pump, e.g., a centrifugal pump, which repeatedly circulates the brine in and out of the mixing tank. Another device consists of a high-speed electric mixer, the shaft of which is long enough so that the propellers come close to the bottom of the tank, insuring a complete circulation of the contents.

Only after the oil is completely dispersed in the brine should the latter be used to cover the pickles.

For diluting the oil, alcohol is occasionally employed, but it can be replaced by glacial acetic acid. In other cases, the oil is reduced to 5 or 10 per cent strength in the form of an emulsion, with gum acacia or any other

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[17] *Am. Perfumer* **48** (February 1946), 65.

[18] *Riechstoff Ind.* (1926), 192.

[19] *Food in Canada,* October (1942).

suitable emulsifying agent. A third method consists of absorbing the oil in some suitable dry medium, such as salt or dextrose.

It has been stated that the oil, and therefore the flavor, will be absorbed more rapidly by the pickles if the brine is not previously acidified; in other words, if the acid be added to the flavored brine after the pickles have stood in it for some time. This is supposed to reduce the "slick" condition, which detracts from the physical appearance of the pickle. On the other hand, this soaking must not be too prolonged, or the pickle may tend to become soft and lose its "snap." The size and variety of the pickle, its condition when flavored, and other factors will necessitate a variation in treatment; the best conditions must be determined experimentally by the individual manufacturer.

This applies also to the proportion of oil employed. In general, 1 oz. of oil of dill herb, dissolved in 3 to 7 vol. of alcohol or similar solvent, supplies the flavor for a 45 gal. cask of dills containing, on the average, 17 to 20 gal. of liquor.

Oil of dill herb enjoys considerable application also in spice oil combinations designed for the seasoning of meat products, relishes, and other condiments.

Use of Dill Seed Oil.—Dill seed oil used to be employed as a flavoring agent by the food industries before the introduction of the now much more popular dill herb ("weed") oil. Since then the consumption of the seed oil has declined considerably. As has been pointed out, dill seed oil, with its high carvone content, resembles oil of caraway seed and may be employed as a substitute for the latter.

Indian and Japanese Dill Seed Oil

For a long time botanists were doubtful as to whether the dill plant cultivated in India and Japan is identical with *Anethum graveolens* L., or whether it represents a different species. Lately, however, the Indian plant has been classified as *Anethum sowa* D.C. The fact remains that the oils distilled from the seed of the two plant types differ in regard to their physicochemical properties and chemical composition. The so-called Sowa plant is a glabrous herb, cultivated in the Punjab plains (India).

The yield of essential oil from the Indian and Japanese seed ranges from 1.20 to 3.5 per cent.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[20] the properties of East Indian and Japanese dill seed oil vary within the following limits:

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[20] "Die Ätherischen Öle," 3d Ed., Vol. III, 533.

Specific Gravity at 15°	0.9480 to 0.9896
Optical Rotation	+41° 30′ to +48° 12′
Refractive Index at 20°	1.491 to 1.499
Carvone Content (Sulfite Method)	19.0 to 22.0%

Chemical Composition.—When distilling Indian or Japanese dill seed, a portion heavier than water separates in the Florentine flask. This fraction, according to Ciamician and Silber,[21] consists of dillapiole (4-allyl-5,6-dimethoxy-1,2-methylenedioxybenzene). Dillapiole occurs also in sea-fennel oil.

Use.—Compared with regular dill seed oil, the East Indian or Japanese kind has attained little commercial importance.

SUGGESTED ADDITIONAL LITERATURE

"Dill Herb Oil," *Ber. Schimmel & Co.* (1928), 23.

J. L. Sarin and M. L. Bari, "Northern India Essential Oils," *Am. Perfumer* **38**, No. 2 (1939), 30, 84.

National Farm Chemurgic Council, Research Division, *Report No. 562* (1940).

OIL OF FENNEL

Essence de Fenouil *Aceite Esencial Hinojo* *Fenchelöl*
Oleum Foeniculi

Botany, Habitat, and Range.—There exist about a dozen varieties of fennel fruit (or seed, as it is called commercially) which differ in appearance, odor, and flavor. The same is true of the volatile oils recovered from the dried ripe fruit by steam distillation. This monograph will deal only with the more important types.

Foeniculum vulgare Miller is divided into two subspecies. The varieties which yield the essential oils described in the following pages belong to the subspecies *capillaceum* (Gilib.) Homboe:

Var. *vulgare* (Miller) Thellung is cultivated and grows wild. It furnishes the oil of *bitter* fennel (I. a and b).

Var. *dulce* (Miller) Thellung is cultivated; it does not occur wild. This variety yields the oil of *sweet* or Roman fennel (II.).

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[21] *Ber.* **29** (1896), 1799.

I. Oil of *Bitter* Fennel.

(a) The plant is *cultivated* chiefly in Roumania and Southern Russia, but also in Czechoslovakia, Hungary,[1] Germany, France, Italy, India, Argentina, Japan, and other countries, among them lately the United States. These regions produce the bulk of seed from which commercial bitter fennel oils are distilled.

(b) The plant grows *wild* in France, Spain, Morocco, and Algeria. The oil is distilled largely from the overground parts, especially the tops, while they bear fruit (seed). Commercially the wild growing plant is of little importance.

II. Oil of *Sweet* or Roman Fennel Seed, also called French *Sweet* Fennel.

This plant is *cultivated* in France, Italy, and Macedonia. The oil is distilled from the seed. Of all the fennel oils, this type possesses the finest odor and flavor.

Foeniculum vulgare Miller is a herbaceous perennial, in some places grown as a hapaxanthic biennial, in others as an annual, 4 to 5 ft. high, which has been known since antiquity in Europe and the Far East. The dried, aromatic fruits, or seeds, are widely employed in culinary preparations for flavoring bread and pastry, in candies, alcoholic liqueurs of French type, as well as in oral and medicinal preparations. Oil of fennel is one of the most important all-round flavoring agents.

The plant bears 3–4 leaves pinnated into almost thread-like segments; the compound umbels of yellow flowers carry 10 to 20 rays, each ray ending in a smaller umbel. Small flowers, containing 5 petals, appear in July. The oval shaped, greenish fruit or seed varies in length from 4 to 10 mm. Odor and flavor are strong and sweet, but possess a somewhat bitter "by-note."

Fennel grows wild on almost any good soil, in sunny localities with a fairly mild climate. It thrives best in rich, well-drained loam, or black, sandy, and sandy-clay soils which contain sufficient lime. Too much dampness or moisture favors excessive development of leaves and stalks rather than seed, a feature undesirable from the producers' viewpoint.

Bauer[2] suggested the following classification of commercial fennel seed:

1. Var. *vulgare* = dark fennel seed, originating mainly from northern (European) countries.
2. Var. *dulce* = light or sweet fennel seed, originating mainly from southern (European) countries.
3. Var. *panmorium* = East Indian fennel seed.

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[1] Guenther, "Hungarian Essential Oils," *Am. Perfumer* **37** (July 1938), 42.

[2] *Pharm. Zentralhalle* **83** (1942), 541.

These varieties, according to Bauer, belong to the subspecies *capillaceum* (garden fennel). However, no sharp distinction from the subspecies *piperitum* can be made, the former being merely a highly developed form of the latter, the result either of very fertile soil or of plant selection. The varieties of the subspecies *capillaceum* differ from one another mainly by the form of their stalks, their fruit (seed), and in regard to flavor (chemical composition of the essential oil).

Planting and Cultivating.[3]—Crooks and Sievers[4] point out that although fennel is readily grown from seed, it can also be propagated by root and crown divisions. The seed may be sown directly in the field, late in the fall or early in the spring. It is sown thickly in drills, 2 or 3 ft. apart, and covered lightly. According to Stockberger,[5] 4 to 5 lb. of seed are required per acre; whereas Willkie and Kolachov[6] suggest 7 to 9 lb. When well established, the plants may be thinned to stand 12 to 15 in. apart in the row. The plants may also be started in a seed bed and transplanted to the field when 3 to 4 in. high. Cultivation required is the same as for ordinary garden crops.

Harvesting and Preparing for the Market.—As a rule, very little seed is produced during the first year, but full crops may be expected in succeeding years. The seed should be harvested in the fall, before it is fully ripe, but sufficiently hard and of greenish-gray color. It is borne on umbels and, although all the seed on an umbel matures within a fairly short time, not all of the umbels develop on the plant at the same time. When harvesting by hand it is possible, according to Crooks and Sievers,[7] to gather the more mature umbels first and go over the plants again once or twice when the remainder have matured. The harvested material must be dried, for which purpose it is spread on a dry floor in some suitable building, or in the open, if the weather is favorable. Harvesting in this manner is tedious and requires much labor, but it appears to be the only way of gathering all the seed at the most desirable stage. Cutting the entire tops at one time with suitable machinery, stacking in the field until fully cured and dried (which takes three to four days) and then threshing with a modified grain thresher, seems to be the only possible procedure for handling the crop at a low labor cost. In this case, however, some seed will undoubtedly

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[3] In this connection, see also Stockberger, "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935), 22. Willkie and Kolachov, "The Domestic Production of Essential Oils from Aromatic Plants," *Natl. Farm Chemurgic Council Bull.*, Columbus, Ohio (1940), 28.

[4] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941), 19.

[5] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935), 22.

[6] "The Domestic Production of Essential Oils from Aromatic Plants," *Natl. Farm Chemurgic Council Bull.*, Columbus, Ohio (1940), 28.

[7] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941), 19.

be lost; if too ripe it will shatter, and if too immature it will not be of good quality when cured.

Yield of Seed.—Crooks and Sievers[8] estimate the yield of fennel seed at 600 to 800 lb. per acre, although small experimental plots have, in some cases, indicated substantially larger yields. Willkie and Kolachov[9] claim 1,000 to 1,400 lb. of seed per acre.

Consideration of Domestic Production.—Crooks and Sievers[10] believe that fennel is adapted to the Central and Northern states and probably to certain sections of California where, in some places, it has escaped from cultivation and grows to a large size. Because the seed can be sown directly in the fields and, after the first year, the plants are of such size that no hand cultivation or weeding is required, introduction of this plant seems indicated. On the other hand, economical harvesting without considerable loss of seed seems improbable, and gross returns are not believed adequate to justify much hand labor. The opportunity for growing fennel is, moreover, limited, since less than 500 acres are needed to supply normal annual domestic requirements. This, however, does not take into account the considerable quantities of fennel oil which the United States used to import before World War II.

Becker, Ister and Goodrich[11] cultivated fennel (*Foeniculum vulgare* Mill.) in the drug garden of the College of Pharmacy, University of Washington, and obtained 4.1 per cent of volatile oil from the ground fruit. The oil met all the requirements of the "United States Pharmacopoeia," Eleventh Revision, except that the solubility in alcohol and the congealing point were slightly low.

Distillation and Yield of Oil.—The seed must be crushed prior to distillation, and then distilled immediately, to avoid loss of oil by evaporation. The yield of oil from best grade seed of eastern European origin ranges from 4 to 5 per cent; it should be at least 2½ per cent. Old seed is liable to give a lower yield than seed from the latest harvest.

According to Clevenger,[12] the yield of volatile oil varies considerably, being highest in seed of German and Roumanian origin and lowest in East Indian seed.

Assaying various types of commercial fennel seed for their content of volatile oils, Fischer, Tornow and Proper[13] found that the yield of oil ranged from 1.0 to 6.0 per cent, the average being 3.51 per cent.

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[8] *Ibid.*

[9] "The Domestic Production of Essential Oils from Aromatic Plants," *Natl. Farm Chemurgic Council Bull.*, Columbus, Ohio (1940), 28.

[10] "Condiment Plants," *U. S. Dept. Agr., Bur. Plant Ind.*, July (1941), 19.

[11] *J. Am. Pharm. Assocn.* **29** (1940), 499.

[12] *J. Assocn. Official Agr. Chem.* **25** (1942), 962.

[13] *Bull. Natl. Form. Comm.* **13** (1945), 6.

Distilling fennel seed in Southern France, the author obtained the following yields of oil:

	Per Cent
French Seed	2.5 to 3.0
Levant Seed	1.4
Spanish Seed	3.75

During distillation it is important to keep the temperature of the condenser sufficiently high to prevent the oil from congealing therein.

The distillation residues, after drying, represent a valuable cattle feed, containing 14.0 to 22.0 per cent of proteins and 12.0 to 18.5 per cent of fat.

Physicochemical Properties.—

I. Oil of *Bitter* Fennel

(a) The properties of oils distilled from *cultivated bitter* fennel seed (*Foeniculum vulgare* Mill.), according to Gildemeister and Hoffmann,[14] vary within the following limits:

Specific Gravity at 15°/15°	0.965 to 0.977
Optical Rotation	+11° 0′ to +24° 0′, usually +11° 0′ to +20° 0′
Refractive Index at 20°	1.528 to 1.539
Congealing Point	Not below +5° and as high as +10° in good oils. Oils of somewhat inferior quality may have a congealing point as low as +3° which must be considered the lowest limit
Solubility	Soluble in 5 to 8 vol. of 80% alcohol (sometimes with slight turbidity), and in 0.5 vol. of 90% alcohol

An oil of fennel distilled at the College of Pharmacy, University of Texas, Austin, and analyzed in the laboratories of Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 25°/25°	0.961
Optical Rotation	+15° 0′
Refractive Index at 20°	1.5320
Congealing Point	+6.2°
Solubility at 20°	Hazy in 7 to 10 vols. of 80% alcohol; clearly soluble in 0.5 to 1 vol. of 90% alcohol and more

Regarding the determination of the congealing point, see Vol. I of this work, p. 253. It is possible to estimate the anethole content of a fennel

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[14] "Die Ätherischen Öle," 3d Ed., Vol. III. 516.

oil from the congealing point; for further data see the monograph "Oil of Anise," Physicochemical Properties.

Oils distilled in the U.S.S.R. from the seed of cultivated bitter fennel, and analyzed in the New York laboratories of Fritzsche Brothers, Inc., had the following properties:

Specific Gravity at 25°/25°	0.971 to 0.973
Optical Rotation	+14° 15′ to +15° 45′
Refractive Index at 20°	1.5331 to 1.5370
Congealing Point	+4.4° to +5.2°
Solubility at 25°	Soluble in 4 to 5 vol. and more of 80% alcohol; soluble in 0.5 vol. and more of 90% alcohol

(b) The oils distilled from the entire overground parts of *wild growing bitter* fennel (*Foeniculum vulgare* Mill.), during the early fruiting period, seldom congeal, even in a freezing mixture, because they contain very little anethole. They usually show a strongly positive phellandrene reaction. As the seed ripens the anethole content increases, for which reason it is advisable to harvest the wild plants as late as possible. This rule, however, is not always followed in Morocco, Algeria, or Spain.

Commercially these oils are unimportant.

In Morocco, *Foeniculum vulgare* Mill. grows spontaneously in most regions where pennyroyal occurs, especially on the great plains between the Sebou and Defale rivers. Since sheep and other herbivorous animals feed on these plants, only limited quantities of oil could be produced—perhaps 4 to 5 tons a year at the most. When distilled during seed formation in July, the plant yields about 0.7 per cent of oil. Distillation of one batch of 100 kg. of plants lasts 1½ to 2 hr. If the material is distilled prematurely, the yield of oil is only 0.5 per cent.

An oil of wild fennel distilled during the author's visit to the Medium Atlas in 1937 from stalks, flowers, and leaves, had these properties:

Specific Gravity at 25°	0.879
Optical Rotation	+57° 50′
Refractive Index at 20°	1.4689
Congealing Point	The oil did not congeal when cooled to −20°
Phellandrene Reaction	Strongly positive
Solubility	Not clearly soluble in 80% alcohol, up to 10 vol.; soluble in 0.5 vol. and more of 90% alcohol

From these properties it appears that the oil contained very little, if any, anethole, the oil having been distilled before seed formation.

An oil of fennel distilled in Spain from wild-growing plants was analyzed by Fritzsche Brothers, Inc., New York:

Specific Gravity at 25°/25°	0.911
Optical Rotation	+43° 18′
Refractive Index at 20°	1.4969
Congealing Point	The oil did not congeal when cooled to −18° and seeded with a crystal of anethole
Solubility	Soluble in 1 vol. of 90% alcohol, hazy in more

The odor of this oil was reminiscent of anethole, but differed from that of both anise seed oil and fennel seed oil.

Gildemeister and Hoffmann[15] gave the following limits for bitter fennel oils distilled from *wild growing* plants:

Specific Gravity at 15°	0.893 to 0.925
Optical Rotation	+40° 0′ to +68° 0′
Refractive Index at 20°	1.484 to 1.508
Solubility	Soluble in 0.5 to 1 vol. of 90% alcohol; sometimes with opalescence

An Italian fennel oil distilled in Calabria during 1939 from the plant tops and the seed-free umbels by Sorgonà Luisi[16] had these properties:

Specific Gravity at 20°	0.9230
Optical Rotation at 21°	+48° 0′
Refractive Index at 21°	1.5030
Acid Number	1.33
Ester Number	30.58
Ester Number after Acetylation	67.90
Solubility	Soluble in 6 vol. of 85% alcohol

II. Oil of French *Sweet* or Roman Fennel Seed (*Foeniculum vulgare* Mill. var. *dulce* Bert.)

The yield of these oils varies from 2.5 to 3.0 per cent. Their odor and flavor are sweeter due to the high anethole content and absence of fenchone. According to Gildemeister and Hoffmann,[17] the properties of sweet fennel oils vary between these limits:

Specific Gravity at 15°	0.976 to 0.980
Optical Rotation	+5° 0′ to +16° 30′
Congealing Point	+10.0° to +14.5°

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[15] *Ibid.*, 522.

[16] *Boll. ufficiale staz. sper. ind. essenze deriv. agrumi* **15** (1940), 38. *Chem. Abstracts* **37** (1943), 3561.

[17] "Die Ätherischen Öle," 3d Ed., Vol. III, 521.

Oils distilled by the author in Southern France from the seed of French sweet fennel possessed the following properties:

Specific Gravity at 25°	0.971 to 0.978
Optical Rotation	+4° 15′ to +5° 4′
Refractive Index at 20°	1.5500 to 1.5519
Congealing Point	+13.3° to +14.8°
Solubility at 25°	Soluble with haziness in 8 to 9 vol. of 80% alcohol; soluble in 1 vol. and more of 90% alcohol

The odor and flavor of these oils were far superior to those of bitter fennel seed oil.

In the course of eight years, Clevenger[18] analyzed representative samples of many shipments of *all types of fennel* seed entering the port of New York. He determined the yield of volatile oil and physicochemical characteristics. The seeds were grouped into six classes: Roumanian, Argentinean, German, French, East Indian, and Italian. The bitter fennel, usually of Italian origin, varied considerably in size and apparent maturity.

The investigations of Clevenger led to these conclusions:[19]

1. The specific gravity found for each group of seed was within the range of expectancy. It ranged from 0.951 to 0.991 at 25°/25°.
2. The optical rotation for each of the oils was positive and ranged from +3° 30′ to +22° 6′ at 25°. In general, the oils of the Roumanian, German and Italian (bitter) fennel gave uniformly high positive rotations. The oils of the Argentinean and French seed gave distinctly lower positive rotations. The optical rotation of the oil from the French seed showed considerable variation.
3. The refractive indexes of all the oils were reasonably uniform. The refractive indexes of oils from the bitter fennel were definitely lower than those of the other varieties.
4. The congealing temperatures for most of the oils were reasonably uniform (from +1.0° to +12.5°), except that the oil from one shipment of seed from Argentina congealed at −3.0°. The oils from the bitter fennel would not congeal even when the temperature was lowered to −15.0°.

Chemical Composition.—The chemical composition of fennel oil varies widely, according to the plant variety from which the oil has been distilled and according to the regions of origin. Needless to say, the seed oils are quite different from the herb oils. In other words, oils distilled exclusively

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[18] *J. Assocn. Official Agr. Chem.* **25** (1942), 962.

[19] For exact figures see the tabulation in the original literature.

from seed are at variance with those distilled from the whole overground herb at different stages of maturity, e.g., blooming or seeding. Our food, beverage, and pharmaceutical industries employ seed oil almost exclusively.

I. Oil of *Bitter* Fennel Seed [*Foeniculum vulgare* Mill. var. *vulgare* (Mill.) Thellung]

(a) The plant is *cultivated* and the oil is obtained from the seed by distillation.

The following constituents have been identified:

d-α-Pinene. Identified by the Schimmel chemists[20] in the fraction b. 155.5°–157.5°, nitrolbenzylamine m. 122°.

Camphene. Conversion with glacial acetic acid-sulfuric acid into isobornylacetate b_{12} 65°, and saponification of this ester to isoborneol m. 208.5°.

d-α-Phellandrene. In the fraction b_7 49.2°–55°, α_D +34° 34′. Identified as nitrite m. 114° by the Schimmel chemists.[21]

Dipentene. Identified in the fraction b. 180° as dihydrobromide m. 94°, and as tetrabromide m. 124°–125°.

Anethole. Investigations of this phenolic ether, the main constituent of fennel seed oil, date back as far as the end of the eighteenth and beginning of the nineteenth centuries. Good fennel seed oil contains 50 to 60 per cent of this compound. It may be isolated by freezing the oil or its corresponding fractions. According to Shchetinin,[22] the total content of anethole separated from fennel oil is approximately 60 per cent. Only half of this amount can be brought to the Pharmacopoeial product by a gradual rectification.

Anethole is a white, crystalline substance, of intensely sweet anise-like odor and flavor. At 22.5° it melts to a colorless, optically inactive, strongly refractive liquid of anise-like odor and very sweet taste.

For further details regarding "Anethole" see Vol. II of this work, p. 508.

It is interesting to note that anethole is not present, or only in small quantities, in oils distilled from the fruiting tops of *wild* growing bitter fennel.

Aside from anethole, bitter fennel seed oil contains another oxygenated compound:

d-Fenchone. According to Wallach and Hartmann,[23] a ketone of intensely bitter, camphor-like odor and flavor. Fenchone is present only in the *bitter* fennel seed oils and responsible for their somewhat coarse, bitter taste. It does not occur in oils distilled from *sweet* or Roman (French) fennel seed (*Foeniculum vulgare* Mill. var. *dulce*).

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[20] *Ber. Schimmel & Co.*, April (1890), 20; April (1906), 29.

[21] *Ibid.* Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 519.

[22] *Trudy Vsesoyuz. Inst. Efirno-Maslichnoĭ Prom.* (1940), No. 8, 137. *Chem. Abstracts* **37** (1943), 3558.

[23] *Liebigs Ann.* **259** (1890), 324; **263** (1891), 129.

A further oxygenated constituent of bitter fennel oil is—

Methyl Chavicol (Estragole). Identified by Tardy.[24] It has a slight anise-like odor, but not the sweet flavor of anethole. Methyl chavicol is liquid at room temperature and, like anethole, optically inactive.

Foeniculin. A phenolic ether, $C_{14}H_{18}O$, of unknown structure was first reported by Takens.[25] It resembles anethole and occurs in the fraction b_{4-5} 150°, d_{15} 0.967, $\alpha_D \pm 0°$, congealing point 21.5°.

More recently Späth and Bruck [26] identified this phenolic ether as *p*-anol prenyl ether. (See Vol. II of this work, p. 512.)

Aldehydes. Traces only.

Basic Constituents. Of disagreeable pyridene-like odor and giving a faint pyrrole reaction, found [27] in the first runnings of fennel seed oil.

Anisaldehyde. In very small quantities.

Anisic Acid. The oxidation products of all oils containing anethole also occur in fennel seed oil.

(b) The plant grows *wild.* Oils distilled from the whole overground parts of the plants during the fruiting period contain little, if any, anethole. Their chemical composition was investigated by Wallach,[28] by the Schimmel chemists,[29] and by Tardy [30] who identified the following constituents:

d-α-Phellandrene. The main constituent.

Pinene.

Anethole. Very little if any.

Fenchone.

Methyl Chavicol.

A Sesquiterpene.

A Compound, $C_{10}H_{14}O_2$. Probably thymohydroquinone.

Ethylfenchyl Alcohol(?). Occurs, according to Dorronsoro,[31] in the highest fractions of oils distilled near Cordoba.

Fenchyl Alcohol. Viguera Lobo [32] investigated the composition of Spanish fennel oil and, reported the presence of fenchyl alcohol.

[24] *Bull. soc. chim.* [3], **17** (1897), 660.

[25] *Riechstoff Ind.* **4** (1929), 8.

[26] *Ber.* **71** (1938), 2708.

[27] *Ber. Schimmel & Co.*, April (1906), 29.

[28] *Liebigs Ann.* **239** (1887), 40.

[29] *Ber. Schimmel & Co.*, April (1901), 12.

[30] *Bull. soc. chim.* [3], **17** (1897), 661. "Etude analytique sur quelques essence du genre anisique," *Thèse,* Paris (1902), 23.

[31] *Mem. acad. cienc. exactas Madrid* **29** (1919). *Ber. Schimmel & Co.*, April (1921), 80.

[32] *Ion* **3** (1943), 410. *Chem. Abstracts* **38** (1944), 1319.

The same author determined the content of anethole and estragole (methyl chavicol) by Zeisel's methoxy method and found that the Spanish oil contains from 27.0 to 34.4 per cent of these two compounds.

Studying the aromatic flora of Morocco, Gattefossé and Igolen[33] investigated also the oil derived from "harvest fennel" (Ridol fa segetum). These authors washed the oil with sodium carbonate solution to remove free acids and phenols and then with metabisulfite solution to remove aldehydes and ketones. The oil was then saponified, washed with water and distilled. The oil was found to consist essentially of about 50 per cent of *d*-α-phellandrene and about 33 per cent of myristicin.

II. Oil of *Sweet* or Roman Fennel Seed, also called French *Sweet* Fennel (*Foeniculum vulgare* Mill. var. *dulce* Bert.)

The plants are *cultivated;* the oils distilled from the seed. According to the Schimmel chemists,[34] the oil contains:

d-Phellandrene. *d*-Limonene. Anethole. The very high percentage of anethole and the absence of fenchone account for the delicate, sweet odor and flavor of these oils. They represent undoubtedly the finest quality of fennel oil produced.

Terpeneless Fennel Oil.—A terpeneless fennel oil prepared by removing the terpenes from sweet or Roman fennel seed oil, and analyzed in the laboratories of Fritzsche Brothers, Inc., New York, had these properties:

Specific Gravity at 25°/25°	0.987
Optical Rotation	Inactive
Refractive Index at 20°	1.5592
Congealing Point	+20.4°
Solubility at 25°	Soluble in 0.5 to 1 vol. of 95% alcohol

The oil had a very characteristic sweet anise odor.

Use.—Oil of fennel is used as a very popular flavoring agent in culinary preparations, bread, pastry, confectionery, liqueurs; furthermore for correcting less pleasant odors and flavors in oral and medicinal preparations.

SUGGESTED ADDITIONAL LITERATURE

B. N. Rutovski and P. P. Leonov, "Constituents of Russian Fennel Oil," *Trans. Sci. Chem.-Pharm. Inst. Moscow* (1923), No. 4, 16. *Chem. Abstracts* **21** (1927), 4020.

L. Rosenthaler, "Microchemical Characterization of Essential Oils," *Pharm. Acta Helv.* **1** (1926), 117. *Chem. Abstracts* **21** (1927), 1870.

D. B. Dorronsoro, "Essential Oils Extracted from Spanish Plants," *Parfumerie moderne* **19** (1927), 175.

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[33] *Bull. soc. chim.* (1946), 361. *Drug Cosmetic Ind.* **61**, November (1947), 684.

[34] Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 522.

N. Sobyanin and S. Saakov, "Investigation of the Essential Oil from Different Kinds of Fennel Cultivated in the Krasnodar District," *Masloboino Zhirovoe Delo* (1929), No. 6, 34. *Chem. Abstracts* **25** (1931), 1631.

V. I. Nilov, "Chemical Variability in Plants and Its Significance for Selection and Systematics," *Bull. Applied Botany, Genetics, Plant Breeding U.S.S.R.* Ser. **A,** No. 11 (1934), 21. *Chem. Abstracts* **29** (1935), 4043.

L. W. Greene, "Chemical Microscopy of Essential Oils," *Drug Cosmetic Ind.* **43** (1938), 156, 174.

A. I. Shavrygin, "Preparation of Fenchone from the Waste of Fennel Oil," *J. Applied Chem. U.S.S.R.* **12** (1939), 1201.

J. F. Clevenger, "Volatile Oils of Anise, Caraway, Celery Fruit, Coriander, Cubeb and Fennel," *Natl. Form. Comm. Bull.* **7** (1939), 293.

J. Sarin and M. L. Bari, "Northern India Essential Oils," *Am. Perfumer* **38,** No. 2 (1939), 30, 84.

"Volatile Oils of Anise, Caraway, Celery Fruit, Coriander, Cubebs and Fennel," Report of the American Pharmaceutical Association Laboratory, *Natl. Form. Comm. Bull.* **7** (1939), 231.

V. V. Klynchevskiĭ and E. N. Tenson, "Improved Method for Treating Raw Materials Yielding Essential Oil. The Reaction of Metals with Essential Oils During Distillation," *Trudy Vsesoyuz. Inst. Efirno-Maslichnoĭ Prom.* (1940), No. 8, 187. *Khim. Referat. Zhur.* **4,** No. 2 (1941), 117. *Chem. Abstracts* **37** (1943), 3559.

J. F. Clevenger, "Determination of Volatile Oils in Spices. Assay of Caraway and Fennel Seeds," *J. Assocn. Official Agr. Chem.* **25** (1942), 700.

OIL OF GALBANUM

Essence de Galbanum   *Aceite Esencial Galbano*   *Galbanumöl*

Galbanum is the air-dried, gum-resin-like exudation of *Ferula galbaniflua* Boiss. et Buhse from the northern sections of Iran (Persia), *Ferula rubricaulis* Boiss. from the southern sections of Iran (Persia), and *Ferula ceratophylla* Regel et Schmalhausen from the mountains of Turkestan, all tall herbs, belonging to the family *Umbelliferae. Ferula galbaniflua* produces the excretion on the base of shoots and leaves, *Ferula ceratophylla* in the flower region.

The trade distinguishes between two types of galbanum, viz., the so-called Levant, or soft, galbanum, and the so-called Persian, or hard, galbanum. The former comes in tears or drops, often agglutinated, translucent, viscous, and of bright or dull yellowish or reddish color. This type of galbanum gum softens on pressing between the fingers. The Persian variety is dry, and consists of agglutinated masses—opaque and whitish inside—which can be broken apart easily. In the heat of summer all galbanum has a tendency to soften and to agglutinate. At 100° C. it becomes sufficiently liquid to permit purification by straining. When rubbed with water, the gum forms a milky emulsion which separates again on standing. High proof alcohol dissolves the greater part of the gum and yields a yellow tincture; addition of water to the tincture forms a milky emulsion.

In former years, galbanum was used as a stimulant, expectorant, and antispasmodic.

The odor of galbanum is characteristic and aromatic; the flavor somewhat bitter, warm, and acrid. Galbanum gum contains a volatile oil which can be isolated by steam distillation; depending upon the age and quality of the drug, the yield of oil varies from 10 to 22 per cent. Efimenko[1] reported that a specimen of dry latex of *Ferula galbaniflua* contained 19.61 per cent of essential (volatile) oil.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[2] the properties of galbanum oil formerly varied within the following limits:

Specific Gravity	0.905 to 0.955
Optical Rotation	+20° 0′ to −10° 0′. According to Hirschsohn,[3] oils distilled from Persian gum are dextrorotatory, while those distilled from Levant gum are laevorotatory
Refractive Index at 20°	1.495 to 1.507
Acid Number	1.0 to 4.7
Ester Number	12 to 28
Ester Number after Acetylation	72 to 99
Solubility	Soluble in 0.5 vol. and more of 90% alcohol

Within the last few years, properties of galbanum oil have changed and old standards no longer hold true. There is no clear explanation for the change, but it may be due to the fact that the merchandise now reaches the market in fresher condition, because of better transportation facilities. This would account for the higher content of low boiling constituents in the oil.

Yield of oil from the gum, according to Schimmel & Co.,[4] varies now from 9.5 to 24.0 per cent.

Schimmel & Co.[5] suggested that the limits for the properties of galbanum oil be modified as follows:

Specific Gravity at 15°	0.8768 to 0.9162
Optical Rotation	+3° 54′ to +16° 2′

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[1] *J. Applied Chem. U.S.S.R.* **12** (1939), 104. *Chem. Abstracts* **33** (1939), 6525.

[2] "Die Ätherischen Öle," 3d Ed., Vol. III, 551.

[3] *Jahresber. Pharm.* (1875), 113.

[4] *Ber. Schimmel & Co.* (1938), 44.

[5] *Ibid.*

Refractive Index at 20°	1.48035 to 1.48712
Acid Number	0.3 to 1.1
Ester Number	8.4 to 26.1
Ester Number after Acetylation	21.4 to 82.1
Solubility	Soluble in 0.5 to 5.5 vol. of 90% alcohol

Two oils distilled by the author in France from imported gum had these properties:

Specific Gravity at 15°	0.873 and 0.875
Optical Rotation	+6° 20′ and +7° 40′
Refractive Index at 20°	1.4799 and 1.4800
Saponification Number	5.4 and 5.7
Solubility	Slightly hazy in 6 to 8 vol. of 90% alcohol; almost clearly soluble in 10 vol.

The specific gravity as well as the refractive index of these oils were slightly below those suggested by Schimmel & Co.

Igolen[6] ventured the opinion that laevorotation in an oil of galbanum indicates Levant origin of the gum, whereas dextrorotation points toward Persian galbanum gum.

Chemical Composition.—The presence of the following constituents has been established in the volatile oil of galbanum:

d-α-Pinene. Identified by Flückiger[7] by conversion to terpin hydrate, and by Thoms and Molle[8] through the hydrochloride m. 125° and the nitrosochloride m. 103°.

β-Pinene. Identified by Semmler and Jonas[9] by conversion to nopinic acid m. 128°.

Myrcene. The same authors[10] proved the presence of myrcene by conversion into camphorene and α-camphorene tetrahydrochloride.

A Compound(?) $C_{10}H_{16}O$. B_{15} 105°–115°, d_{20} 0.951, α_D +6°, n_D^{20} 1.4918.

According to Semmler and Jonas,[11] this substance is possibly a ketone which can easily be enolized. The fraction in which this compound occurs possesses the typical odor of galbanum oil in highly concentrated form. Oxidation yielded a ketonic acid, $C_{10}H_{16}O_3$, whereas treatment with alkaline bromine solution gave a dicarboxylic acid, $C_9H_{14}O_4$.

Cadinene. Identified by Wallach[12] by means of the hydrochloride m. 117°–118°.

Semmler and Jonas[13] obtained *l*-cadinene hydrochloride by passing hydrogen chloride gas through the fraction b_{10} 132°–138°, d_{19} 0.9282, α_D^{19} +33°, n_D^{19} 1.50526, which they had obtained by repeated fractionation over metallic sodium. How-

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[6] *Parfums France* **14** (1936), 300.

[7] "Pharmakognosie des Pflanzenreiches," 3d Ed., Berlin (1891), 65.

[8] *Ber. deut. pharm. Ges.* **11** (1901), 90. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 552.

[9] *Ber.* **47** (1914), 2068.

[10] *Ibid.*

[11] *Ibid.*

[12] *Liebigs Ann.* **238** (1887), 81.

[13] *Ber.* **47** (1914), 2068.

ever, these authors expressed some doubt whether this dextrorotatory fraction actually contained *l*-cadinene whose laevorotation was probably concealed by a strongly dextrorotatory compound. It is quite possible that the dextrorotatory sesquiterpene occurring in this fraction was converted into *l*-cadinene by the action of hydrochloric acid.

α-Cadinol. Semmler and Jonas[14] found in the fraction b_{15} 155°–165° a new tertiary sesquiterpene alcohol which they named cadinol. It split off water easily and formed cadinene. The dihydrochloride of the latter, m. 117°–118°, was identical with that of cadinol.

Ruzicka and Stoll[15] came to the conclusion, offered with reservation however, that the *d*-cadinol occurring in galbanum oil consists of a mixture of at least two forms in which α- or β-cadinol, or a mixture of the two, predominates over the γ-form.

Oil from Galbanum Fruit.—Steam distilling the ripe fruit of *Ferula galbaniflua* (*Ferula Badra-Kema*), Rutovski and Vinogradova[16] obtained 2.35 per cent of a volatile oil possessing an odor of turpentine oil and these properties:

Specific Gravity at 20°/20°	0.8736
Optical Rotation	+16° 10′
Refractive Index at 20°	1.4765
Acid Number	1.2
Ester Number	6.65
Ester Number after Acetylation	31.78

This oil was composed of

	Per Cent
d-β-Pinene	30
dl-α- and *d*-α-Pinene	40
d-Limonene	1.5
An Alcohol Not Further Identified	3
A Ketone	1
Esters of Acetic, Butyric and Isovaleric Acids, and of an Acid m. 114°–116°	...

The occurrence of *d*-β-pinene in this oil is remarkable, as the dextrorotatory form of β-pinene has been observed only rarely in nature.

Use.—Medicinally, oil of gum galbanum is today employed as an external stimulant. To a limited extent it is used as an adjunct in perfumes of the oriental type.

SUGGESTED ADDITIONAL LITERATURE

N. P. Kiryalov, "Peculiarities of the Chemistry of Resins and Oils of *Ferula*," *Soviet. Botan.* **14**, No. 3 (1946), 163. *Chem. Abstracts* **40** (1946), 7310.

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[14] *Ibid.*

[15] *Helv. Chim. Acta* **7** (1924), 94.

[16] *J. prakt. Chem.* [2], **120** (1928), 41.

OIL OF LOVAGE

Essence de Livèche *Aceite Esencial Levistico* *Liebstocköl*
Oleum Levistici

Botanical Description.—*Levisticum officinale* Koch, syn. *Angelica levisticum* Baillon, is a tall perennial, growing under favorable conditions to a height of almost 6 ft. All parts of the plant are strongly aromatic. The roots, which constitute the commercially most important part of the plant, are composed of a vertical rhizome, 5 to 10 cm. long and 2 to 4 cm. thick, from which spring forth numerous lateral rootlets, up to 20 mm. long and a few millimeters thick.

All parts of the plant contain a volatile oil, which can be recovered by steam distillation, the root oil being the most important one.

According to The Herb Society of America,[1] lovage, a once popular but now somewhat neglected herb, is distinguished by its strong celery-like flavor and aroma. It was, indeed, used as a celery substitute by our forefathers. In old New England the root used to be candied in sugar syrup in the same way as sweet flag root. Lovage is easy to grow and adaptable to almost any soil, although it thrives best in a rather moist, heavy soil with a good deal of shade. Here it will grow to a height of 7 to 8 ft. and send up a flower stalk another foot high.

The roots have long been supposed to possess medicinal properties; they are administered in the form of infusions as a stimulant aromatic, and as a carminative, diaphoretic, and emmenagogue. The seeds (fruits) are used for flavoring confectionery and notably in liqueurs of French type. The leaves are sometimes blanched, like celery, and relished in the form of salads.

Habitat and Range.—Lovage is a native of Southern Europe, where it grows wild in the mountain regions of Southern France (Dauphiné and Provence). It thrives best in damp and strong soils. Lovage is cultivated in Germany (Thuringia and Bavaria), also in Hungary, Czechoslovakia, and other central European countries. The perennial has been introduced to the United States as a garden plant and is now grown as a crop in a few localities of New England and the West.

Planting, Cultivating, and Harvesting.—Stockberger[2] recommends propagating lovage by root division or from seeds. The seeds may be planted in the fall in drills 18 in. apart or sown in early spring in a hotbed, green-

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[1] *The Herbarist,* No. 10, Boston, Mass. (1944).

[2] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935), 27.

house, or well-prepared seedbed, in a sheltered portion of the garden. They should be covered very lightly with sand or fine-sifted soil. To prevent the soil from drying out before the seeds germinate, it is advisable to spread old burlap or sacking over the bed. The sacking may be sprinkled occasionally, if the weather is dry, and should be removed when the first seedlings break the soil. The plants should reach a size suitable for transplanting by the end of May, when they may be set at intervals of 8 in., in rows far enough apart for convenient cultivation. Lovage grows well in almost any deep, well-drained soil, such as will produce a fair crop of corn or potatoes, and is benefited by the liberal use of fertilizer, although heavy application of manure tends to produce excessive top growth.

The roots may be dug in October of the second or third year after setting the plants. Numerous offshoots will generally be found; if these have good roots they may be used to renew the plantings, without recourse to seed. Such shoots should be reset immediately at the usual distances apart. The freshly dug roots should be well washed, cut into slices about one-half inch thick, and carefully dried. If necessary, artificial heat not exceeding 125° F. may be used to hasten drying.

According to Stockberger,[3] returns from experimental areas indicate that under good conditions a yield of about 1,000 lb. of dried root to the acre may be expected every third year.

Distillation of Lovage Root.—Age of the root material affects the quality of the recovered oils, oils from fresh roots being considered superior. Distillation of dried roots gives rise to the formation of a yellow, gummy, and sticky mass in the condenser and oil separator, especially toward the end of operation. The resulting oils are brown in color. Distillation of green, especially of freshly harvested, roots, on the other hand, proceeds without any gum formation; the oils are then of yellowish color. Rectification of oils from old root material leaves as residue considerable quantities of resinous matter, whereas oils from fresh roots are almost entirely volatile.

Yield of Lovage Root Oil.—Distillation of very fresh root material with direct steam yields 0.1 to 0.2 per cent of oil, semidried roots 0.3 to 0.6 per cent, and dried roots 0.6 to 1.0 per cent of oil. It is advisable to granulate the root material prior to distillation; otherwise the yield will be subnormal.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[4] the properties of lovage root oil vary within the following limits:

Specific Gravity at 15°	1.00 to 1.05
Optical Rotation	Inactive to slightly dextrorotatory, up to +6° 0′; seldom laevorotatory, up to −1° 0′

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[3] *Ibid.*

[4] "Die Ätherischen Öle," 3d Ed., Vol. III, 540.

Refractive Index at 20°	1.536 to 1.554
Acid Number	2 to 16
Ester Number	175 to 232
Ester Number after Acetylation	Around 227
Solubility	Clearly soluble in 2 to 4 vol. of 80% alcohol, sometimes with slight turbidity

Oils of lovage root distilled by the author in France had properties varying within these limits:

Specific Gravity at 15°	1.034 to 1.057
Optical Rotation	+0° 40′ to +1° 20′
Refractive Index at 20°	1.5502 to 1.5591
Acid Number	2.8 to 16.5
Saponification Number	238.0 to 257.6
Solubility	Soluble in 1 to 2 vol. of 80% alcohol; clear to opalescent with more

It is an interesting fact that, on storing and in the course of time, oil of lovage root, like oil of angelica, changes its optical rotation, from dextro- to slight laevorotation. With age the oil also becomes darker and more resinous.

The odor of lovage root oil resembles that of angelica root oil and, in a way, the odors of celery seed and opopanax oils. It is warm, aromatic, pungent and lasting.

Analysis of Lovage Root Oil.—According to Naves,[5] the analysis of lovage root oil should be carried out with proper consideration of its content of lactones and phthalides. If possible, it should comprise a fractional distillation test of a sample of oil or of the lactones after isolation through their corresponding alkali salts. The interpretation of the composition of the lactone fractions can be based quite reliably upon the values of the refractive indices, n_D^{20}:

n-Butylidene Phthalides	1.5780
n-Butyl Phthalides	1.5260
Sedanolide	1.4943
n-Butyl Hexahydrophthalides	1.4719

(For further details the reader should consult the original literature.)

Chemical Composition.—Very little was known about the chemistry of lovage root oil until Naves[6] found that the oil consists largely (about 70 per cent) of butylidene phthalides and of hydrophthalide derivatives which are mainly responsible for the odor and the high saponification number of the oil. The presence of the following compounds in lovage root oil has been reported:

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[5] *Helv. Chim. Acta* **26** (1943), 1286.

[6] *Ibid.* **26** (1943), 1281.

d-α-Terpineol. The Schimmel chemists[7] isolated from the main fraction b_{15} 107°–115°, a compound b. 217°-218°, α_D +79° 18′ which crystallized on cooling. It possessed the characteristic properties of solid *d*-α-terpineol. Phenylurethane m 112°, nitrolpiperidine m. 151°-152°.

A Terpene(?) $C_{10}H_{18}O$. Braun[8] steam distilled an oil after saponification with alcoholic potassium hydroxide, fractionated the distillate first *in vacuo*, then at atmospheric pressure, and obtained a fraction b. 176°, d_{15} 0.8534, α_D +5° 0′, which seemed to be a terpene.

The same author isolated from the distillation residue:

Acetic Acid, Isovaleric Acid and Benzoic Acid.

Haensel[9] observed in an old oil:

Myristic Acid.

Octyl Aldehyde(?).

Extracting lovage root with benzene and steam distilling the resinoid, Naves[10] reported the presence of:

n-Butylidene Phthalide. Identified by hydrolysis into the corresponding acid, and preparation of the phthalazone m. 156°.

n-Butyl Phthalide. Identified by hydrolysis into *o*-[α-hydroxyamyl]-benzoic acid m. 73°, and preparation of the mononitro derivative m. 54°-55°.

Sedanonic Anhydride. Identified by the preparation of tetrahydro-*n*-butyl phthalazone m. 136° from sedanonic acid

n-Butyl Dihydrophthalide and *n*-Butyl Tetrahydrophthalide. Presence probable but in small quantities only.

The same author also observed that the volatile fraction contained:

Eugenol. Identified as benzoate.

Carvacrol. Identified as phenylurethane m 136°.

Coumarin.

Sesquiterpenes.

n-Butyric Acid. Identified as phenyl phenacyl *n*-butyrate m. 83.5°.

Regarding the chemistry of sedanonic anhydride and the various phthalides see Vol. II of this work.

The nonvolatile fraction of the resinoid (obtained by extraction of the root with benzene), according to Naves,[11] contains among several unidentified compounds:

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[7] *Ber. Schimmel & Co.*, April (1897), **27**; October (1897), 9, Footnote 3.

[8] *Arch. Pharm.* **235** (1897), 2, 18.

[9] *Geschäftsbericht,* April–September (1908).

[10] *Helv. Chim. Acta* **26** (1943), 1281.

[11] *Ibid.*

Palmitic Acid. Free.

Hydrophthalide Acids.

Bergaptene. M. 189°–190°.

Use.—Oil of lovage root finds its principal use as a minor ingredient in many flavoring compositions, for tobaccos, liqueurs, and cordials, confectionery, and food products of various kinds, as well as in medicinal products.

It is also employed, to a limited extent, in modern perfumes where it produces novel effects when skillfully handled. The powerful odor of lovage root oil requires that it be used very sparingly and with great discretion.

Lovage Seed and Herb Oils.—For the sake of completeness, we should add a few words about oils distilled from the seed (yield 0.8 to 1.1 per cent) and from the fresh herb (yield 0.05 to 0.15 per cent). The odor of both oils resembles that of the root oil. Gildemeister and Hoffmann[12] reported the following properties for a few samples of these types of oil:

	Fruit (Seed) Oil	*Herb Oil*
Specific Gravity at 15°	0.935 to 0.936	0.904 to 0.945
Optical Rotation	+11° 10′	+16° 0′ to +46° 0′
Refractive Index at 20°	1.51308	1.484 to 1.487
Acid Number	2.8	2.8 to 4.6
Ester Number	125.2	152.6 to 152.7
Solubility	Soluble in 0.5 vol. of 90% alcohol; not clearly soluble in 10 vol. of 80% alcohol	Soluble in 0.5 to 1 vol. of 90% alcohol; in 3 to 10 vol. of 80% alcohol, sometimes with opalescence and flocculation

Distilling the whole overground parts of lovage in the flowering stage, Chiris[13] obtained (yield 0.248 per cent) a volatile oil of celery- and angelica-like odor; it had these properties:

Specific Gravity at 15°	0.9252
Optical Rotation	+25° 11′
Refractive Index at 20°	1.4890
Acid Number	7
Ester Number	79.26
Ester Number after Cold Formylation	148.7
Solubility	Soluble in 0.5 to 2 vol. of 90% alcohol; turbid above 2 vol. Soluble in 0.1 to 6 vol. of 95% alcohol; turbid above 6 vol.

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[12] "Die Ätherischen Öle," 3d Ed., Vol. III, 541.

[13] *Parfums France* **14** (1936), 12.

Two oils of lovage leaves distilled in Hungary (by Dr. Jules de Bittera, Budapest), and analyzed by Fritzsche Brothers, Inc., New York, had the following properties:

	I	*II*
Specific Gravity at 15°	0.925	0.925
Optical Rotation	+4° 34′	+37° 40′
Refractive Index at 20°	1.4829	1.4841
Acid Number	2.6	3.5
Saponification Number	166.7	159.8
Solubility at 20°	Clearly soluble in 0.5 vol. and more of 90% alcohol	

The odor of these oils was suggestive of root oil, but harsher and more terpene-like

An oil of lovage seed submitted by the same producer in Hungary had the following properties:

Specific Gravity at 15°	0.885
Optical Rotation	+12° 32′
Refractive Index at 20°	1.4970
Acid Number	1.1
Saponification Number	60.7
Solubility at 20°	Turbid in 10 vol. of 90% alcohol

The specific gravity of this oil was low, the solubility poor. The odor suggested celery, parsley, and lovage root

Suggested Additional Literature

G. Igolen, "Lovage," *Parfums France* **14** (1936), 70.

W. Struhk, "The Cultivation of Lovage," *Nachr. Reichsverb. Heil-, Duft- und Gewürzpflanzenanb.* **10** (1944), 49. *Ber. Schimmel & Co.* (1944/47), 36.

OIL OF MASTERWORT

Essence d'Impératoir *Aceite Esencial Imperatoria* *Meisterwurzelöl*

Peucedanum ostruthium (L.) Koch (= *Imperatoria ostruthium* L.), a perennial, is a native of the Alps, but occurs also in other European mountain lands. It has a root with a pungent, aromatic, warm taste and an odor resembling that of angelica. Upon distillation the dried root yields from 0.2 to 0.8, and in some cases even 1.4 per cent of oil.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[1] the physicochemical properties of masterwort oil are as follows.

Specific Gravity at 15°	0.8632 to 0.8766
Optical Rotation	+59° 30′ to +66° 30′
Acid Number	0.8
Saponification Number	17.9
Ester Number after Acetylation	38.34

Chemical Composition.—According to Lange[2] about 95 per cent of masterwort oil consists of terpenes, the balance of alcohols, esters, free acids, and lactones. Lange reported the presence of the following compounds:

Dipentene. Identified by means of its dihydrochloride m. 50°.

d-Limonene. Nitrolbenzylamine m. 92°–93°.

α-Pinene. Nitrolbenzylamine m. 122°–123°.

d-Phellandrene. Nitrite m. 103°–104°.

An Alcohol(?) $C_{10}H_{20}O$. This unidentified alcohol formed a phenylurethane m. 145°–146°.

A Sesquiterpene(?). It gave a dihydrochloride m. 157°–157.5°.

Palmitic Acid. In free form.

Formic Acid, Acetic Acid, Isobutyric Acid, and Isovaleric Acid. Free and as esters

Isopropylidene Acetic Acid (β,β-Dimethylacrylic Acid). It is questionable whether this acid is present as such in the original oil or whether it is formed in the course of distillation.

Other important constituents of masterwort oil are lactones, although their presence has not been noted by Lange.[3] Extracting roots of masterwort with hot benzol and treating the extracts, Butenandt and Marten[4] isolated three lactones:

Hydroxypeucedanin $C_{16}H_{14}O_5$. M. 141°.

Osthole. M. 85°.

Ostruthin. M. 119°.

Some of these lactones occur also in angelica root oil, hence the similarity of odor.

Use.—Oil of masterwort has not attained any commercial importance.

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[1] "Die Ätherischen Öle," 3d Ed., Vol. III, 560

[2] *Pharm. Inst. Univ. Berlin* **8** (1911), 98. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 560.

[3] *Ibid*

[4] *Liebigs Ann.* **495** (1932), 200.

OIL OF PARSLEY

Essence de Persil *Aceite Esencial Perejil* *Petersilienöl*
Oleum Petroselini

Botany.—*Petroselinum sativum* Hoffm. (*Apium petroselinum* L., *Carum petroselinum* Benth. et Hook.), a native of Mediterranean countries, has been cultivated as a garden herb since antiquity. It was used by the Greeks and Romans for festive garlands, its deep green color being exceptionally lasting.

Petroselinum hortense, as the common garden variety may be classified, is widely cultivated in temperate countries and extensively employed as a culinary herb for garnishing and seasoning. The cuisine of France seldom offers a dish without a sprig of parsley.

Parsley is a hardy biennial, bearing greatly divided pinnately-compound leaves; the flowering and fruiting plant reaches a height of from 2 to 3 ft. The fruit, commercially called seed, consists of two dried mericarps joined along the center commissure when fresh (but usually separated in the commercial lots).

All parts of the plant, particularly the seed, contain a volatile or essential oil which is responsible for the pronounced odor and flavor of parsley; the oil can be recovered by steam distillation.

Commercially there exist two types of parsley oil, viz., parsley seed oil and parsley herb oil, the latter possessing a superior odor and flavor, characteristic of the fresh leaves.

French Parsley Oil

A. Parsley Seed Oil

Producing Regions.—The herb is cultivated on a large scale by truck farmers throughout France, particularly in the environs of big cities. Truck farmers usually buy their seed from special seed growers.

The bulk of French parsley seed originates from the Département Seine et Loire, especially around Angers. The south of France (St. Rémy-en-Provence) also produces parsley seed; but, in general, it can be stated that outside of Seine et Loire in France, little seed is grown in Europe for export and distillation purposes. Because of the reduced demand and the low prices prevailing during the years preceding World War II, parsley seed production in France fell off considerably. This condition, however, was only temporary; increased production may be expected when prices become sufficiently attractive.

Planting and Harvesting.—The growing and harvesting of the parsley plant in France resembles that of celery (see also "Oil of Celery Seed"). Depending upon the year, 800 to 1,500 kg. of parsley seed are obtained per hectare. The surplus seed which cannot be sold by the seed growers to truck farmers in various parts of France or abroad is usually sold to distillers as superannuated seed at about half price. Parsley seed loses its germinating power in a relatively short time and becomes practically worthless so far as planting is concerned. This lower price creates a considerable difference in the cost of the essential oil; therefore distillers are interested primarily in the superannuated seed, especially since the oils distilled from the two qualities of seed are similar.

The quantity of chaff resulting from the winnowing of the seed is so small that it can hardly be considered as distillers' material. Besides, oil distilled from chaff is of inferior quality.

Distillation.—The distillation of parsley seed demands considerable experience and attention.

Yield, as well as quality, of the oil is considerably influenced by the maturity of the seed.

Fully ripe seed gives the highest yield of oil; superannuated seed, a somewhat lower yield. Gildemeister and Hoffmann[1] report that the yield from normal seed ranges within 2.0 and 7.0 per cent of oil. Distilling parsley seed in Southern France, the author obtained yields from 1.5 to 3.5 per cent.

Yield and flavor of the oil depend greatly upon the method of distillation, even minor factors—such as slow starting of distillation, duration, speed, and other variations in the procedure—affecting yield and quality of the oil considerably.

Physicochemical Properties of Parsley Seed Oil.—According to Gildemeister and Hoffmann,[2] the properties of parsley seed oil vary within the following limits:

Specific Gravity at 15°	1.043 to 1.110
Optical Rotation	$-4° 0'$ to $-10° 0'$
Refractive Index at 20°	1.512 to 1.528
Acid Number	Up to 6
Ester Number	1 to 11
Ester Number after Acetylation	4 to 20
Solubility	Soluble in 4 to 8 vol. and more of 80% alcohol, in exceptional cases with turbidity

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[1] "Die Ätherischen Öle," 3d Ed., Vol. III, 476.

[2] *Ibid.*

Certain types of oil, especially those distilled from German seed, contain so much apiole that they are semisolid at room temperature. Oils distilled from French seed, on the other hand, contain much less apiole. Small, poorly developed and immature seeds yield oils of lower specific gravity and higher rotation, than oils from normal seed, the result probably, of the predominance of terpenes in such oils.

Genuine parsley seed oils distilled in France, and analyzed by Fritzsche Brothers, Inc., had these properties:

Specific Gravity at 15°	1.054 to 1.080
Optical Rotation	−4° 50′ to −7° 42′
Refractive Index at 20°	1.5139 to 1.5200
Saponification Number	0 to 3.7
Solubility at 20°	Soluble in 4 to 5 vol. and more of 80% alcohol, in some cases with separation of solids

Parsley seed oils distilled by the author in Southern France had the following properties:

	Superannuated Seed	*Mixed Seed*	*Fresh Seed*
Specific Gravity at 15°	1.099	1.120	1.106
Optical Rotation	−4° 32′	−3° 35′	−2° 30′
Refractive Index at 20°	1.5259	1.5271	1.5282
Saponification Number	6.0	5.6	2.8
Ester Number after Acetylation	18.7	17.7	17.7
Solubility	Soluble in 6 and more vol. of 80% alcohol with slight turbidity	Soluble with turbidity in 6 to 7 vol. and more of 80% alcohol. Separation of paraffin	Soluble in 5 to 5.5 vol. and more of 80% alcohol

Chemical Composition of Parsley Seed Oil.—The following compounds have been identified in parsley seed oil:

α-Pinene. As nitrosochloride m. 105°, in the lowest boiling fractions b. 158° 160°, by Thoms.[3]

Aldehydes, Ketones and Phenols(?). In the course of the same investigation, Thoms also proved the presence of traces of other compounds, among them aldehydes, ketones, and phenols, none of them further identified, and

Palmitic Acid. M. 62°.

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[3] *Ber.* **36** (1903), 3453.

A large portion of the oil was found to consist of:

Myristicin (1,2-Methylenedioxy-6-methoxy-4-allylbenzene). This phenol ether was identified in parsley seed oil as dibromomyristicin dibromide m. 130°, and as isomyristicin m. 44°-45°.

Apiole (1,2-Methylenedioxy-3,6-dimethoxy-4-allylbenzene). This important constituent of parsley seed oil was identified by Ciamician and Silber,[4] and by Thoms.[5]

1-Allyl-2,3,4,5-tetramethoxybenzene. When cooling the corresponding fraction with "dry ice" (carbon dioxide), Thoms[6] later isolated from the oil still another phenol ether, viz., 1-allyl-2,3,4,5-tetramethoxybenzene m. 25°.

Petrosilane(?). Matthes and Heintz[7] observed in the fatty oil of parsley seed small quantities of a solid hydrocarbon m. 69° which they named petrosilane. Being partly volatile with steam, the presence of such a paraffin also in the volatile oil of parsley seed is probable.

B. Parsley Herb Oil

It must be admitted that in general parsley seed oil is not quite characteristic of parsley leaves, which alone are used as flavoring ingredient and garnish in culinary preparations. Parsley seed oil is, therefore, only a sort of substitute for the more expensive herb or leaf oil.

The latter, which truly represents the odor and flavor of parsley leaves, is obtained by steam distilling the flowering tops of the plants. Unfortunately, the yield of oil from leaves and flowers exclusively is so low (about 0.06 per cent) that prices become prohibitive.

It is advisable, therefore, to distill the overground parts of the plant in a rather advanced state of maturity. The herb should be harvested, like dill, when seed has formed but not yet matured; in other words, the herb bearing unripe seed should be distilled. The yield of oil from such plant material is about 0.25 per cent. The more developed the seed, the higher the yield of oil, but its odor and flavor will then approach that of seed oil.

Physicochemical Properties of French Parsley Herb Oil.—According to Gildemeister and Hoffmann,[8] the properties of parsley herb oil vary within the following limits:

Specific Gravity at 15°	0.9023 to 1.0157
Optical Rotation	+1° 16′ to +4° 10′
Refractive Index at 20°	1.509 to 1.526

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[4] *Ibid.* **21** (1888), 913, 1621; **22** (1889), 2481; **23** (1890), 2283.

[5] *Ibid.* **36** (1903), 1714.

[6] *Ibid.* **41** (1908), 2753.

[7] *Ber. deut. pharm. Ges.* **19** (1909), 325. Cf. Gildemeister and Hoffmann, "Die Ätherischen Öle," 3d Ed., Vol. III, 478.

[8] "Die Ätherischen Öle," 3d Ed., Vol. III, 479.

Acid Number	Up to 1
Ester Number	5 to 14
Ester Number after Acetylation	19 to 68
Solubility	Soluble in 95% alcohol. Not always clearly soluble in 90% alcohol, sometimes opalescent to turbid with 2 to 4 vol. of 90% alcohol

Genuine oils distilled in France from the overground parts of parsley during seed formation and analyzed by Fritzsche Brothers, Inc., New York, had properties which varied within these limits:

Specific Gravity at 15°	0.948 to 0.967
Optical Rotation	−2° 55′ to −6° 10′
Refractive Index at 20°	1.5087 to 1.5159
Saponification Number	0.9 to 7.0
Solubility at 20°	Usually not clearly soluble in 90% alcohol up to 10 vol. Some oils clearly soluble in 1 to 1.5 vol. and more of 90% alcohol

Two lots of oil distilled by the author in Southern France had the following properties:

	I	*II*
Specific Gravity at 15°	0.979	1.002
Optical Rotation	−4° 50′	−5° 0′
Refractive Index at 20°	1.5155	1.5150
Acid Number	1.4	1.4
Ester Number	2.3	7.9
Ester Number after Acetylation	26.1	50.4
Solubility	Soluble in 1 vol. of 90% alcohol; turbid with more	Soluble in 0.5 vol. and more of 90% alcohol

A comparison of these figures with those of Gildemeister and Hoffmann for herb oil and for seed oil confirms the fact that parsley leaves and stalks bearing immature seed were used in these two distillation experiments. Laevorotation of an oil indicates the presence of seed in the distillation material. Yet, the two oils mentioned above possessed the characteristic odor and flavor of parsley leaves to a very pronounced degree. It is, therefore, not advisable to pay too much attention to analytical properties, but rather to consider the odor and flavor of the oil.

The author also distilled in Southern France parsley leaf material *without any seed* and obtained a yield of only 0.066 per cent. The oil had these properties:

Specific Gravity at 15°	0.911
Optical Rotation	+6° 0′

Refractive Index	1.5029
Acid Number	1.4
Ester Number	8.9
Ester Number after Acetylation	44.8
Solubility	Insoluble in 90% alcohol; soluble in 95% alcohol with opalescence

The physicochemical properties of parsley herb oil are thus greatly influenced by the maturity of the plant material. The presence of seed in the leaf and stalk material changes the rotation from dextro- for leaf oil exclusively, to laevo-.

Oil of parsley herb has been distilled mainly in France and on a small scale, because its high price has prevented more general application of this interesting and valuable oil.

Chemical Composition of Parsley Herb Oil.—No investigation has been undertaken on this type of oil, according to available literature.

AMERICAN PARSLEY OIL

Planting, Cultivating, and Harvesting.—Stockberger[9] recommended a rich, rather moist soil for the growing of parsley. Because the seeds germinate slowly, they are frequently sown early in spring in cold frames or seedbeds, from which the young plants are removed later and set in the open at distances of 6 in. in rows 1 ft. or more apart. When fully grown, the leaves may be collected and dried in the usual manner. The plants flower in the second year. As soon as the seed is ripe, it should be harvested and carefully dried.

Yield of Seed per Acre.—According to Stockberger,[10] yields of seed at the rate of 185 lb. per acre have been obtained on small areas.

Harvesting of the Overground Parts.—Slessman[11] suggests preparing the ground just as for dill weed. In fact, the growing of parsley closely resembles that of dill. The seed is spaced at 22 in.; 8 lb. of seed are required to sow one acre. The raising of parsley, a biennial, involves considerable hand work, as it is necessary to weed twice and sometimes three times. For distillation of the herb oil the overground parts of the plants are harvested in the second year when the seed is well formed and just starting to turn brown.

Physicochemical Properties of American Parsley Herb Oil.—Parsley herb oils produced in Fremont, Ohio, during 1942 and 1943 and examined by Fritzsche Brothers, Inc., had the following properties:

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[9] "Drug Plants under Cultivation," *U. S. Dept. Agr., Farmers' Bull.* No. 663 (1935), 28.

[10] *Ibid.*

[11] Private communication from Mr. A. E. Slessman, Fremont, Ohio.

	I	*II*	*III*	*IV*
Specific Gravity at 15°	0.945	0.966	1.046	0.909
Optical Rotation	−4° 39′	−5° 40′	−2° 13′	−7°40′
Refractive Index at 20°	1.5080	1.5107	1.5179	1.5123
Saponification Number	0.0	3.7	3.1	6.1
Solubility at 20°	Soluble in 0.5 to 1 vol. of 90% alcohol and more	Hazy in 2 vol. of 90% alcohol and more	Soluble in 0.5 vol. of 90% alcohol, opalescent with more	Turbid in 4.5 vol. of 90% alcohol. Hazy in 10 vol.

These oils possessed a typical parsley leaf flavor.

HUNGARIAN PARSLEY SEED AND HERB OIL

In Hungary, substantial quantities of superannuated parsley seed are offered occasionally on the market and purchased for distillation purposes. In 1947 one producer had about 40 hectares of parsley under cultivation which served exclusively for distillation of the flowering plant (herb oil). The Hungarian parsley oils offered on the world market prior to and after World War II have usually been of very good quality.

Three samples of pure Hungarian parsley herb oil examined by the author prior to World War II had these properties:

	I	*II*	*III*
Specific Gravity at 15°	0.965	0.987	0.975
Optical Rotation	−2° 47′	−2° 3′	−1° 46′
Refractive Index at 20°	1.5210	1.5250	1.5232
Acid Number	0.1	0.2	0.1
Ester Number	2.0	6.1	2.5
Ester Number after Acetylation	11.5	22.2	15.8
Solubility	Soluble in 3.5 vol. of 90% alcohol; slightly hazy with more alcohol		

Two additional samples of Hungarian parsley herb oil submitted in 1947 had these properties:

	IV	*V*
Specific Gravity at 15°	0.948	0.970
Optical Rotation	−6° 18′	−5° 47′
Refractive Index at 20°	1.5053	1.5165
Saponification Number	7.7	7.4
Solubility at 20°	Slightly hazy in 10 vol. of 90% alcohol	

Odor and flavor of all these oils were normal; the odor of No. V was perhaps somewhat "heavier" than in other parsley herb oils.

Use of Parsley Seed and Herb Oil.—As has been pointed out, only parsley herb oil represents the true odor and flavor of the garnish which is so widely employed in culinary preparations. The seed oil is merely a lower priced substitute for the herb oil. Both oils are employed for the flavoring of all kinds of food products, particularly meats, sausages, and table sauces in general.

SUGGESTED ADDITIONAL LITERATURE

A. Bänninger, "Investigations of the Influence of Mountain Climates on the Content of Active Components of Pharmaceutical Plants," *Ber. schweiz. botan. Ges.* **49** (1939), 239. *Chem. Abstracts* **35** (1941), 6735.

OIL OF SEAFENNEL

Essence de Criste-marine *Aceite Esencial Hinojo Maritimo*
Seefenchelöl

Crithmum maritimum L. occurs wild in coastal sections of Mediterranean countries, also on the Crimean peninsula, and along the Atlantic Coast of France and England. All parts of the plant contain a volatile oil, but the quantity as well as the physicochemical properties and chemical composition of the oil vary considerably according to locality and soil conditions on which the plant grows. The oil has not attained any commercial importance, and only experimental lots have been distilled occasionally.

Yield of Oil.—The causes of the great variations in yield of oil have been investigated by Delépine and de Belsunce,[1] by Borde,[2] and by Francesconi and Sernagiotto.[3]

According to season, the yield of oil from the different plant parts varies within 0.16 and 0.90 per cent; in general it is greatest from the umbels.

Physicochemical Properties.—The above-named authors also described the properties of various types of seafennel oil they investigated.

Richter and Wolff[4] reported these properties for a French oil distilled from whole plants, which had been gathered on the beach near Biot (A.M.):

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[1] *Bull. soc. chim.* [4], **23** (1918), 24.

[2] *Bull. sci. pharmacol.* **16** (1909), 132. *Chem. Zentr.* I (1909), 1566.

[3] *Atti accad. Lincei* [5], **22,** I (1913), 231, 312, 382. *Chem. Zentr.* I (1913), 1685, 1686, 1687.

[4] *Ber.* **60** (1927), 477. *Ber. Schimmel & Co.* (1927), 95.

Specific Gravity at 15°/15°	0.8780
Optical Rotation	+4° 4′
Refractive Index at 20°	1.48296
Acid Number	0.4
Ester Number	8.4
Ester Number after Acetylation	15.8
Solubility	Soluble in 4.3 vol. and more of 90% alcohol

Chemical Composition.—The following compounds have been reported as occurring in seafennel oils of various origin:

d-Pinene. According to Delépine[5] this terpene occurs in the French, but not in the Italian, oil. Terpin hydrate m. 116°; pinene hydrochloride m. 130°.

β-Phellandrene. Conversion of the nitrosochloride into dihydrocuminaldehyde. *β*-Phellandrene occurs in the Italian but not in the French oil.

p-Cymene. Both oils, however, contain *p*-cymene, according to Delépine.[6] Oxidation to *p*-hydroxyisopropylbenzoic acid m. 157°, and to *p*-toluic acid m. 177°.

Limonene(?) and Sabinene(?). Investigating an oil from the Crimean peninsula, Pevtzov[7] found that it contained 90 per cent of terpenes, among them *p*-cymene, limonene, and sabinene.

γ-Terpinene. The "crithmene" reported in the oil by Francesconi and Sernagiotto[8] was shown by Richter and Wolff[9] to consist in reality of *γ*-terpinene. Oxidation of the "crithmene" fraction b_{20} 69°–73° with potassium permanganate, according to Wallach's[10] method, yielded the corresponding erythritol m. 235°.

Thymolmethyl Ether. Its presence in the fraction b. 210°–214° was reported by Delépine.[11] Treatment of the methyl ether with hydrogen bromide in glacial acetic acid solution yielded thymol.

Phenols(?), a Fatty Acid(?), and an Alcohol(?). Delépine[12] found in the same fraction small quantities of other compounds (phenols, a high molecular fatty acid and an alcohol of rose-like odor) which, however, were not identified.

A Tertiary Alcohol(?). The occurrence of a tertiary alcohol $C_{10}H_{17}OH$ (b. 205°) in a Crimean oil was reported by Pevtzov.[13]

Dillapiole (1,2-Methylenedioxy-5,6-dimethoxy-4-allylbenzene). The most important constituent of the French oil, present also in the Italian oil, is dillapiole, accord-

[5] *Compt. rend.* **150** (1910), 1061. *Bull. soc. chim.* [4], **7** (1910), 468.

[6] *Ibid.*

[7] *J. Gen. Chem. U.S.S.R.* **5** (1935), 1185. *British Chem. Abstracts* **B** (1936), 171.

[8] *Atti accad. Lincei* [5], **22**, I (1913), 231, 312, 382. *Chem. Zentr.* I (1913), 1685, 1686, 1687.

[9] *Ber.* **60** (1927), 477.

[10] *Liebigs Ann.* **362** (1908), 303.

[11] *Compt. rend.* **150** (1910), 1061. *Bull. soc. chim.* [4], **7** (1910), 468.

[12] *Ibid.*

[13] *J. Gen. Chem. U.S.S.R.* **5** (1935), 1185. *British Chem. Abstracts* **B** (1936), 171.

ing to Delépine.[14] It gave a tribromo compound m. 110°. Conversion with sodium ethylate into dillisoapiole m. 44°.

Delépine and de Belsunce[15] found that the content of dillapiole varies considerably in the different types of seafennel oil; it ranges from 8 per cent in the umbels to 90 per cent in the roots.

A Paraffin(?). The high boiling fractions of French or Italian seafennel oil contain a paraffin m. 63°.

RUSSIAN SEAFENNEL OIL
(*Crithmum maritimum* L.)

Investigating a seafennel oil distilled on the Crimean peninsula, Pevtzov[16] established the presence of—

Limonene.

p-Cymene.

Sabinene.

A Tertiary Alcohol(?) $C_{10}H_{17}OH$. B. 205°.

OIL OF SUMBUL
(Muskroot)

Essence de Sumbul	*Aceite Esencial Sumbul*	*Moschusöl* or *Sumbulöl*
	Oleum Sumbuli	

The name sumbul is derived probably from the Arabian word "sunbul" = hyacinth. The commercial muskroot (*Radix sumbul*) originates from *Ferula sumbul* (Kauffm.) Hook. f. and from *Ferula suaveolens* Aitch. et Hemsl., both *Umbelliferae* plants of the subgenus *Eryangium.* They are natives of Samarkand and Buchara and possess a thick root which contains about 9 per cent of a gum or resin, and 0.2 to 1.37 per cent of a volatile oil possessing a faint musk-like odor.

In India aromatic roots of other plants, too, are named "sumbul," especially two of the family *Valerianaceae,* namely, *Valeriana celtica* L., a native of Europe (*Sumbul ekleti, S. ekelti, S. italicus*), and *Nardostachys*

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[14] *Compt. rend.* **149** (1909), 215. See also F. Borde, "Étude pharmacognostique du *Crithmum maritimum* L.," Lons-le-Saunier (1910).

[15] *Bull. soc. chim.* [4], **23** (1918), 24.

[16] *J. Gen. Chem. U.S.S.R.* **5** (1935), 1185. *British Chem. Abstracts* **B** (1936), 171.

jatamansi D.C. from the Himalaya Mountains. *Dorema ammoniacum* Don., fam. *Umbelliferae,* furnishes "Bombay Sumbul," or "Boi."

The two first named *Ferula* species are the true sumbul roots, the other roots often being employed as adulterants in commercial shipments from India.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[1] the physicochemical properties of sumbul root oil are as follows:

Specific Gravity at 15°	0.941 to 0.96
Optical Rotation (Two Determinations Only)	−6° 20′
Refractive Index at 20°	About 1.50
Acid Number (Three Determinations)	4.1 to 14.9
Ester Number (Two Determinations)	29.9 to 31.7
Ester Number after Acetylation (One Determination Only)	72.8
Saponification Number	24.0 to 92.0
Solubility	Not completely soluble in 10 vol. of 80% alcohol; soluble in 90% alcohol

Chemical Composition.—Nothing is known about the composition of sumbul root oil except that it contains a sesquiterpene which yields cadinene hydrochloride on treatment with hydrogen chloride and which has been named *sumbulene* by Dyson.[2] For details see Vol. II of this work, p. 97.

Use.—Because of its musk-like odor, sumbul root oil has possible application for all kinds of perfume mixtures, but the oil has actually attained no commercial importance.

OIL OF WATER FENNEL

Essence de Fenouil d'Eau *Aceite Esencial Hinojo Acuatico*
Wasserfenchelöl *Oleum Phellandrii Aquatici*

Phellandrium aquaticum L. (*Oenanthe phellandrium* Lam.) is a biannual or perennial European water plant, the seed of which contains 1.0 to 2.5 per cent of volatile oil.

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[1] "Die Ätherischen Öle," 3d Ed., Vol. III, 556.

[2] *Perfumery Essential Oil Record,* Annual Special Number (1936), 6.

Physicochemical Properties.—According to Gildemeister and Hoffmann,[1] the properties of water fennel oil vary between these limits:

Specific Gravity at 15°	0.850 to 0.890
Optical Rotation	+12° 42′ to +19° 0′
Refractive Index at 20°	1.4840 to 1.4950

When distilled under atmospheric pressure, the oil starts to boil at about 170°. Fifty to sixty per cent distills below 172°; the temperature then rises to 300°, and finally a black resin remains in the distilling glass.

The oil possesses a strong penetrating odor and a somewhat burning taste.

Chemical Composition.—The following compounds have been identified in water fennel oil:

d-β-Phellandrene. Years ago Pesci[2] showed that 80 per cent of the water fennel oil consists of a terpene, viz., phellandrene, which yields a nitrite. Later it was found that phellandrene exists in two modifications, the one in water fennel oil being *d*-β-phellandrene.

According to Wallach,[3] β-phellandrene from water fennel oil has these properties:

b_{11}	57°
d_{20}	0.8520
d_{18}	0.8480
$[\alpha]_D$	+14° 45′
n_D^{20}	1.4788
n_D^{18}	1.4759

The optical rotation of phellandrene changes considerably under the influence of light and age.

The presence of *d*-β-phellandrene in water fennel oil was confirmed by Berry, Macbeth and Swanson.[4]

Pinene(?). When investigating the hydrochloride of phellandrene, Kondakov and Schindelmeiser[5] noticed the presence also of pinene hydrochloride which might have been derived from pinene originally present in the oil.

Sabinene(?). Wallach[6] expressed the opinion that sabinene is possibly a constituent of seafennel oil.

Camphene. Wienhaus and Presting[7] reported the occurrence of camphene in this oil.

Phellandral (Tetrahydrocuminaldehyde). Laevorotatory phellandral α_D −36° 30′ was discovered by the Schimmel chemists[8] in the fractions boiling above phellandrene. Its odor recalls cuminaldehyde.

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[1] "Die Ätherischen Öle," 3d Ed., Vol. III, 534.

[2] *Gazz. chim. ital.* **16** (1886), 225.

[3] *Liebigs Ann.* **336** (1904), 43; **340** (1905), 2.

[4] *J. Chem. Soc.* (1937), 1448.

[5] *J. prakt. Chem.* [2], **75** (1907), 141.

[6] "Terpene und Campher," 2d Ed., Leipzig (1914), 485, footnote.

[7] *Inaugural Dissertation, Univ. Leipzig* (1930). *Ber. Schimmel & Co.* (1932), 134.

[8] *Ber. Schimmel & Co.,* October (1904), 91; October (1905), 71.

Later investigations of Berry, Macbeth and Swanson[9] showed that water fennel oil contains phellandral in dextrorotatory modification α_D +116° 13′.

Androl (*n*-1-Nonen-3-ol). Years ago the Schimmel chemists[10] found in the fraction b. 197°–198° of water fennel oil an alcohol b. 197°–198°, d_{15} 0.858, α_D −7° 10′, which possessed the characteristic odor of this oil to a marked degree and which they named "androl." Later Wienhaus and Presting[11] declared it to be a primary terpene alcohol $C_{10}H_{20}O$; α-naphthylurethane m. 80.5°.

Wienhaus and Striegler[12] finally proved that androl has the empirical molecular formula $C_9H_{18}O$ and that this low boiling laevorotatory alcohol is actually *n*-1-nonen-3-ol.

n-2-Nonen-1-ol(?), *n*-4-Undecen-3-ol(?), and 4-Isopropyl-2-cyclohexen-1-ol(?). Probably present in water fennel oil, according to Wienhaus and Striegler.[13]

4-Isopropyl-2-cyclohexen-1-one. Also identified by Wienhaus and Striegler, and later confirmed by Berry, Macbeth and Swanson.[14]

The presence of citronellol in water fennel oil, first suggested by Wienhaus and Presting[15] was later disproved by Wienhaus and Striegler.[16]

Use.—Oil of water fennel has not attained any commercial importance, but its use has been suggested in cases of chronic pectoral afflictions, such as bronchitis and asthma, and as a remedy for dyspepsia, intermittent fever, obstinate ulcers, etc.

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[9] *J. Chem. Soc.* (1937), 1448.

[10] *Ber. Schimmel & Co.*, October (1904), 91; October (1905), 71.

[11] Presting, *Inaugural Dissertation, Univ. Leipzig* (1930).

[12] Striegler, *Inaugural Dissertation, Univ. Leipzig* (1936).

[13] *Ibid.*

[14] *J. Chem. Soc.* (1937), 1448.

[15] Presting, *Inaugural Dissertation, Univ. Leipzig* (1930).

[16] Striegler, *Inaugural Dissertation, Univ. Leipzig* (1936).

CHAPTER VI

ESSENTIAL OILS OF THE PLANT FAMILY *GERANIACEAE*

OIL OF GERANIUM

Essence de Géranium *Aceite Esencial Geranio* *Geraniumöl*
Oleum Geranii

Introduction, Botany, and Development.—The taxonomy of the plants which are cultivated in various parts of the world for the production of commercial geranium oil has been a matter of much controversy and has given rise to considerable confusion. In fact, the name geranium oil itself is a misnomer, since the commercial types of geranium oil are derived not from any *Geranium,* but from several species, varieties, and strains of *Pelargonium. P. graveolens, P. roseum, P. radula, P. capitatum, P. odoratissimum, P. fragrans,* and *P. terebinthinaceum* have been stated as the source of geranium oil. According to Beckley,[1] it is questionable whether some of these terms are not fancy horticultural names, with no real botanical meaning. Neither the true *P. odoratissimum* nor *P. fragrans* is suitable for cultivation for the purpose of oil production. The former consists of a mass of radical leaves with a few long, trailing, flowering branches, possessing a most unattractive odor. *P. fragrans* is a small, bushy shrub of pleasant odor, but the odor differs from that of geranium oil. The term *P. roseum* is most probably a garden name for *P. graveolens* and *P. radula* types. The *Pelargonium* plants readily cross, and soon after their introduction into Europe so many hybrids were developed that today the numerous existing varieties and strains can hardly be distinguished from one another.

"Geranium" has now become a rather vague horticultural term which has no relation to the botanical term *Geranium.* The only true *Geranium* species, from which an essential oil is derived (and in very small quantities), is *G. macrorrhizum* L. (*G. lugubre* Salisb., *Robertium macrorrhizum* Picard). The latter grows wild in Bulgaria and other Balkan countries and is occasionally used for the distillation of an oil said to be employed for the adulteration of rose oil (cf. the monograph on "Oil of *Geranium macrorrhizum*").

The only region in which *Pelargonium* grows wild is the Cape Province (Union of South Africa). According to Holmes,[2] there are about 600 species of the genus *Pelargonium* in the Cape Province, many of which possess an agreeable odor. During the last years of the seventeenth century (1690),

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[1] *Perfumery Essential Oil Record* **28** (1937), 235.

[2] *Ibid.* **4** (1913), 239, 372. Cf. A. Engler, "Das Pflanzenreich," IV, 129. R. Knuth "*Geraniaceae,*" Leipzig (1912). Cf. also Piesse, "The Art of Perfumery," London, 4th Ed. (1879), 124.

cuttings were exported to Europe (particularly to Kew Gardens in England), where they were crossed and hybridized in botanical institutes, greenhouses, and private gardens. It seems probable that all the species and varieties of *Pelargonium,* which yield the various types of commercial geranium oils (i.e., the Réunion, Algerian, Moroccan, Belgian Congo, Spanish, French, Corsican, and East African oils) are descendants of the hybrids created in Europe and re-exported, particularly from Southern France, to the colonies. The theory of hybridization would explain the difficulty of germinating the seeds of the *Pelargonium* plants. Moreover, when germination is actually attained, the new plants do not grow true to their parent plants, but develop into "sports," or different varieties. For this reason commercial propagation of *Pelargonium* is now effected by means of cuttings.

The parent plant of all *Pelargonium* varieties and strains used today for the commercial production of geranium oil seems to be *P. graveolens* Ait. For the sake of simplicity we shall refer to the essential oil derived from this plant simply as oil of geranium—the name by which it has been known to the trade for many years.

Owing to its agreeable and very pronounced strong rose-like odor, oil of geranium is one of the most important ingredients in perfumery. If pure, the oil is almost a perfume by itself and blends well into all kinds of scents, floral as well as oriental. Being stable and lasting, even in a slightly alkaline medium, the oil is widely used in the scenting of soaps.

Because of its importance, many attempts have been made to produce geranium oil in various parts of the world, but not all of these have been successful. Commercial production of the oil from plantations was started in the Grasse region of Southern France, during the first decades of the nineteenth century. In 1847 plants were exported from there to newly conquered Algeria, and slowly a new geranium oil industry developed in the fertile plain of Mitidja. About 1880 plants, also from the Grasse region, were transferred to the island of Réunion in the southwestern Indian Ocean, whence the bulk of geranium oil originates today. Small quantities have been produced in Spain, Corsica, and Madagascar. At present, efforts are being made to develop a geranium oil industry in Morocco, the Belgian Congo, East Africa, and the southern part of the U.S.S.R. Substantial quantities of these oils, more or less of good quality, have reached the world markets, and a few of these types will undoubtedly attain considerable commercial importance. In recent years great changes have taken place in the geranium oil industry, and production has gradually shifted from region to region, the changes being caused by the prices of the oil on the world market and by economic conditions in the production areas. Thus, Southern France and Corsica, once important producers, have been reduced almost to insignificance. Spain, which had suffered a similar decline, experienced a slight revival during World War II; Algeria, once a heavy producer of the oil, is gradually being eliminated, Morocco and the Belgian Congo taking its place. The so-called mawah oil (derived from a hybrid) of Kenya Colony has not met with much success. Comparatively little is known about production in the southern U.S.S.R. Efforts to raise *Pelargonium* in the United States have so far been unsuccessful. (Details will be given in the monographs on the various types of geranium oil.)

The same species, exported from Southern France, appears to have been used originally for starting plantings in various subtropical and tropical countries; but ecological factors strongly influence the morphological and physiological characteristics of *Pelargonium.* Small wonder, then, that after a few years of growth in a different soil and climate, the plant seems to change and develop in the direction of a special local or new variety. The influence of climate, soil, altitude, and actinism, not to mention the method of distillation, tends to create marked differences also among the essential oils derived from these local varieties.

In general, *Pelargonium* grows well in temperate, subtropical and tropical climates, and at a variety of altitudes. It thrives best in a subtropical (but not too warm) climate. Temperatures below +3° C. kill the plant, for which reason it is grown as an annual in temperate countries, such as Southern France, and must be replanted each year. In warmer climates, *Pelargonium* becomes a perennial, lasting on the average from five to six years. The plant requires a certain amount of moisture, either by rain, irrigation, or atmospheric humidity. This is why it flourishes in certain parts and altitudes of Réunion Island that are exposed to the moisture-laden monsoon winds. The plant itself is quite resistant to drought, but may wither under conditions of excessive drought. After a long spell of dry weather the yield of oil diminishes greatly.

Pelargonium thrives well in porous, light soil which does not retain moisture in the winter or during the rainy season. A water-logged soil causes root-rot, and, in conjunction with excessive rain, may be as deadly to the plant as frost.

Pelargonium is easily propagated by means of cuttings.[3]

The essential oil is contained in small glands, $\frac{1}{15}$ to $\frac{1}{18}$ mm. long, distributed over the green parts of the plant, particularly over the surface of the leaves. Many of these glands can be seen with the naked eye and impart to the surface a silvery satin-like shine. According to Bourquelot and Bridel,[4] the essential oil occurs in the glands partly as oil in free form and partly as β-geranyl glycoside. This may explain the fact that the yield of

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[3] For details pertaining to cultivation, see an article by A. Rolet in *L'Eclaireur agricole et horticole,* November 1, 1931, through *Bull. Kew* (1932), 205.

[4] *Compt. rend.* **157** (1913), 72.

oil seems to be higher when the plants are permitted to dry and wither for a few hours, prior to distillation.

For distillation the overground parts of the plant, chiefly the leaves, are used, after the heavier stalk material has been removed. In fact, in most producing regions the plant material is harvested in such a way that the woody parts are excluded, the cutting being done by hand and with short sickles, a very tedious and "back-breaking" task.

Charabot and Laloue[5] expressed the opinion that the essential oil is located entirely in the leaves and not in the flowers. Blandini,[6] however, obtained 0.150 to 0.158 per cent of oil from the flowers, and only 0.07 to 0.08 per cent from the leaves; Prioris[7] reported a yield of 0.29 per cent of oil from the flowers, the oil being comparable with that from the leaves of the same batch of plants.

In actual field practice harvesting takes place within a period of a few days, at the beginning of the flowering period, when the originally lemon-like odor of the leaves has changed to a pronounced rose scent.

It is said that plants from dry soil yield less oil, but an oil of better quality, than plants from irrigated soil. Agronomic conditions, in general, exert a considerable influence upon the quality of the oil.

Reviewing the character, the particular merits, and principal use of each commercial type of geranium oil, we may summarize as follows:

1. The Réunion oil, by far the most important one commercially, and very rich in citronellol, is used for the extraction of commercial rhodinol. The oil possesses a very strong, somewhat "minty" odor and is widely employed for the scenting of soaps.
2. The Algerian oil has a more delicate odor and recommends itself for use in high-grade cosmetics, particularly powders and creams.
3. The Moroccan oil, developed only recently, seems to combine the advantages of the Réunion and the French oils—a product of supreme quality in every respect.
4. The French oil, now produced in small quantities only, possesses the finest and most rose-like odor. It is employed where high odor value, not price, is a principal consideration.
5. The Spanish oil, produced on a very limited scale, and absorbed by the home market, approaches the quality of the French oil.
6. The Tunisian, Sicilian, and Calabrian oils, produced in very small quantities, approach the character of the Algerian type.

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[5] *Ibid.* **136** (1903), 1467.

[6] *Bull. de l'Office du Gouv. de l'Algérie* **12** (1906), 277.

[7] *Parfumerie moderne* **20** (1927), 125.

7. The Madagascar oil, produced in very limited quantities, resembles the Réunion oil.

8. The Congo oil has an odor somewhat different from that of the other types. Annual production is small, but flexible, and depends upon market price.

9. The Russian oil possesses a weaker odor than the Réunion and the Algerian oils. It may be classified as standing between the Algerian and the mawah oil (see below).

10. The East African mawah oil exhibits an odor quite different from that of the Réunion and the Algerian oils and may be classified as standing between geranium oil in general and palmarosa oil It differs from all other geranium oils also in regard to its chemical composition and physicochemical properties.

Oil of Geranium Réunion

Introduction.—By far the greater part of the world's total supply of geranium oil comes from Réunion (formerly called Bourbon), a picturesque and fertile island located in the Indian Ocean, about 400 miles east of Madagascar. For a long time, England and France fought for the two neighboring islands, Réunion and Mauritius, until the issue was decided by assigning Réunion to France, and Mauritius to England. During the eighteenth century, Réunion, like Haiti, Guadeloupe, and Martinique in the West Indies, contributed greatly to the wealth of France by the export of valuable tropical produce, such as sugar, spices, coffee, vanilla, and rum, and absentee landlords living in Paris enjoyed the fruit of slave labor on the distant island. Since the French revolution conditions have changed, however, and today the liquid capital of the island seems to be frozen in the vaults of St. Denis' banks. Sugar interests dominate the island economically. Large dividends are paid to the stockholders of powerful concerns, but the money does not circulate freely and the white settlers in the highlands remain in abject poverty. Little is spent on modern improvements, and the living standard of the peasantry has remained what it was in the days of early colonization. A "paillotte," or straw hut, is all the wealthy landowner offers his sharecroppers or "colons" for living quarters; and, as in the "tobacco road" area of the United States, a sharecropper draws upon advanced funds, which he tries to repay—but seldom succeeds—with the crops he wrests from the overworked rented land.

High up in the mountains, on the plateaus and plains, the original French population has remained almost purely white; but, down in the coastal lowlands, it has intermingled with the descendants of Negro slaves and Asiatic immigrants and developed into a population of all shades from Nordic white to African dark.

The visitor to the highlands will be shocked to find the descendants of early immigrants from the north of France fallen into utter poverty, a result, perhaps, of the tropical climate and of economic conditions. He may wonder whether the white man is endowed at all by nature to survive in the tropics and to compete, on an equal economic basis, with the colored races—unless he is assisted by the modern conveniences of our scientific and mechanical age.

So far as the colored native is concerned, he has always been apathetic, and even high wages do not easily induce him to improve his standard of living. He prefers to spend his earnings on trinkets or rum, or to work fewer days a week. He seems to be happier in a hut than in a clean stone house. Most of the retail shops are Chinese-owned, and the shrewd Chinaman supplies the rum against the earnings of the ignorant native.

The visitor must realize the existence of these conditions before he can understand the primitiveness of Réunion's geranium oil industry which, next to sugar, rum, and tobacco, supplies one of the islands most important export articles. The oil is produced almost entirely by the poverty-stricken descendants of the early French immigrants, who settled in the more healthful highlands of the island.

Historical Development.—The geranium plant was introduced to Réunion about 1880. Some of the older growers remember that their fathers distilled small quantities of geranium oil. But the plant grown at that time (locally known as *Petit géranium à feuilles minces*) was probably of a species (*Pelargonium capitatum?*) different from that cultivated today. It was smaller and, although yielding less herb material per acre, seems to have given a higher yield of oil. The odor of the oil was much more mint-like than that of the oil produced today. (The old type of plant is still found growing wild in some parts of the island.)

About 1900, another *Pelargonium* species, probably *P. graveolens* (or *P. roseum,* according to other sources), was introduced from the Grasse region in Southern France. It grows more luxuriantly and taller (whence the local name *Gros géranium*) and yields a sweeter, more rose-like oil than the species originally cultivated on Réunion. Under the influence of climatic and soil conditions, the newly introduced species gradually developed into a definite local type, which today is cultivated on a large scale. It yields an oil possessing a high citronellol content and an odor quite different from that of the oil derived from the parent plants in Southern France.

Climate, Soil, and Altitude.—The plant grows well in those parts of Réunion Island which are neither too moist nor too dry. Excessive moisture causes rust (*Uredo* Pers.) which may destroy a planting in a few days. Prolonged spells of drought, on the other hand, retard the growth of the plant. The temperate sections of the island, where the atmosphere contains sufficient moisture (slight sea breezes or dew), are those best suited for cultivation of geranium. Such conditions exist in the southern, southwestern, and western parts of Réunion, which are not exposed to the heavy rains of the southeast monsoons during the "winter" months (July to September).

At the present time most of the geranium plantations are located at altitudes ranging from 400 to 1,200 m., or even higher. In former years geranium was also cultivated in the lowlands, extending from the coast to ten or fifteen miles inland; but of late it has been replaced there by more remunerative crops, chiefly sugar cane. As a result of this trend, geranium has been gradually driven up into the highlands. Today it is grown largely on the timber line, i.e., the demarcation line between private land and government-owned wooded lands high on the mountain slopes. The highlands of the island are thus dotted with countless small plots of geranium, here and there laid out in clearings in the forest, often on steep hill slopes of the rugged volcanic mountains, or wedged into canyons, but usually with exposure to the sea. Sugar cane cannot be grown here, where the roads are few and poor, as the bulky cane cannot be hauled to the refineries.

The spectacle of these mountains, covered by luxuriant tropical vegetation and set against the luminous Indian Ocean, is of overwhelming beauty; and, were it not for the poverty in which the rural population lives, the highlands of Réunion Island would be a terrestrial paradise. The climate resembles that of Southern France, but the difference in the temperature of day and night is less pronounced.

Producing Regions.—Réunion Island is divided into two districts. (1) Arrondissement "Du Vent," the windward part of the island, is exposed to the moist, southeast monsoons and frequent rains from July to September. This region stretches from St. Denis, the capital, to the east, and toward St. Pierre in the south. The climate in this district is too moist for the cultivation of geranium. (2) Arrondissement "Sous le Vent," the leeward, and larger, side of the island is much drier throughout the year and, particularly during the "winter," is well suited for the growth of geranium.

The principal localities of geranium cultivation are: St. Leu, Tampon, St. Pierre, St. Paul, Entre-Deux, Avirons, Trois Bassins, St. Joseph, St. Louis, and Plaine des Caffres. St. Leu and Tampon produce about half of the total crop. The oils of best quality come from Tampon and St. Louis.

The total area planted with geranium varies from year to year; on the average it is about 1,500 hectares. In 1948 about 1,400 hectares were planted with geranium.

Planting, Cultivating, and Harvesting.—Geranium does not grow wild on the island, and all the plant material used for distillation of the oil originates from plantings, which range from small patches to a few acres.

To start a plantation, slips are prepared from May to October, depending upon the altitude, and immediately planted in the field, at distances of 30 cm. between the plants and between the rows. The soil should be slightly moist, the result of a light previous rain. Provided they receive sufficient moisture by moderate rains, the young plants develop rapidly and, depending upon weather conditions, reach a height of 20 to 60 cm. (in some cases even more).

The first harvest may take place six months after planting, or after eight months, if the weather is dry. The plants are cut by hand with a short knife at the time of blossoming. Some growers still cut the entire overground part of the plant. Since this often causes the plant to perish, a better method of harvesting was introduced some years ago; it permits the plant to continue its metabolic functions. By the new method, one branch with all its adhering leaves is left on each plant stock. One month after cutting, the plant has developed new branches and leaves sufficiently large to absorb carbon dioxide from the air and keep the plant alive. The one branch left from the first cutting may then be harvested. Two or three months later the new branches and leaves have grown sufficiently large to be cut; but again one branch with all its leaves is left standing, etc.

Theoretically four harvests are possible each year. Actually, however, only three are obtained, i.e., two harvests in "summer" (November to April), and one in "winter" (July to September), at which time plant growth is retarded. Moreover, from May to October, slips are prepared from the older plants for the purpose of replanting, which diminishes the amount of plant material available for distillation. Thus the most important months, so far as production of the oil is concerned, are those between November and April (particularly January to March). From May to October (particularly July to September) the fields yield fewer and smaller plants and correspondingly less oil. However, distillation of oil goes on also between seasons, continuing, in fact, all year around, but on a much smaller scale. Thus a certain amount of herb material is harvested throughout the year from plants which start to bloom.

Exporters in Réunion usually speak of two harvests only—the summer crop from January to March, and the winter crop from August to September. The former represents roughly four-fifths of the total quantity of geranium oil distilled in the year, the latter amounts to one-fifth only.

A geranium planting requires considerable care if it is to remain productive for several years. Otherwise it will perish. In addition to stable manure, the distilled plant material is dumped in the fields for fertilization. All plants which show signs of decay must be removed and replaced during the "winter" months. If planted in new ground and well taken care of, a geranium field may last up to ten years; five years, however, is considered the average, as older plantings decline in productivity. If planted in ground which previously had served for geranium, the field will not be very productive and will decline within two or three years.

Like every crop on Réunion Island, geranium is occasionally ravaged by cyclones which appear to strike annually for several years, then spare the island for a few years. The cyclone season lasts from the middle of January to the end of March. A cyclone, always unpredictable in its course, may devastate a whole region, or only parts; it may hit a field and destroy the crop in whole, or only in part. The earlier in the season it appears, the more havoc a cyclone will play with the standing crop; later in the season a good portion of the geranium may have been harvested, and the damage will be less. However, even then great destruction may be wrought in the fields, because after a severe cyclone it is often difficult to prepare sufficient slips for a new planting. Frequently the cyclones are preceded by very hot winds which dry up the crop. (The geranium plant, in general, is very sensitive to wind.) The heavy rains which follow a cyclone also inflict much damage upon the fields; but, if they are short, the plants have a chance to recuperate. Under these circumstances, it is not surprising that the whole geranium industry of Réunion Island has always suffered from instability; there have been years in which parts of the crop, or, indeed, almost the entire geranium production, were wiped out. In others there has been overproduction. Such fluctuations obviously encourage a great deal of price speculation.

Since 1944, particularly in 1945 and 1947, the cyclones have been so frequent and severe that growers have become quite discouraged, and production of geranium oil has fallen to very low levels (less than 20 metric tons in 1948). The worst cyclone since 1900 was that of January 25, 1949. It killed 150 people, destroyed 70 per cent of the dwellings in the area where it struck, 50 per cent of the cattle, and 80 per cent of the geranium plantings.

Distillation.—Because of the extreme ruggedness of the volcanic mountains on the slopes of which geranium is grown, roads are difficult to construct—hence, few in number. Plant material, therefore, cannot be hauled to centrally located distilleries, and the stills must follow the plant material. Distillation is carried out in hundreds of small field stills operated near the plantings. Where abundant herb material and running water are available, a distillation post may comprise several field stills. They are usually of the primitive directly-fired type, made of copper. According to estimates by the local Bureau of Internal Revenue there are about 1,700 geranium stills in Réunion Island, but not all of them are operated every year.

The most annoying handicap confronting the geranium distillers on the island is the lack of water (specifically running water) in many parts of the producing regions. Traveling through the villages of Réunion's geranium areas, the visitor frequently notices water tanks along the roads, from which the villagers draw their supply. They collect the water in tin cans, which they carry suspended on a pole held across their shoulders, often for long distances. The geranium distillers likewise find it easier to haul the water in barrels and cans to their distillation posts rather than transport the bulky plant material from the fields to a distant distillery conveniently placed near a brook or spring. In some sections of the island running water is plentiful, but even under such conditions distillation is always carried out in simple field stills, because of the difficulty of hauling the herb material over long distances.

The stills, mounted above a walled-in fire hearth, are usually set up beneath a palm shelter and, if possible, on a steep slope to permit easier charging and discharging of the plant material. Such an arrangement also makes the fire hole more accessible and facilitates the flow of the distillate into the oil separator and the flow of the separated oil into the receiving vessel (the latter often an old wine bottle).

Wood collected from the nearby mountain forests serves as fuel for the fire beneath the still. The distilled and exhausted plants are not used for the heating of the stills, as this material has to be dumped in the geranium fields, particularly the older fields, for fertilization.

The average still measures 1 m. in diameter, and 1.5 m. to 2 m. in height, including the hearth. The stills hold about 200 or 250, the larger ones 450, kg. of plant material. The 250 kg. type has been found most practical, because it can be operated by one man. It seems to be more economical also as regards consumption of fuel. Large stills are difficult to move, whereas the smaller ones can be transported more easily from field to field, after the crop of one planting has been processed.

The plant material is distilled as soon as possible after the harvest; and, since most of the plants of one field bloom at about the same time, much herb material is then available. Distillation thus goes on day and night.

The plants are charged into the still, above the perforated grid, and tramped down tightly. The space beneath the grid contains water up to a height of about 1 ft., the water being brought to boiling by a fire beneath the still. The still head is clamped down and all joints are sealed with a kind of paste made of water, mud, and dried, crushed plant matter, the paste hardening on heating of the still. To enable the distiller to watch the flow of oil, an empty sardine can is often placed between the outlet of the condenser and the oil separator. Distillation of one charge requires about 1½ hr., when practically all the oil has been distilled over. By that time the cooling water in the condenser (if not replaced by flowing water) has become hot, especially the upper portion. The residual water beneath the false bottom in the still (which has not been vaporized during the distillation) at the end of the operation is of dark color and contains some polymerized and empyreumatic compounds of sharp, unpleasant odor. In normal distillation this water would be thrown away and replaced with fresh water, before a new batch is started. This, however, is not possible in regions where water is scarce, and working conditions are then much more difficult.

Courtesy of Fritzsche Brothers, Inc., New York.

Fig. 38. Geranium oil production on Réunion Island. A distillation post in the mountains. Owing to the lack of running water the distiller stores water for his condenser tank in a barrel.

In such a case, the distiller must improvise his water supply by storing reserve water in one or two drums or barrels. All the distillation water, running off the condenser, quite warm, is collected in a drum, where it cools. The stationary cooling water in the condenser tank becomes increasingly warm as distillation proceeds. To prevent the distillate from flowing too hot, the distiller then draws some of the warm water from the top of the condenser tank and replaces it with cool water from his reserve drum. The residual water in the still bottom beneath the grid is left in the still, despite its objectionable odor; but the quantity of water that has been distilled over during the process is replaced with warm water drawn from the top of the condenser tank. Since this water has a temperature of about 70° C., fuel will be saved, as the water beneath the grid in the still then needs to be heated only from 70° to the boiling point during the following operation.

The water drawn from the top of the condenser tank is again replaced with water from the drum (which has already served for distillation), etc. In other words, the same limited water supply serves again and again for distillation and is therefore repeatedly cohobated. Actually, fresh water is added only as the old water supply dwindles by gradual evaporation in the course of many operations. The whole procedure is abnormal, and certainly not beneficial to the odor of the oil. It may be one of the reasons why Réunion geranium oil often exhibits a somewhat harsh odor and is, in general, not as soft and rose-like as the oils produced by modern methods in Algeria, Morocco, and France. Years ago, Garnier and Défaud[8] experimentally distilled geranium leaves in a modern steam distillery located in St. Paul (Réunion Island) and obtained oils with a softer, more pleasing odor than that of the country-distilled oils. However, the venture had to be abandoned, as the cost of transport of the plant material from the hills, and of fuel, was much too high.

During off-seasons the field stills are partly dismantled; and the more valuable and easily movable parts, such as helmet and gooseneck, are stored in the villages against theft.

Yield of Oil.—The yield of oil varies greatly, depending upon climatic, weather, and soil conditions, altitude, exposure to the sea, age of the planting, and other factors. Plant material from the same field may not always give the same yield, atmospheric conditions probably being responsible for the variations. A cloudy sky during the time of harvest seems to bring about a good yield of oil, whereas rain or humidity lowers the yield. After a thunderstorm the yield is very poor, and several days of dry weather are required before the plantation again produces a normal yield of oil. When a cyclone is approaching, the yield of oil often increases heavily and may reach twice the amount of a normal yield. The plant then seems to protect itself by storing up certain elements of biological importance.

During the "winter" harvest (July to September), the yield is about one-third lower than during the more important "summer" harvest (November to April). According to de Palmas,[9] 250 kg. of freshly cut herb material yield from 600 to 700 g. of oil in "summer," and 400 to 500 g. in "winter," as the plants then are much smaller. In the southern part of the island 250 kg. of fresh plant material yield 300 to 400 g. of oil in September and October, and 500 to 800 g. from January to April. One kilogram of oil per 600 kg. of plant material is generally considered normal.

According to Défaud,[10] the yield of geranium oil averages 0.15 per cent;

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[8] Private communication of Mr. Robert Garnier, Paris.

[9] Conversation with Mr. Richard de Palmas in Moka, Rivière des Pluies, St. Marie, Réunion Island.

[10] Conversation with Mr. Justin Défaud in St. Paul, Réunion Island.

0.20 per cent is considered very satisfactory. These figures refer to freshly cut plant material; the yield from plants dried in the fields is higher.

The yield of oil per hectare varies greatly; it depends upon the age and condition of the planting and the weather conditions. With favorable weather a well-kept, vigorous plantation may yield 30 kg. of oil per year and hectare, but this is exceptional. At present the average yield amounts to 18 kg. In former years higher yields of oil per year and hectare were obtained. The present much lower yields must be attributed to the generally poor condition of the geranium fields in Réunion.

Economic Set-up and Oil Trade.—The entire geranium oil industry of Réunion Island owes its peculiar character to the fact that the ruggedness of the mountainous countryside necessitates dividing and subdividing the land into numerous small patches and plots. These are tilled by settlers, many of whom live under impoverished conditions.

A small landowner may cultivate a few fields of geranium and do his own distilling, perhaps employing a laborer on daily wages; but the larger landowners usually exploit their fields with the help of tenants, who operate on a sharecrop basis. The sharecroppers then do all the work, including planting, cultivating, harvesting and distilling, in return for two-thirds of the oil produced; the landowner receives one-third. The sharecropping system generally prevails in Réunion, not only with reference to geranium, but to other crops as well.

When entering a working agreement with a sharecropper, the landowner lends him a hut as living quarters and advances funds in the form of cash or produce (food, seed, etc.), so that he may start a crop. The stills are the property of the landowner, who also supplies the necessary wood for fuel.

Considering the tenant's low standard of living and his usual apathy, the old-fashioned and semifeudal sharecropping arrangement has worked quite well—at least for the landowner. It relieves him of many inconveniences (administrative duties, for example), and he does not have to worry about the labor problem. In the highlands of Réunion, labor is difficult to obtain, as most of the unskilled agricultural labor has been absorbed by the better paying sugar industry in the coastal lowlands. So long as the tenant is hardworking and honest, the landowner has no reason for complaint; and, after a year, the sharecropping arrangement is usually renewed for another year. The tenant often remains on the same land for years. The landowner confines his activities to routine visits to the fields and distillation posts, in order to check up on the actual yield of oil, since a tenant-distiller might be tempted to sell a part of the oil output "on the side."

Every Saturday during the harvest the tenants bring their weekly oil production to the landlord's house, where the oil is divided into shares, one-third for the owner, and two-thirds for the sharecropper. The latter may sell his share, for cash, to a field dealer, or to a shopkeeper in the nearest village. More frequently, however, the tenant turns his own share over to the landlord, in payment against advanced funds. It may happen that at the end of the year the sharecropper has managed to produce just enough to pay off his debts, and new funds have to be advanced for the ensuing year. As long as the landowner treats him in a decent way, the tenant is content to stay on, and the semifeudal system continues.

From the large landowners and their tenants, and from the small landowners (who do their own distilling), the oil goes into the hands of field dealers, who continuously travel through the producing regions, and, on their own account, buy up small lots of oil. These field dealers are intimately familiar with the condition of each planting, the quality of oil produced in each locality, and particularly with the oil prices, which fluctuate daily. Whenever they have acquired quantities of oil amounting to a few hundred kilograms, they bring the bulked lot to a town broker in St. Pierre or St. Denis, who holds the lot as the property of the field dealer. There are several certified brokers in St. Paul and St. Denis, the principal geranium oil markets on Réunion Island, and a few who operate without a license.

The town brokers, in their turn, supply the exporters in St. Denis with oil, when the latter receive shipping orders from abroad. Whenever an inquiry for the price of geranium oil arrives in Réunion, the exporting houses in St. Denis first contact the town brokers, who in turn must consult the field dealers for whom they hold the stocks in custody, and, asking permission, often by telephone, sell the lot at a certain price. Price options are usually given only for a very few days, and, in case of a rising market, often for only 24 hr., as oil prices fluctuate greatly and constantly. An oil exporter in St. Denis thus finds himself in about the same position as a Wall Street broker buying stocks for an out-of-town customer. He cannot grant long options; he may buy "at best," or below a margin specified by his customer. The geranium oil market in St. Denis is so confined and so small, relatively, that any price difference among the few town brokers would be immediately made known and rendered almost impossible. In order to book a shipping contract, the exporters must therefore content themselves with small profits.

While the bulk of oil thus reaches the exporters through many field dealers and a few town brokers, there is also a limited number of large landowners whose tenants produce annually several tons of oil. These large producers may sell their output directly to the exporters in St. Denis on occasions when there exists a sufficiently wide and attractive margin between the prices offered by the field dealers and the prices paid by the exporters in St. Denis. In other words, by excluding the field dealers and absorbing their profits, the large producers become oil dealers themselves, and occasionally they even buy up oil produced by neighboring small landowners.

As a part of the over-all picture of the geranium oil trade, we should also mention the many shopowners in the villages, usually Chinese, who purchase or barter small lots of oil across the counter from sharecroppers or independent small producers. These Chinese merchants may even operate as field dealers and town brokers. In general they do not constitute a very desirable element in the trade, and much of the speculative element that permeates the Réunion geranium oil industry must be blamed on them. They often hold back what are known as "invisible stocks," i.e., lots that, for the purpose of speculation, have been stored for a number of years under very poor conditions, in unclean. half-filled containers, exposed to air and heat. No wonder, then, that these old oils are of subnormal quality, possessing particularly a low optical rotation (see "Physicochemical Properties"). Appearing unexpectedly, these lots present a constant menace to the normal price structure of geranium oil and, flooding the market, may upset all predictions. When they do reach the market, they are usually offered at a substantial discount. Exhibiting substandard physicochemical properties, these lots are often bulked with lots of normal properties, which practice does not contribute to the quality of the Réunion oil in general. This has been the case particularly in the years immediately following World War II, when geranium oils with low optical rotation have been shipped from the island. These were the result of bulkings with oil lots produced as early as 1940–1941.

At present, before any export license is granted, a sample of the intended shipment must be analyzed by the "Service de Conditionnement" in St. Denis which, after approval of the quality, will issue a "Certificat de Conditionnement," accompanied by a report of the official analysis.

As regards the price of the Réunion geranium oil, it is influenced chiefly by three factors:

1. The supply of the oil, which depends upon the acreage planted, the condition and age of the plantings, weather conditions, the yield of oil, and the damage done to the fields by cyclones.
2. Unpredictable factors, for example, the sudden appearance, on the market, of "invisible stocks," or a change in the franc-dollar exchange ratio.
3. The demand from abroad. Next to devastation of the fields by cyclones, this factor exercises the most profound influence upon the price movement of the oil. Exporters in St. Denis are not entirely wrong if they claim that oil prices are basically determined abroad. A single inquiry for, say,

2 tons of oil directed to several competing importers in New York, London, Paris, or Grasse by a large soap manufacturer may entirely upset the price structure on the island. Cable lines to St. Denis and telephone lines from St. Denis to St. Paul and the producing regions in the interior will buzz with competing inquiries, and the original inquiry for 2 tons of oil may quickly assume the importance of an inquiry for 10 tons. Prices will thus be stimulated artificially.

Geranium oil should be purchased quietly, so to speak, through a reliable source. The most advantageous period for buying the oil is toward the end of January. The bulk of the "summer" harvest has been distilled by then, stocks are abundant, and the producers need cash for the next harvest and are willing to liquidate their stocks. The full season of the cyclones has not arrived yet; it comes usually in February or March, if at all. If a cyclone should really hit the producing regions during these two months, oil prices most probably will rise, and heavy profits are to be had.

Annual Total Production.—It is very difficult to obtain exact figures on the actual production of geranium oil on Réunion Island. According to Barbot,[11] the only way to arrive at even approximate figures is to deduct the so-called "hidden stocks" held by the speculators (which always amount to 15 to 20 metric tons) from the export figures in a given year. Taking the production of 1936–37 as an example, we arrive at this calculation:

	Metric Tons
Exports of 1936–1937	113
"Hidden Stocks"	15
Actual Production	98

As usual, about 80 per cent of this amount was obtained from the "summer" crop, and 20 per cent from the "winter" harvest.

Pursuing the above method, we arrive at the following approximate figures:

Year	*"Summer" Harvest in Metric Tons*	*"Winter" Harvest in Metric Tons*
1936–1937	78.5	19.6
1937–1938	82.9	20.7
1938–1939	93.8	23.4
1939–1940	67.0	19.0
1940–1941	65.0	13.0
1941–1942	60.0	12.0
1942–1943	55.0	11.0

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[11] Private communication of Mr. André Barbot, St. Denis, Réunion Island, through the courtesy of Mr. Jean Duclos, Paris.

Year	*"Summer" Harvest in Metric Tons*	*"Winter Harvest in Metric Tons*
1943–1944	50.0	10.0
1944–1945	35.0	7.0
1945–1946	35.0	7.0
1946–1947	35.0	7.0
1947–1948	10.0	2.0

Annual Exports.—In 1910 Réunion Island exported about 61 metric tons of geranium oil, in 1924 about 110 tons, and in 1926 about 126 tons. Since 1936–1937 the exports have been approximately as follows:

	Metric Tons
1936–1937	113.1
1937–1938	118.6
1938–1939	132.3
1939–1940	100.1
1940–1941	53.1
1941–1942	0.1
1942–1943	2.5
1943–1944	72.9
1944–1945	71.2
1945–1946	95.3
1946–1947	57.2
1947–1948	34.1

A study of the figures quoted above will show that within the last few years the exports have been substantially higher than the actual production in a given year. The reason is simply that, since the end of World War II, a great amount of oil has been exported that had accumulated on the island during the war years when exports were not regular. Many of these old lots have been of substandard quality (see "Physicochemical Properties").

Physicochemical Properties.—The Réunion geranium oil possesses a very strong, heavy rose-like odor, occasionally slightly harsh and minty. The oil is valued particularly on account of its high citronellol content, which makes the Réunion type of geranium oil the best starting material for the extraction of commercial "rhodinol."

According to Gildemeister and Hoffmann,[12] the physicochemical properties of the Réunion geranium oils vary within these limits:

Specific Gravity at 15°	0.888 to 0.896
Optical Rotation	−7° 40′ to −13° 50′
Refractive Index at 20°	1.461 to 1.468
Acid Number	1.5 to 12
Ester Number	50 to 78
Ester Content, Calculated as Geranyl Tiglate	21 to 33%

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[12] "Die Ätherischen Öle," 3d Ed., Vol. II, 897.

Ester Number after Acetylation	206 to 233
Total Alcohol Content, Calculated as Geraniol	67 to 77.6%
Solubility	Usually clearly soluble in 2 to 3 vol. of 70% alcohol; often separation of paraffin crystals on addition of more alcohol

Naves[13] reported the following values for several hundred batches of Réunion geranium oil imported into France from 1924 to 1934:

	In Most Batches	*Extreme Limits*
Specific Gravity at 15°/15°	0.8905 to 0.8945	0.8884 to 0.8960
Optical Rotation	−11° 30′ to −13° 0′	−7° 40′ to −14° 10′
Refractive Index at 20°	1.4630 to 1.4655	1.4612 to 1.4677
Acid Number	Up to 3.9	Up to 12
Ester Number	62.3 to 72.8	53.2 to 75.2
Ester Content, Calculated as Geranyl Tiglate	26.2 to 30.7%	22.4 to 31.7%
Ester Number after Acetylation	213.1 to 220.5	207.9 to 224
Total Alcohol Content, Calculated as Geraniol	66.2 to 67.7%	65.5 to 69.2%
Free Alcohol Content	46.9 to 50.8%	45.7 to 52.8%
Ester Number after Formylation	145.6 to 171.1	139.3 to 179.8
Apparent Citronellol Content	43.7 to 52%	41.7 to 55%
Ketone Content, Calculated as Isomenthone (Hydroxylamine Hydrochloride Method)	About 6 to 13.5%	...
Solubility	Soluble in 3 to 4 vol. of 75% alcohol, sometimes with opalescence or slight turbidity on dilution. Soluble in 0.5 to 2 vol. of 70% alcohol, rarely with opalescence on dilution	

Shipments of numerous lots of pure geranium oils imported and examined before World War II by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.890 to 0.894
Optical Rotation	−10° 12′ to −12° 48′
Refractive Index at 20°	1.4630 to 1.4661
Acid Number	1.4 to 9.8
Ester Content, Calculated as Geranyl Tiglate	22.4 to 30.7%
Total Alcohol Content, Calculated as Geraniol	64.6 to 72.7%
Formate Content, Calculated as Geranyl Formate	13.4 to 16.5%
Ketone Content, Calculated as Isomenthone (Hydroxylamine Hydrochloride Method)	9.2 to 11.6%

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[13] *Parfums France* **12** (1934), 179.

Solubility	Soluble in 2 to 2.5 vol. and more of 70% alcohol

Some of the lots arriving from Réunion shortly after the end of the war had somewhat different properties—for example, a specific gravity as high as 0.900, an optical rotation as low as −6° 48′, and a formate content as low as 11.5% were observed. A few lots were soluble in two volumes of 70 per cent alcohol, but hazy in ten volumes. Undoubtedly these rather abnormal properties were the result of admixture of old lots which had accumulated on the island during the war. Since 1948 the properties of the shipments have again been normal, approaching those supplied in prewar years.

Some lots of Réunion geranium oil show a positive test for dimethyl sulfide, others react negative to this test. On removal of the dimethyl sulfide from the oil, either by aging or by exposure to air, the odor generally improves.

The properties of genuine Réunion oils usually vary within rather narrow limits because of the fact that all commercial shipments consist of bulkings of numerous small lots (see above). Any marked deviations in physicochemical properties may indicate that a commercial lot contains an admixed lot of old, partly resinified oil which had been stored for several years.

Improper storage for a prolonged period, particularly in half-filled containers and in Réunion's warm climate, causes a marked lowering of the optical rotation and ester content, as well as an increase in the specific gravity, refractive index, acid number, and evaporation residue. Freshly distilled oils exhibit an optical rotation of −11° or slightly higher. Analyzing numerous lots of freshly distilled Réunion geranium oil (amounting to more than 100 metric tons) in 1937, Barbot[14] found an average optical rotation of −11° 40′ and an average saponification number of 72.07. After several years of improper storage the optical rotation may fall to as low as −7° 30′. (In this connection it should be pointed out, however, that storage of the oil under carefully controlled conditions improves the odor of the oil substantially, freshly distilled oils possessing a somewhat "green" odor. Proper aging of the oil for one or two years results in a more mellow and richer odor.) The decrease in the optical rotation of geranium oils on prolonged standing is caused chiefly by the inversion of the *l*-isomenthone present in the lower boiling fractions of the oil (cf. "Chemical Composition of Geranium Oil").

While surveying the production of geranium oil on Réunion Island, the author collected a number of samples of authentic oils. With the exception of one (Montvert, No. 1), all samples were taken from freshly distilled batches. They exhibited the following properties:

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[14] Private communication of Mr. André Barbot, St. Denis. Réunion Island, through the courtesy of Mr. Jean Duclos, Paris.

Location	*Specific Gravity at 15°*	*Optical Rotation*	*Refractive Index at 20°*	*Acid Number*	*Ester Content, Calculated as Geranyl Tiglate* (%)	*Total Alcohol Content, Calculated as Geraniol* (%)	*Isomenthone Content (Hydroxylamine Hydrochloride Method)* (%)
Entre-Deux..	0.892	−11° 0′	1.4640	7.0	28.9	68.6	10.1
Montvert (No. 1)....	0.899	−9° 28′	1.4671	7.0	26.6	66.1	10.1
Montvert (No. 2)....	0.893	−13° 40′	1.4640	7.0	28.5	64.8	13.5
Petite Ile (No. 1)....	0.895	−12° 0′	1.4642	8.4	28.7	67.9	13.3
Petite Ile (No. 2)....	0.896	−11° 20′	1.4649	8.4	29.9	68.4	11.6
St. Louis.....	0.893	−11° 52′	1.4643	7.0	30.9	66.9	10.1
St. Joseph....	0.895	−11° 20′	1.4650	8.4	28.7	66.9	11.6
Tampon (No. 1)....	0.894	−11° 48′	1.4629	7.0	31.7	66.1	12.3
Tampon (No. 2)....	0.893	−11° 20′	1.4631	7.0	30.9	68.3	11.2
Tampon (No. 3)....	0.894	−11° 20′	1.4630	8.4	30.3	67.3	11.9
Tampon (No. 4)....	0.894	−11° 12′	1.4639	5.6	31.1	68.7	10.8
St. Leu (No. 1)....	0.892	−11° 4′	1.4635	5.6	30.7	67.3	9.6
St. Leu (No. 2)....	0.891	−11° 20′	1.4635	5.6	29.5	68.1	10.0

All of these oils were soluble in 2 to 2.5 vol., and more, of 70 per cent alcohol.

According to Bertrand,[15] oils distilled early in the season are richer in terpenes and, hence, are less soluble and of lower specific gravity than oils distilled later.

For the analysis of Réunion geranium oil, the reader is referred to the section on "Oil of Geranium Algerian."

Adulteration.—Outright adulteration of geranium oil is rarely practiced on the island. Synthetic isolates or aromatics are almost unknown, and distillers would not know how to employ them. Neither would dealers and exporters run the risk of using these products. The island is small, imports are very limited, and any incoming shipments of geraniol or citronella oil fractions would immediately arouse the suspicion of the custom officials. A form of adulteration practiced occasionally by the small distillers, and particularly by the Chinese middlemen, consists in the addition of small

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[15] Conversation with Mr. René Bertrand, formerly chemist in charge of the official control laboratory in St. Denis, Réunion Island.

quantities of kerosene or cheap alcohol derived from rum. (For methods of detection see Vol. I of this work, pp. 332 and 338.) Very few exporters on the island have an analytical laboratory, and most of the shippers examine small lots arriving from the interior simply by olfactory tests. In doubtful cases a sample of the questionable batch is sent to the official laboratory in St. Denis for a chemical analysis, which also has to pass on all outgoing shipments.

The addition of old, partly resinified lots (see above) to batches of newly distilled oils cannot be considered actual adulteration, although it lowers the quality and value of the fresh oil considerably. The buyer abroad should beware of this practice, which has become quite frequent since the end of the Second World War. In trade an optical rotation ranging from −10° 30′ to −13° 0′, or occasionally a little higher, is a good safeguard against the presence of inferior old lots in newly distilled oils. In purchasing Réunion geranium oil, one should always demand shipments of oil derived from the latest harvest.

Oil of Geranium Madagascar

For years small quantities of geranium oil (2 to 3 metric tons) have been produced in the highlands of Madagascar, particularly in the region of Moramanga, near Lac Alaotra. Climatic and soil conditions there resemble those of Réunion Island. Cultivation and distillation are carried out by native sharecroppers working for large landowners. Most of the oil has always been shipped to France. The characteristics of the Madagascar oil resemble those of the Réunion.

A sample (about one year old) collected by the author in Madagascar had these properties:

Specific Gravity at 15°	0.895
Optical Rotation	−8° 48′
Refractive Index at 20°	1.4660
Acid Number	5.6
Ester Content, Calculated as Geranyl Tiglate	26.6%
Total Alcohol Content, Calculated as Geraniol	70.3%
Solubility	Soluble in 2 and more vol. of 70% alcohol

The odor of the oil was not quite as strong and pronounced as that of the Réunion oil.

According to Naves,[16] the citronellol content of Madagascar geranium oils

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[16] *Parfums France* **12** (1934), 179.

examined by Établissements Antoine Chiris in Grasse (A. M.), France, never exceeded 45 per cent; the optical rotation in most cases was high (−13° to −14° 40′).

OIL OF GERANIUM ALGERIAN
(African Geranium Oil)

History and Development.—The plant from which the Algerian geranium oil is derived has been described variously as *Pelargonium roseum* Willd.,[17] *P. graveolens* Ait., and *P. graveolens* × *P. terebinthinaceum*. It was introduced to Algeria from the Grasse region (Southern France) in 1847, being first planted in the region of Cheragas and Chebli. Later, commercial plantations were started in the plain of Mitidja and greatly expanded after the turn of the century. At the peak of development Algeria produced very large quantities of geranium oil per year, exceeding production in Southern France by far. The Mitidja Plain, in classical times one of the great granaries of the Roman empire, is today again one of the most productive and beautiful agricultural regions in the world, intensively cultivated by modern methods of agriculture for the growing of all kinds of produce—grain, grapes, tobacco, olives, citrus, almond, many other fruit trees, and a great variety of vegetables. Bordered on the north by the low coastal hills of the Mediterranean shore, and on the south by the barren high mountains of the Atlas, with its crags and peaks often enshrouded in a light mist, the radiant Mitidja Plain recalls California in more than one aspect. Under an azure, luminous sky the visitor drives for hours over excellent roads, through prosperous villages which have retained their French character, and through vast vineyards, olive, almond, and citrus groves, all well cultivated and in excellent condition. The development of the Mitidja Plain into France's most important agricultural region has been made possible by a combination of several favorable factors, i.e., good soil, excellent climate, artificial irrigation, and, until World War I, low-priced native labor. Agriculture here is organized largely along the lines of cooperatives, which have contributed much toward the introduction of advanced methods of cultivation, high yielding plants and modern equipment, and price stabilization by sound marketing policies.

As regards geranium, the plantations in former years centered around Boufarik and Blida, where most of the distilleries were located. Being a strong, quickly growing plant, geranium grew well on the virgin soil, large areas of which were then available. The low cost of native labor used in

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[17] Naves and Angla, *Ann. chim. anal.* **23** (1941), 201. Cf. Ducellier, "Le Geranium rosat, sa culture en Algérie," Algiers, 1913.

planting and harvesting, and the facility of transport of the plant material over good roads to centrally located distilleries contributed to the success, and Algeria's geranium oil industry prospered, reaching its peak in 1925. About 120 metric tons of oil were produced in favorable years. Since 1925, however, the industry has declined steadily; in 1938 only about 2,000 hectares were under cultivation, yielding approximately 35.5 tons of oil, and in 1944 the acreage shrank to 640 hectares yielding 5.3 metric tons of oil. At the time of this writing (1949) the situation has become worse, the Mitidja Plain producing only a few tons of oil annually.

The steady decline of Algeria's geranium oil industry has been caused by several factors. In 1926 the production on Réunion Island reached such proportions that competition brought about a severe drop in the price of the oil on the world's markets. At the same time, many of the older geranium plantations in the Mitidja Plain had reached a point where they yielded very little oil and had to be renewed on other ground. Virgin land, however, was no longer available in the Mitidja Plain, all arable land having been taken up for the cultivation of more vital and remunerative crops, such as grapes and tobacco. (About 60 per cent of the tobacco crop was regularly bought up by the French government monopoly which assured a steady outlet.) Moreover, Algeria, a Département of France, had developed into one of its most important wine producers, and large quantities were shipped to the mother country every year, to be blended with choice wines from Bordeaux and Burgundy, or sold under the Algerian label. Small wonder then, that many growers in the Mitidja lost interest in geranium, and changed to more profitable crops. For a time the "Geranium Coopérative Mitidja," located at Oued-el-Alleug, offered brave resistance by rallying the growers and by a strict analytical control over all outgoing shipments, which assured buyers abroad of excellent quality; but in the end external factors were too powerful, and after World War II production of the oil diminished almost to the vanishing point. It must be remembered that Algeria is not a colony, but a Département of France, and all the labor and social laws (wages, forty hour week, etc.) enacted in France prior to the outbreak of World War II apply automatically also to Algeria. Cost of production therefore has risen tremendously, and the Algerian oil can no longer compete with the oil from Réunion Island, except in quality, which makes it still desirable for certain purposes—the scenting of high-grade cosmetics, for example. If it is to be produced in substantial quantities in future, the oil will therefore have to be sold at a premium price. Otherwise Algeria's geranium oil industry may soon disappear. Land in the Mitidja is now too expensive to permit cultivation of such relatively short-lived crops as geranium.

Planting, Cultivating, and Harvesting.—The warm climate of Algeria, where the winter temperature averages from 10° to 12° C. and no winter frosts endanger the plant, permits cultivation of geranium as a perennial. A plantation is good for from five to six years, after which the crop must be rotated.

The plant grows rapidly and well, forming thick clusters of leaves on a rather heavy woody stock, and attaining a height of 2.5 or 3 ft. The plant itself is quite resistant to drought, but prolonged spells of dry weather lower the yield of oil substantially.

Cuttings are usually prepared in September and planted immediately in nurseries, where they take root. About two months later the young plants are transferred to the fields and planted 1 ft. apart, in rows 3.5 ft. apart. A calcareous light soil containing gravel seems to produce more oil in the plant than a heavier soil (such as clay). In the Mitidja the land best suited for geranium extends from Beni Mered to Manzaya; here gravel soil predominates. Years ago two-thirds of the Mitidja's geranium plantations were located in this section. The terrain near Boufarik, Chebli, Bouinan, and Rovigo consists to a great extent of clay soil.

Fertilizers are, as a rule, not applied before the third or fourth year, preference being given to nitrogen-containing organic compounds. Inorganic (particularly acid) fertilizers should be avoided.

The harvesting of geranium, a very tedious task, is carried out by natives. White labor can hardly be found for this sort of work. It means stooping for hours in the sun and heat of Algeria, while cutting the tough geranium with a small sickle.

As a rule, two cuttings are undertaken per year. The first lasts from the latter part of April to the end of June, when the plants are in full bloom. At this stage the originally somewhat lemonlike odor of the leaves has changed to a pronounced rose note. The second cutting lasts from October to the middle of November, depending upon the growth of new leaves. The plants then bear no flowers, and the leaves have turned slightly yellow. Another, intermediate, cutting takes place from June to July, but only of plants six months old, which had been newly planted during the preceding December. These young plants are not cut in May and October, as are the regular plants in the older fields.

Distillation.—After cutting, the plants are loaded on trucks and hauled to the distillery, which usually belongs to the owner of the field. The plant material is then stacked near the stills for about 24 hr. to dry and reduce in volume. Apparently this 24-hr. storage results in a slight fermentation ("curing") and splitting of glycosides, which latter reaction supposedly increases the yield of oil.

Distillation is carried out in regular steam stills, the steam being generated in a separate boiler. The stills, usually holding 550 to 650 liters, are arranged in batteries, one battery comprising three stills. One such battery is considered necessary for the processing of the plant material from 10 hectares of geranium. Each battery is provided with only one condenser, so that only one still is actually distilling at a time, the other two stills being discharged and charged, respectively.

Before distillation is started, 20 to 25 liters of water are poured into the still. Then the plant charge is distilled for about ½ to ¾ of an hour, the length of distillation depending upon the steam pressure and the condition of the plant material. During the peak of the harvest, operation in the distilleries continues day and night. At least, this was necessary formerly, when huge quantities of plant material had to be processed.

Yield of Oil.—From observations made by the author on the occasions of his visits to the Mitidja Plain, it appears that during the spring harvest 1,000 kg. of plant material (chiefly leaves and short stalks) yield on the average 1 kg. of oil; during the fall harvest 800 kg. of plants yield 1 kg. of oil.

The yield of oil per acre depends obviously upon the amount of plant material that the area produces, and therefore chiefly upon the age of the planting. A young field produces more oil than an old field. Generally speaking, three factors influence the yield of oil: the weather (dry or wet), the soil (calcareous or clay), and the age of the plantation, which in the seventh year of existence yields so little oil that it becomes unprofitable. The yield of oil per hectare (= 2.471 acres) and per year may be estimated as follows:

	Kilograms
First Year.............	10
Second Year...........	30–35
Third Year............	30–35
Fourth Year...........	25–28
Fifth Year.............	20–25
Sixth Year.............	15–20
Seventh Year..........	6–10

These yields include the two cuttings, the spring harvest always giving more oil than the fall cutting because of the dryness prevailing in the latter part of the year.

Exports.—In 1910 Algeria exported 33.8 metric tons of geranium oil, in 1925 about 66.5 tons, in 1928 almost 143 tons. Since then production and exports have been declining steadily as can be seen from the following figures:

Year	*Exports of Oil in Metric Tons (Gross Weight)*
1936	51.3
1937	50.5
1938	22.9
1939	61.8
1940	35.2
1941	24.9
1942	18.2
1943	...
1944	0.4
1945	3.2
1946	12.0
1947	4.5
1948	8.6 *

* = 6.3 metric tons in net weight.

Physicochemical Properties.—The Algerian geranium oil possesses a strong rose-like odor, not quite as delicate as that of the French oil, but finer than that of the Réunion oil.

According to Gildemeister and Hoffmann,[18] the physicochemical properties of the Algerian (African) geranium oil vary within these limits:

Specific Gravity at 15°	0.892 to 0.904
Optical Rotation	−6° 30′ to −12° 0′
Refractive Index at 20°	1.464 to 1.472
Acid Number	1.5 to 9.5
Ester Number	31 to 70
Ester Content, Calculated as Geranyl Tiglate	13 to 29.5%
Ester Number after Acetylation	203 to 234
Total Alcohol Content, Calculated as Geraniol	66 to 78%
Solubility	Soluble in 2 to 3 vol. of 70% alcohol; usually separation of paraffins on dilution

Sabatié and Angla[19] reported the following values for Algerian oils produced during the 1932 and 1933 harvest:

Specific Gravity at 15°/4°	0.8900 to 0.9015
Optical Rotation	−7° 58′ to −12° 0′
Refractive Index at 20°	1.4634 to 1.4704
Acid Number	1.4 to 8.4
Ester Number	59 to 74.2

[18] "Die Ätherischen Öle," 3d Ed., Vol. II, 897.

[19] *Ann. fals.* **27** (1934), 70. *Ber. Schimmel & Co.* (1935), 35.

Ester Content, Calculated as Geranyl Tiglate	24.5 to 31.2%
Ester Number after Acetylation	202 to 219
Free Alcohol Content	42 to 51%
Total Alcohol Content	62 to 68.5%
Citronellol Content	30 to 40%

According to Naves,[20] the properties of Algerian geranium oil vary within these limits:

	In Most Batches	*Extreme Limits*
Specific Gravity at 15°/15°	0.8945 to 0.9024	0.890 to 0.905
Optical Rotation	−9° 20′ to −12° 40′	−6° 30′ to −13° 0′
Refractive Index at 20°	1.468 to 1.472	1.4635 to 1.4725
Acid Number	Up to 5.6	Up to 12.0
Ester Number	54.6 to 74.1	. . .
Ester Content, Calculated as Geranyl Tiglate	23 to 31.2%	. . .
Ester Number after Acetylation	211.7 to 227.5	204.2 to 228.2
Total Alcohol Content	66.0 to 71.3%	61 to 72%
Free Alcohol Content	46 to 52%	42 to 61%
Ester Number after Formylation	89.2 to 134	Up to 143.5
Apparent Citronellol Content	26 to 40%	Up to 43%
Isomenthone Content (Hydroxylamine Hydrochloride Method)	About 10.5 to 16%	. . .
Solubility	Soluble in 0.5 to 2.5 vol. of 70% alcohol, with separation of paraffins	

Shipments of genuine Algerian geranium oils imported and analyzed by Fritzsche Brothers, Inc., New York, had properties varying within the following limits:

Specific Gravity at 15°/15°	0.894 to 0.904
Optical Rotation	−7° 40′ to −12° 0′
Refractive Index at 20°	1.4665 to 1.4702
Acid Number	Up to 10.3
Ester Content, Calculated as Geranyl Tiglate	22.5 to 31.2%
Total Alcohol Content, Calculated as Geraniol	69.0 to 73.0%
Formate Content, Calculated as Geranyl Formate	10.0 to 15.9%
Ketone Content, Calculated as Isomenthone (Hydroxylamine Hydrochloride Method)	7.7 to 12%
Solubility	Usually soluble in 2 vol. of 70% alcohol, occasionally slightly opalescent and separation of paraffins with more alcohol

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[20] *Parfums France* **12** (1934), 175.

Studying the influence of age upon the physicochemical properties of Algerian geranium oil, Angla[21] observed the following changes after the oil had been stored for one year in well-closed bottles, protected from light:

1. A substantial diminution in the optical rotation.
2. A substantial increase in the acid number.
3. A diminution in the content of esters.
4. A substantial increase in the content of free alcohol.
5. A substantial increase in the evaporation residue.

In the author's own opinion, storage of geranium oil under carefully controlled conditions for one or two years improves the odor of the oil, notwithstanding the changes mentioned above. The odor of freshly distilled oils, originally "green" and somewhat coarse, gradually becomes mellow, richer, and more rose-like.

Analysis.—Methods of analysis applicable to all types of geranium oils will be discussed here. It is true that most of the new and more effective methods of analysis have been developed upon Algerian oils, but such methods may be used for other types as well. Routine analysis of geranium oil (specific gravity, optical rotation, refractive index, solubility, acid number, ester number, etc.) is successful for the detection of gross frauds, but it fails completely to reveal systematic and skillful adulteration, whereby the physical properties mentioned above are kept within permissible limits. Geranium oil today is often adulterated by the addition of geraniol and citronellol fractions derived from the much lower priced citronella oil, or with the low and high boiling fractions of geranium oil obtained as byproducts in the isolation of "rhodinol" from this oil. By a clever combination of these fractions the adulterator is able to prepare "geranium oils" which will meet the requirements of a simple routine analysis.

In view of this fact the analysis of a geranium oil should therefore include the following assays:

1. Determination of the total alcohol content (calculated as geraniol) by acetylation (cf. Vol. I of this work, p. 271).

2. Determination of the citronellol content by formylation (cf. Vol. I of this work, p. 278).

3. Determination of the ketone content (calculated as isomenthone), by the hydroxylamine hydrochloride method (cf. Vol. I of this work, p. 285).

4. Determination of the ester content (cf. Vol. I of this work, p. 265). For a long time it was assumed that the esters present in geranium oil con-

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[21] *Ibid.* **11** (1934), 266.

sisted chiefly of tiglates, and even today many commercial analyses of geranium oil express the ester content as tiglates. However, Dodge[22] has proved that the percentage of tiglates in geranium oil has been overestimated and that the oil contains a substantial amount of formates. Dodge found 12.7 per cent of formates in an Algerian geranium oil, 11.3 per cent in a Réunion oil, and 8.9 per cent in a French oil. The amount of "actual formate" in geranium oil is best determined by saponification in the cold (cf. Vol. I of this work, p. 271). The relatively large percentage of formates occurring in the oil appears to be characteristic and should be taken into consideration in the commercial examination of the oil.

Angla,[23] Naves,[24] and Naves and Angla[25] suggested still other methods which may come to have considerable practical value in the examination of geranium oils, once the methods proposed by these authors have been applied to a sufficiently large number of genuine oils (for details the reader is referred to the original literature).

For example, the dispersion of the rotatory power appears to be helpful in the analysis of essential oils, since their optical rotation varies with the solvent used. In the opinion of Naves and Angla,[26] an oil of geranium that does not exhibit a noticeable exaltation in the optical rotation after the oil has been dissolved in chloroform (20 to 25 per cent solution) is suspect. Naves and Angla reported these values for an Algerian geranium oil:

$[\alpha]_D$ without Solvent................	−9.35°
$[\alpha]_D$ in Chloroform Solution..........	−10.50°
$[\alpha]_D$ in Alcohol 70%................	−8.26°
$[\alpha]_D$ in Benzyl Alcohol..............	−8.76°

So far as the ketones in the oil are concerned, the same authors[27] suggest collecting the terpenic ketones in the first fractions (20 per cent) of the oil, in order to submit them to a closer investigation. The optically most active fractions attain a rotation as high as −29°. Since in many cases not more than 50 g. of oil are available for analysis, Naves and Angla recommend using a 721 Pyrex distillation flask, of the Claisen-Vigreux type (125 cu. cm. capacity), and distilling over 20 per cent of the oil by volume, at 10–15 mm. pressure, at a temperature up to 100°.

The optical examination of this fraction permits the detection of certain

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[22] *Soap* **17** (March 1941), 33. Cf. Béhal, *Bull. soc. chim.* [4], **15** (1914), 306.
[23] *Parfums France* **11** (1933), 180.
[24] *Ibid.* **12** (1934), 168.
[25] *Ann. chim. anal.* **23** (1941), 201. Cf. Naves, *Fette und Seifen* **49** (1942), 183.
[26] *Ann. chim. anal.* **23** (1941), 234. Cf. *Ber. Schimmel & Co.* (1942–1943), 12.
[27] *Ibid.*, 231.

forms of adulteration. Depending upon the content of ketones in the oil, the optical rotation of the head fraction varies from α_D −15° to −18° for Algerian oils, and from α_D −18° to −22° for Réunion oils. The ketone content of the fraction (determined by oximation—cf. Vol. I of this work, p. 285) amounts to 20 to 32 per cent; the refractive index and the value α_v/α_j are characteristic, as can be seen from these two examples:

n_D^{20}	1.4608	1.4612
α_v	−25.86°	−23.88°
α_j	−22°	−20.33°
α_v/α_j	1.17_5	1.17_2

It may be possible to "arrange" a normal ketone content in an adulterated oil by incorporating head fractions of geranium oils which result from deterpenation and extraction of "rhodinol." Such manipulations, however, alter a large part of the isomenthone originally present, which during the process of deterpenation (distillation) is isomerized to menthone.

Additional ketones commercially available for the purpose of adulteration are menthone, piperitone, isopulegone, and in exceptional cases, carvone. The properties of these ketones, as obtained from readily accessible raw materials, are:

	Menthone	*Piperitone*	*Isopulegone*	*Pulegone*	*Isomenthone*
n_D^{20}	1.451	1.486	1.467	1.488	1.453
α_v	−30.10°	−56.31°	−23.81°	−22.18°	−70.34°
α_j	−26.30°	−47.58°	−20.05°	−18.33°	−59.23°
α_v/α_j	1.14_4	1.18_3	1.18_7	1.21_0	1.18_7

For common adulteration, natural pulegone (dextrorotatory, α_v about +24° to +28°) or isopulegone (also dextrorotatory, α_v about +2° to +14°) is usually employed, as the corresponding laevorotatory products have to be prepared by special methods.

The rotatory dispersion of isomenthone is quite characteristic, and only that of piperitone and isopulegone resemble it. These latter two ketones, however, differ from isomenthone in regard to their refractive indices. Menthone differs in its low rotatory dispersion.

Naves and Angla arrived at the conclusion that those geranium oils should be considered abnormal the head fractions of which (20 per cent of the total oil) exhibit a ketone content lower than 20 per cent, an optical rotation (α_D) less than −15° in Algerian oils (or less than −18° in Réunion oils), a refractive index (n_D^{20}) higher than 1.4610, and a rotatory dispersion (α_v/α_j) lower than 1.17.

When oils exhibit such abnormalities, the ketones should be isolated from the head fraction by means of Girard and Sandulesco's reagent P, and further examined. Details will be found in the original paper of Naves and Angla.

SUGGESTED ADDITIONAL LITERATURE

Y. R. Naves, "Carbonyl and Peroxide Number in the Analysis of Ethereal Oils," *Fette u. Seifen* **48** (1941), 677. *Chem. Zentr.* (1942), II, 109.

CHEMICAL COMPOSITION OF GERANIUM OIL

As Dodge[28] has pointed out, the composition of geranium oil, like that of most essential oils, is complex; in fact, the number of constituents so far discovered would appear to be limited only by the amount of time spent on their examination.

The chief constituents of geranium oil are *geraniol* and *citronellol*, the mixture of these two terpene alcohols comprising 75 to 80 per cent of the oil, depending upon its origin. There has been a prolonged controversy regarding the structure of geraniol and citronellol, details of which will be found in Vol. II of this work, pp. 171 and 178.

Geraniol $C_{10}H_{18}O$ was first observed in geranium oil by Gintl,[29] and by Bertram and Gildemeister.[30] The other terpene alcohol occurring in the oil —the Réunion product contains the largest amount—was recognized as citronellol $C_{10}H_{20}O$ by Tiemann and Schmidt.[31] Barbier and Bouveault[32] assigned to the geraniol-citronellol mixture the name "Rhodinol de Pélargonium," whereas Hesse[33] called it "Réuniol."

[In this connection it should be pointed out that the present-day commercial term "Rhodinol" applies to mixtures of various alcohols isolated from geranium oil on a technical scale, i.e., citronellol and geraniol, accompanied by very small quantities of phenyl ethyl alcohol, linaloöl, terpineol, menthol, 3-hexen-1-ol, and often by traces of the ketone, isomenthone (see below). Commercial *l*-citronellol is simply a purer form of commercial rhodinol. According to Rosenthal,[34] rhodinol is prepared by saponification of geranium oil, by steam distillation of the saponified oil, and by fractionation, *in vacuo*, of the distillate. The commercial term rhodinol must not be confused with the word employed in its strict chemical sense. The pure compound consists of a mixture of *l*-*β*- and *dl*-*β*-citronellol.]

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[28] *Soap* **17**, No. 3 (1941), 33.
[29] *Jahresber. Chem.* (1879), 941.
[30] *J. prakt. Chem.* [2], **49** (1894), 191.
[31] *Ber.* **29** (1896), 924.
[32] *Compt. rend.* **119** (1894), 281, 334.
[33] *J. prakt. Chem.* [2], **50** (1894), 472; **53** (1896), 238.
[34] *Deut. Parfümerieztg.* **27**, No. 14 (1941), 153.

The quantities of geraniol and citronellol, and their ratio, vary in the different geranium oils and depend upon the origin of the latter. Tiemann and Schmidt,[35] for example, reported these approximate proportions:

Réunion Oil....	80% total alcohols, of which 50% was geraniol and 50% citronellol
Algerian Oil....	75% total alcohols, of which 80% was geraniol and 20% citronellol
Spanish Oil.....	70% total alcohols, of which 65% was geraniol and 35% citronellol

In these three oils the citronellol was present as a mixture of the *d*- and of the *l*-modification. As has been said above, the geraniol and citronellol present in geranium oil are accompanied by small quantities and traces of other alcohols; therefore, the percentage figures given by Tiemann and Schmidt for geraniol and citronellol are not absolute. Besides, these researchers used the phosphorus trichloride method for the assaying of the citronellol and geraniol content, but this method is not exact since it gives somewhat confusing results because of the presence of other alcohols in the oil—linaloöl and terpineol, for example.

Gildemeister and Hoffmann[36] cite a few figures reported by various sources, indicating the content of citronellol in geranium oils of different origin:

Origin	*Satie*[37] (%)	*Simmons*[38] (%)	*Anonymous*[39] (%)
French Oil...........	37–43	...	39.8
Algerian Oil.........	37–43	32–43	32.9
Réunion Oil.........	50–65	44–51	44.3
Corsican Oil.........	...	30.3	45.9

The content of citronellol, in the presence of geraniol and linaloöl, is best determined by (hot) formylation (cf. Vol. I of this work, p. 278).

Using this method, Naves[40] determined the content of rhodinol (citronellol!) in geranium oils to be as follows:

	Usual Limits (%)	*Extreme Limits* (%)
French Oil..........	40–44.4	35.3–44.4
Algerian Oil........	26–40	26–43
Réunion Oil........	43.7–52	41.7–55

Assay of the citronellol content is a very important feature of the evaluation of geranium oil.

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[35] *Ber.* **29** (1896), 924.

[36] "Die Ätherischen Öle," 3d Ed., Vol. II, 901.

[37] *Am. Perfumer* **1,** No. 12 (1907), 12.

[38] *Pharm. J.* **91** (1913), 143.

[39] *Perfumery Essential Oil Record* **4** (1913), 328.

[40] *Parfums France* **12** (1934), 171.

The same author established the proportion of rhodinol (citronellol!) to the total alcohols present in the oils of various origin:

	Usual Limits (%)	*Extreme Limits* (%)
French Oil..........	0.56–0.60	0.51–0.64
Algerian Oil........	0.39–0.55	0.38–0.60
Réunion Oil........	0.64–0.71	0.63 0.80

The rhodinol (citronellol!) which can be extracted from geranium oil is partly racemized, the optical rotation varying from $-2° 0'$ to $-2° 30'$; it consists of a mixture of *dl-β*-citronellol and *l-β*-citronellol.

As regards the geraniol content, Naves[41] estimates the percentages in the Algerian and in the Réunion oils as follows:

	Free Geraniol (%)	*Esterified Geraniol* (%)
Algerian Oil..	16–30	26–46
Réunion Oil	10–15	16–25

The proportion of geraniol in the alcohols—whether free or combined—is fairly constant (Naves).

The alcohols listed above, particularly geraniol and citronellol, occur in the oil chiefly in the free state, and in a substantial proportion combined with fatty acids as esters. Barbier and Bouveault[42] identified *acetic acid,* the Schimmel chemists[43] *butyric-, valeric-,* and *tiglic* acids. For a long time it had been supposed that tiglic acid is the principal acid present in geranium oil, until Dodge[44] showed that the amount of this acid in normal oils had been overestimated. Dodge examined a precipitate in a Réunion geranium oil which had been shipped in a zinc-lined container, and found the precipitate to be zinc formate. Further work proved that all geranium oils contain substantial quantities of formates: in an Algerian oil Dodge observed 12.7 per cent of formates, in two Réunion oils 11.3 and 8.9 per cent. Dodge concluded that the relatively large amount of formic acid found in geranium oil appears to be characteristic, and suggested using the determination of the content of formic esters in the technical analysis of the oil (cf. above, "Physicochemical Properties"). It is arbitrary to express the ester content as geranyl tiglate.

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[41] Private communication of Dr. Y. R. Naves, Geneva, Switzerland, 1949.

[42] *Compt. rend.* **119** (1894), 281.

[43] *Ber. Schimmel & Co.,* April (1894), 31.

[44] *Perfumery Essential Oil Record* **13** (1922), 184. *Soap* **17,** No. 3 (1941), 33. As early as 1914 Béhal [*Bull. soc. chim.* [4], **15** (1914), 308] had observed that the larger percentage of the esterified alcohols in geranium oil is present in the form of formates. Béhal, however, did not indicate by which means he had identified the formates.

Aside from the chief constituents, viz., geraniol and citronellol, and their esters (mainly formates) the following substances have been found in geranium oil:

Dimethyl Sulfide. Observed in the lowest boiling fractions of Algerian and Réunion geranium oils by Schimmel & Co.[45] Although present in traces only, dimethyl sulfide (b. 37°) nevertheless exerts a considerable influence upon the odor of the oil.

Ethyl Alcohol. Identified, by means of its α-naphthylurethane m. 79°–80°, in the foreruns of Réunion geranium oil by Bohnsack.[46]

Diacetyl. Identified through its disemicarbazone m. 278°–280° in the foreruns of the same oil (Bohnsack [47]).

Isoamyl Alcohol. Years ago Schimmel & Co.[48] reported the occurrence, in the fraction b. 100°–140°, of a cough-provoking amyl alcohol, the phenylurethane of which melted at 41°–43°. More recently, Bohnsack [49] identified the alcohol as isoamyl alcohol, in the fraction b. 129°–131° of the Réunion oil; α-naphthylurethane m. 63°–64°. Oxidation gave isovaleric acid; amide m. 131°–133°.

l-α-Pinene and Phellandrene (probably β-). Investigating the terpenes present in the Réunion as well as in the Algerian type of oil, Schimmel & Co.[50] observed *l*-α-pinene, which yielded a nitrolbenzylamine m. 122°–123°; and traces of what was probably β-phellandrene, which gave a nitrite m. 114° 115°.

d-3-Methyl-1-pentanol. In his work on Réunion geranium oil Bohnsack [51] examined the low boiling alcohols particularly. Removing the geraniol and citronellol from 5,000 kg. of the total oil by the phthalic ester method, Bohnsack obtained 225 g. (= 0.004 per cent of the total oil) of a fraction b. 153°–154°, which was cough-provoking and had an odor reminiscent of fresh green leaves and amyl alcohol (see above). In this fraction Bohnsack identified *d*-3-methyl-1-pentanol b. 154°, b_9 52°–54°, d^{18}_{15} 0.826, $[\alpha]^{20}_D$ about +2° 24′, by progressive oxidation to optically active *d*-3-methyl-1-pentanoic acid, which yielded an amide m. 123.5°–124°.

3-Hexen-1-ol. In the same alcohol fraction b. 153°–154° Bohnsack [52] also observed the presence of an unsaturated hexyl alcohol (amounting to 55.2 per cent of the alcohol fraction), which on hydrogenation yielded 1-hexanol (α-naphthylurethane m. 60°–61°), and which on oxidation with potassium permanganate gave propionic acid and oxalic acid. For details regarding 3-hexen-1-ol the reader is referred to Vol. II of this work, p. 158.

n-1-Hexanol. In a supplementary investigation of the low boiling alcohols present in Réunion geranium oil, Bohnsack [53] found that *d*-3-methyl-1-pentanol and 3-hexen-1-ol are accompanied by three other alcohols, viz., the lower boiling isoamyl alcohol (see above), the higher boiling *n*-1-hexanol b_{14} 65°–66°, and methyl hexyl carbinol. The *n*-1-hexanol was identified by means of its α-naphthylurethane m. 60°–61°.

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[45] *Ber. Schimmel & Co.*, April (1909), 50.

[46] *Ber.* **75** (1942), 502.

[47] *Ibid.*

[48] *Ber. Schimmel & Co.*, April (1904), 51.

[49] *Ber.* **75** (1942), 502.

[50] *Ber. Schimmel & Co.*, April (1904), 51.

[51] *Ber.* **74** (1941), 1575.

[52] *Ibid.*

[53] *Ibid.* **75** (1942), 502.

Methyl Hexyl Carbinol. This alcohol b_{12} 72°–74° was isolated from the foreruns of Réunion geranium oil by treatment with phthalic anhydride after the addition of pyridine. Oxidation with chromic acid-sulfuric acid yielded methyl hexyl ketone (semicarbazone m. 120°–122°); oxidation with potassium permanganate gave *n*-caproic acid (amide m. 96°–98°).

l-Isomenthone. Years ago Flatau and Labbé,[54] investigating the foreruns of geranium oil, observed *l*-menthone, which they identified through its semicarbazone. More recently Schimmel & Co.[55] noted that in all cases where *l*-menthone had previously been characterized by means of its semicarbazone or oxime, the researchers had not considered the pronounced tendency of the menthones toward inversion. Considering the fact that mere saponification of the oil would cause fundamental changes in any menthone present, the Schimmel chemists submitted the menthone fraction of Réunion geranium oil to a careful examination and arrived at the conclusion that the original, untreated oil contains *l*-isomenthone α_D −74° 15′, but not *l*-menthone.

In a still later investigation of Algerian geranium oil, Angla[56] found that the ketone fractions of this type of oil, too, consist chiefly of *l*-isomenthone, more or less racemized, accompanied by other ketones or aldehydes. Isomenthone is very sensitive to acid or alkaline treatments, which produce or intensify its racemization. Racemization may also occur during the aging of the oil. This would account for the decrease in optical rotation of the geranium oil with time. Rectification of the oil *in vacuo* at relatively low temperature does not affect *l*-isomenthone; this furnishes a means of easily obtaining head fractions containing about 30 per cent of *l*-isomenthone.

It is sufficient to examine the first fractions amounting to 10 per cent of the oil. These head fractions contain from 20 to 40 per cent of unchanged isomenthone. The latter influences the characteristic optical properties of this fraction, viz., the refractive index n_D^{20} 1.4590 (which should be lower than that of the original oil), the optical rotation α_j −20° (which is higher than that of the original oil), and the very exalted dispersion of the rotation $\alpha_v/\alpha_j = 1.18$.

Other Ketones (or Aldehydes?). In 1946 Sfiras[57] observed that, in addition to isomenthone, Réunion geranium oil contains other ketones or aldehydes. He isolated two ketones, one of which had a second functional oxygen. Fractionating 3 kg. of an oil which contained 9.3 per cent of ketones (calculated as isomenthone) Sfiras obtained four fractions:

The first fraction contained isomenthone, the second fraction a ketone which was not isolated. 183 g. of the third fraction, b_3 112°–135°, d_{15}^{15} 0.9178 – 0.9427, n_D^{20} 1.4759 – 1.4812, on treatment with the reagent T of Girard and Sandulesco, yielded 12 g. of a ketone b_3 112°–114°, d_{15}^{15} 0.9839, α_D −34° 50′, n_D^{20} 1.4856, which had the molecular formula $C_{15}H_{22}O_2$; semicarbazone m. 153°–154°.

28 g. of the fourth fraction b_3 155°–200°, d_{15}^{15} 0.9096 – 0.9218, n_D^{20} 1.4832 – 1.4944, on treatment with reagent T, gave 1 g. of a ketone b_3 130°–175°, d_{15}^{15} 0.9566, n_D^{20} 1.4963, the dinitrophenylhydrazone of which melted at 88°–89°. The semicarbazone could not be crystallized.

Sfiras[58] arrived at the conclusion that geranium oil contains at least four substances with a functional carbonyl group:

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[54] *Bull. soc. chim.* [3], **19** (1898), 788.

[55] *Ber. Schimmel & Co.* (1932), 34.

[56] *Chimie & industrie* **41** (1939), 234.

[57] *Ind. parfum.* **1** (1946), 154.

[58] *Ibid.*

Traces of aldehydes or ketones occurring in the head fractions; isomenthone amounting to 90 per cent of the oil's ketone fraction; another ketone or aldehyde (distilling right after the isomenthone) which Sfiras did not investigate; and finally two other ketones which he isolated (see above).

Linaloöl. This terpene alcohol was observed in geranium oil first by Barbier and Bouveault,[59] and later identified by Schimmel & Co.[60] in the fraction d_{15} 0.872, α_D $-1°\ 40'$, n_D^{20} 1.4619, by means of its phenylurethane m. 65°–66°.

α-Terpineol, Menthol, and Borneol(?). In the course of their investigations of geranium oil the chemists of Schimmel & Co.[61] isolated optically inactive α-terpineol m. 34°–36° (phenylurethane m. 109°–111°, nitrosochloride m. 114°–115°).

During the purification of the terpineol, they also found menthol and traces of an alcohol with a borneol-like odor.

According to Naves,[62] the optically most active fraction he isolated from geranium oil had a rotation of α_D $+25°\ 8'$. The phenylurethane melted at 113.5°–114°. Oxidation with the Beckmann mixture yielded *l*-menthone, α_D $-12°\ 30'$; its semicarbazone melted at 186°.

Phenyl Ethyl Alcohol. Although present in small quantities only, this alcohol nevertheless is in large part responsible for the rose-like odor of the oil. Identified by means of its phenylurethane m. 80° (Schimmel & Co.[63]).

Geraniol and Citronellol. Regarding these chief constituents of geranium oils, see above.

Eugenol. Sabetay and Trabaud [64] observed small quantities of eugenol in seven samples of geranium oil. Identified by means of its benzoate.

Using the method of Zeisel for the determination of the methoxy content, these authors obtained the following results:

Origin of the Oil	*Methoxy Content* (%)
Réunion Island	0.20 [65]
Madagascar	0.18
Algeria	0.16
Morocco	0.16
Egypt	0.28
France (Grasse)	0.15
Morocco (Absolute, fraction volatile *in vacuo*)	0.19

Sabetay and Trabaud arrived at the conclusion that eugenol is present in all the geranium oils listed above, because none of the previously known constituents of geranium oil (with the possible exception of dimethyl sulfide) reacted in the Zeisel determination.

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[59] *Compt. rend.* **119** (1894), 281.

[60] *Ber. Schimmel & Co.*, April (1904), 50; October (1910), 52.

[61] *Ibid.*, October (1910), 52; October (1911), 46.

[62] *Parfums France* **12** (1934), 171.

[63] *Ber. Schimmel & Co.*, October (1910), 52.

[64] *Ann. chim. anal.* **27** (1945), 191. *Chem. Abstracts* **40** (1946), 2588.

[65] Equivalent to about 1 per cent of eugenol.

Sesquiterpenes and Sesquiterpene Alcohols. In their work on the elucidation of the azulenes, Pfau and Plattner [66] saponified 20 kg. of Réunion geranium oil, removed the sesquiterpene alcohols, and obtained 500 g. of sesquiterpenes b_{10} 127°–129°, n_D^{20} 1.4971, which on dehydrogenation with sulfur or selenium yielded S-guaiazulene.

A Paraffin(?). The last runs of geranium oil contain a crystalline substance m. 63°, the properties of which resemble the stearoptene present in oil of rose. Judging from its solubility in 70 per cent alcohol, the Spanish type of geranium oil seems to be particularly rich in this paraffin (Gildemeister and Hoffmann [67]).

Treating the oil obtained by redistillation of the distillation waters (oil of cohobation or water oil) with sodium bisulfite, Charabot and Laloue [68] isolated *citral.*

Barbier and Bouveault [69] attributed the green color of some geranium oils, especially those from Réunion, to the presence of a liquid substance ($[C_{10}H_{17}]_2O$?), b_{10} 165°–170°.

Use.—Because of its powerful, rose-like odor, oil of geranium is one of the most important essential oils, employed widely for the scenting of soaps and cosmetics, and for the isolation of rhodinol which forms part of most high-grade perfumes. The oil is stable in soaps, imparting to them a characteristic and strong rose odor. As regards the use of the various types of geranium oil, the reader is referred to the section on "Introduction, Botany, and Development" (see above).

OIL OF GERANIUM MOROCCAN

The geranium oil industry of Morocco is of recent date; it shows great promise, however. In time, Morocco may develop into the second largest geranium oil producer in the world (Réunion Island holding first place).

The first attempts to cultivate geranium in Morocco were made near Fez, Meknès, Serrat, and Marrakech, but were largely unsuccessful because of occasional frosts in winter, excessive heat in summer, general lack of water, and inexperience on the part of growers, particularly in regard to the proper use of fertilizers. The oil produced in those early years amounted to only a few hundred kilograms annually.

Renewed and more serious efforts were made in 1935 when new plantings were started in the region of Chaouia, near the coast of the Atlantic Ocean, and in certain sections of the Atlas Mountains where local conditions are much more favorable to geranium.[70] The average annual rainfall in Chaouia

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[66] *Helv. Chim. Acta* **19** (1936), 858.

[67] "Die Ätherischen Öle," 3d Ed., Vol. II, 903.

[68] *Compt. rend.* **136** (1903), 1467.

[69] *Ibid.* **119** (1894), 281.

[70] See P. A. Muller, *Parfumerie moderne* **30** (1936), 198.

ranges from 400 to 500 mm.; additional moisture is provided by irrigation. As a result, geranium flourishes in these sections. The soil is generally sandy, or quite light.

The usual method of propagation is by cuttings, which take root in September and are planted out in November. The rows are laid out 0.9 to 1 m. apart. One hectare contains from 15,000 to 25,000 stocks, which Muller considers insufficient. Harvesting takes place at the end of April–May and in September. All the work of planting, cultivating, and harvesting is done by hand, chiefly by women, the cost of labor consequently being very low.

Courtesy of M. Pierre Chauvet, Seillans (Var), France.

FIG. 39. Geranium oil production in Morocco. Harvesting of the plant material.

The plants are cut at an early hour and carted to the distilleries, which, during the harvest, are kept going day and night. The stills have to be operated at full capacity in order to distill the crop before June, as after June the yield of oil may drop from the normal 0.1 per cent to 0.03 or even 0.02 per cent.

On the average, one hectare produces 15 to 18 kg. of oil, but the yield varies greatly with the age and condition of the plantings.

The stills are of the same type as those employed in Algeria, one battery consisting of three tanks, heated with direct steam from a separate steam generator. Three tanks can process daily (in 24 hr.) 3 to 4 metric tons of plant material. There are also a number of small field stills which are directly fired with wood (and hence can operate at low cost). Their daily capacity is obviously lower than that of the stationary (Algerian) type.

In 1935 about 800 kg., and in 1936 more than 1,000 kg., of geranium oil were produced in Morocco. This increase over previous years resulted chiefly from renewed interest in the production of geranium oil on the part of several growers who had become discouraged with the prevailing low prices of cereals and other elementary crops. World War II, however, changed the picture again, and the settlers in Morocco lost interest in geranium oil, directing their activities toward the cultivation of vital food crops.

An entirely new chapter in the story of Morocco's geranium industry began shortly after World War II, when a very enterprising and experienced producer of essential oils from the Grasse region in Southern France entered the field. Impressed with the many advantages which Morocco offers for the cultivation of aromatic plants (vast tracts of land at low prices, cheap labor, excellent climate, good soil in certain localities, possibility of irrigation by means of artesian wells, etc.), he laid out extensive plantations of all kinds of aromatic plants—jasmine, rose, tuberose, bitter orange, geranium, etc.—near Khémisset, about 40 km. east of Rabat, on the road to Meknès. A modern distillery and a building equipped for the extraction of oils with volatile solvents were constructed in the center of the plantations. The stills, of very large capacity (about 20 metric tons), are provided with labor-saving devices which permit the mechanical charge and discharge of the plant material by means of electrically driven hoists. The powerful steam boilers are heated by oil burners. Agricultural work, too, is mechanized by the use of modern American farming equipment (tractors, cultivators, harvesters where possible, etc.).

Courtesy of M. Pierre Chauvet, Seillans (Var), France.

FIG. 40. Geranium oil production in Morocco. Charging of a modern still with plant material. The stills have a capacity of 20.000 liters.

As regards geranium in particular,[71] only the most select plant material was collected in the Grasse region of Southern France, Corsica, Algeria, and Morocco. The cuttings were then planted in Khémisset, and a further selection was made, so that only the best plants were used in the final plantations.

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[71] The author is greatly obliged to his good friend and close collaborator for many years, Mr. Pierre Chauvet, Seillans (Var), France, for details given in this section.

In this section of Morocco frost is unknown. The fields do not have to be irrigated as the soil (generally sandy) retains the moisture very well, particularly if the principles of "dry farming" are applied.

In general, the cultivation of geranium undertaken in Khémisset closely resembles that of lavandin in Southern France (for details, see the monograph on "Oil of Lavandin," Vol. III of this work). Toward the end of the year, when the vegetative growth stops, cuttings are taken and planted in nurseries. As soon as the new roots are sufficiently developed, the young plants are set out in the fields, 50 cm. apart, in rows 1 m. apart. One hectare thus contains about 20,000 stocks.

Cultivation is along the lines of dry farming, i.e., as many light plowings as possible are practiced. The plants grow rapidly to such a size that tractors no longer can pass between the rows.

It has not yet been possible to construct a mechanical harvester which does not injure the plants; therefore the cutting is done by hand. The harvested plant material is distilled immediately, as the warm climate of Morocco would cause evaporation and a serious loss in the yield of oil.

There are two harvests per year, one in May–June, and the other in October. Two-thirds of the annual yield of oil originates from the May–June crop, and one-third from the October harvest.

On distillation, 1,200 kg. of plant material yield about 1 kg. of oil. One hectare of a planting in full productivity yields about 20 kg. of oil per year.

The development of geranium plantations near Khémisset has not been without setbacks. During the spring of 1947, for example, 50 hectares of nursery beds were ravaged by locusts. Fortunately, 5 hectares located at some distance from Khémisset were not attacked, and the plants from this field could be used for the starting of new plantations.

The production in 1948 amounted, therefore, to only one metric ton of oil, but the new fields will produce about 6 tons of oil annually. Provided conditions remain favorable, the newly established geranium oil industry near Khémisset will be second only to the production on Réunion Island. In fact these plantations are by far the largest and most modern in the world, as the plantings in Réunion consist only of small, scattered fields, cultivated by antiquated methods. The same is true of the equipment for distillation.

Physicochemical Properties.—According to Naves,[72] the Moroccan geranium oils which he examined resembled the Algerian oils. An oil produced in the Marrakech region exhibited an exceptionally high citronellol content (47 per cent); the total alcohol content (calculated as geraniol) was 67 per cent.

Moroccan geranium oils produced in Khémisset on the above-mentioned

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[72] *Parfums France* **12** (1934), 175.

new plantations, and analyzed by Fritzsche Brothers, Inc., New York, had an exceptionally fine rose odor; they were of superb quality, equaling the oils from Southern France. Two typical lots of the 1948 harvest had these properties:

	I	*II*
Specific Gravity at 15°/15°	0.893	0.893
Optical Rotation	−11° 50′	−11° 41′
Refractive Index at 20°	1.4650	1.4650
Acid Number	3.3	2.2
Ester Content, Calculated as Geranyl Tiglate	25.1%	25.6%
Formate Content, Calculated as Geranyl Formate	14.7%	13.6%
Total Alcohol Content, Calculated as Geraniol	71%	72.8%
Citronellol Content (Hot Formylation [73])	45.2%	55.6%
Ketone Content, Calculated as Isomenthone (Hydroxylamine Hydrochloride Method, 2 hr.; Stillman-Reed Procedure [74])	10.6%	15.6%
Solubility	Soluble in 2 to 2.5 vol. and more of 70% alcohol	

The physical properties of this oil resemble those of the Algerian type, the odor that of the French oil. The citronellol content, however, is very high, approaching that of the Réunion type. The Moroccan oil thus combines the virtues of the French, Algerian, and Réunion geranium oils.

CONCRETE AND ABSOLUTE OF GERANIUM

A portion of the geranium crop cultivated in the Grasse region of Southern France, and in Khémisset (Morocco) is not submitted to steam distillation, but to extraction with volatile solvents (chiefly benzene, or petroleum ether —cf. Vol. I of this work, pp. 188, 200, 211). Five hundred kilograms of plant material yield about 1 kg. of concrete of geranium, which, on conversion, gives 600 to 700 g. of alcohol-soluble absolute.

The concrete is a waxy, solid mass of dark green color, only partly soluble in high-proof alcohol. The absolute is liquid, of green color, soluble in high-proof alcohol. Both products, the concrete as well as the absolute, possess a very fine, smooth, geranium odor, softer than that of the distilled oil, and much more lasting.

In many preparations, the green color of the absolutes and concretes is considered objectionable; partly decolorized products of light brown color have, therefore, been developed and are available.

Concretes of geranium are to be recommended in preparations where solubility in alcohol is not required; the absolutes in products which demand

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[73] Cf. Vol. I of this work, p. 287.

[74] *Ibid.*

solubility. Properly used, the concretes and absolutes give excellent results, imparting long lasting, smooth, geranium notes to soaps, perfumes, and cosmetics.

OIL OF GERANIUM FRENCH

The geranium oil produced in the Grasse region of Southern France has always been highly esteemed for its very fine, rose-like odor. Many years ago, before the emergence of Algeria and Réunion as heavy producers of geranium oil, a large acreage in the Grasse region was devoted to the cultivation of geranium, and up to 2,000,000 kg. of herb were annually harvested and distilled. The perfume, cosmetic, and soap industries of the world then depended almost entirely upon the French production for the supply of geranium oil.

The plant was cultivated by numerous growers in the beautiful region between Cannes and Grasse, particularly in the lovely and fertile Siagne Valley, near Pégomas, Auribeau and Mandelieu.

In late years conditions have changed fundamentally in this respect. No longer can the French oil, despite its supreme quality, compete with the oils from Algeria, Morocco, and particularly Réunion Island. Labor in France is now high priced, and the French Riviera has developed into one of the world's most fashionable resorts. Much land has been withdrawn from agricultural use; the delightful climate has attracted a great many people from other parts of France, and the Côte d'Azur has become the paradise of the sun lovers and the retired. Countless homes dot the countryside, and what agricultural land remains is devoted largely to the growing of vegetables for the increased population and the tourists. No wonder then that production of geranium oil in the Grasse and Pégomas region has declined to a few hundred kilograms per year.

Because of occasional frosts (a temperature below +3° C. destroys the plant), geranium in Southern France has to be grown as an annual, i.e., it has to be replanted every spring, which of course increases the cost of the oil unreasonably.

Physicochemical Properties.—The oils produced in the Grasse region of Southern France (Grasse geranium oils) possess a very delicate, fine and rose-like odor.

According to Gildemeister and Hoffmann,[75] their physicochemical properties vary within these limits:

Specific Gravity at 15°	0.896 to 0.905
Optical Rotation	−7° 30′ to −10° 15′
Acid Number	6 to 10

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[75] "Die Ätherischen Öle," 3d Ed., Vol. II, 898. Cf. Jeancard and Satie, *Bull. soc. chim.* [3], **31** (1904), 43.

Ester Number	46 to 66
Ester Content, Calculated as Geranyl Tiglate	19.4 to 28%
Ester Number after Acetylation	217 to 228
Total Alcohol Content, Calculated as Geraniol	71.3 to 75.6%
Citronellol Content	37 to 40%
Solubility	Soluble in 2 to 3 vol. of 70% alcohol; usually separation of paraffins on dilution

Naves[76] reported the following values for pure French oils produced from 1924 to 1934:

	In Most Batches	*Extreme Limits*
Specific Gravity at 15°/15°	0.895 to 0.901	0.894 to 0.9035
Optical Rotation	−9° 50′ to −11° 30′	−9° 0′ to −12° 40′
Refractive Index at 20°	1.4686 to 1.4725	1.4670 to 1.4730
Acid Number	1.9 to 3.08	Up to 5.4
Ester Number	44.8 to 63	39.9 to 72
Ester Content, Calculated as Geranyl Tiglate	18.9 to 26.5%	16.8 to 30.3%
Ester Number after Acetylation	215.6 to 224	Up to 229.1
Total Alcohol Content, Calculated as Geraniol	68 to 71.4%	Up to 74%
Ester Number after Formylation	134.4 to 147.7	119.3 to 147.7
Apparent Citronellol Content	40.1 to 44.4%	35.3 to 44.4%
Ketone Content, Calculated as Isomenthone (Hydroxylamine Hydrochloride Method)	8 to 10%	...
Solubility	Soluble in 2 to 6 vol. of 65% alcohol Soluble in 1 to 4 vol. of 68% alcohol	

A genuine oil distilled by the author in Southern France had these properties:

Specific Gravity at 15°	0.903
Optical Rotation	−11° 34′
Refractive Index at 20°	1.4710
Acid Number	4.2
Ester Content, Calculated as Geranyl Tiglate	28.6%
Total Alcohol Content, Calculated as Geraniol	69%
Solubility	Soluble in 2 to 2.5 vol. of 70% alcohol; turbid with more alcohol

For analysis of the oil, the reader is referred to the monograph on "Algerian Geranium Oil."

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[76] *Parfums France* **12** (1934), 175.

OIL OF GERANIUM CORSICAN[77]

Years ago small quantities of geranium oil were produced near the northeastern coast of Corsica, in the regions of Brando, Luri, Borga, and Erbalunga. The Corsican oil, much esteemed for its high quality which approximated that of the French oil, was used chiefly in France.

Today production of geranium oil in Corsica (if any) is negligible.

As regards the physicochemical properties, Gildemeister and Hoffmann[78] state that only few oils of geranium from Corsica have been examined; their properties vary within these limits:

Specific Gravity at 15°	0.896 to 0.901
Optical Rotation	−8° 0′ to −10° 30′
Acid Number	3.6 to 5
Ester Number	56 to 63
Ester Content, Calculated as Geranyl Tiglate	23.6 to 26.5%
Solubility	Soluble in 2 to 3 vol. of 70% alcohol; usually separation of paraffins on dilution

OIL OF GERANIUM SPANISH

Spanish geranium oil, although produced in very small quantities only, has always been esteemed for its fine, rose-like odor, which resembles that of the French oil. Some connoisseurs, indeed, consider it superior to the French product.

For years geranium has been cultivated as a perennial in various parts of Spain, but on a very limited acreage, the total production varying from one hundred to several hundred kilograms of oil. Because of the very high price of the oil (in 1948 about six times the price of the Réunion or Algerian oil) the annual output of the oil has always been absorbed chiefly on the local market, exchange restrictions in Spain preventing the import of geranium oils from abroad.

Prior to the outbreak of the civil war in 1936, Spain produced yearly 800 to 900 kg. of geranium oil; 500 to 600 kg. of this total output came from Malvarrosa (Valencia), 200 kg. from Gandia (Valencia), and 100 kg. from Medina-Sidonia (Cádiz). The oil produced in ancient and picturesque Medina-Sidonia was known as "Geráneo rosa," and was usually purchased by one of the leading perfume houses in Paris.

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[77] For details see Gattefossé, *Parfumerie moderne* **3** (1910), 73.

[78] "Die Ätherischen Öle," 3d Ed., Vol. II, 898.

After the outbreak of the civil war in Spain most of the plantations in the places mentioned above, particularly those in Medina-Sidonia, were abandoned, to be replaced by other, more vital crops. Food then fetched very high prices on the black market, and growers lost interest in geranium.

Since the end of World War II new geranium plantations have been developed, chiefly in the province of Murcia, and to a small extent in the province of Valencia.

The new plantings in the province of Murcia (about 70 acres) are located near Cartagena on very fertile, well irrigated soil. These, in 1947, yielded about 300 kg. of oil.[79] At the time of this writing (1949) these geranium fields are being increased, and in 1950 a production total of 700 to 800 kg. of oil is anticipated.

The new plantings in the province of Valencia are located near Gandia (40 to 50 kg. of oil per year, but declining), near Malvarrosa (also 40 to 50 kg. of oil per year, likewise declining), and a little further along the coast on a property called "Corinto" (about 100 kg. of oil per year, with little prospect of an increase). Even at the high prices paid at present for geranium oil, the crop offers no great inducement to growers, in view of the high labor cost and the great profits to be made from vegetables and other alimentary products, particularly on the black market.

The geranium fields have to be protected as much as possible against frost by laying them out along the Mediterranean coast, in localities sheltered by mountains against cold winds from the north. Even so, the plants, being very delicate, are often damaged by winter frost; some fields are destroyed almost every two years. It is estimated that only two out of every three years in Spain are free from frost.

The geranium plant flourishes on sandy soil. On fertile soil it seems to develop more resistance to frost. If frosts do not prevent, the plant is grown as a perennial for a period of five years, after which the land is permitted to lie fallow for one year. Then geranium can be grown again. Plantings are started in February or March. If well irrigated, the plants develop rapidly and can be cut twice every year. The first harvest takes place in June–July, producing the best quality and the highest yield of oil (about 70 per cent of the total annual harvest). The second cutting takes place in September and yields about 30 per cent of the yearly crop. On the average, one hectare produces from 20 to 25 kg. of oil. Old plantings yield less oil than younger ones. Irrigation seems to be an important factor in the successful cultivation of geranium; without it, a planting may be destroyed during a spell of excessively hot and dry weather.

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[79] The author is greatly indebted to his friend, Mr. Ramon Bordas, Sevilla, Spain, for much of the data contained in this monograph.

So far as the physicochemical properties of Spanish geranium oil are concerned, Gildemeister and Hoffmann[80] reported these limits:

Specific Gravity at 15°	0.894 to 0.907
Optical Rotation	−7° 0′ to −14° 0′
Refractive Index at 20°	1.466 to 1.473
Acid Number	1.5 to 11
Ester Number	64 to 99
Ester Content, Calculated as Geranyl Tiglate	27 to 42%
Ester Number after Acetylation	204 to 234
Total Alcohol Content, Calculated as Geraniol	66 to 78%
Solubility	Not always clearly soluble in 2 to 3 vol. of 70% alcohol

A sample of genuine Spanish geranium oil distilled in 1947 near Cartagena (Murcia), and analyzed by Fritzsche Brothers, Inc., New York, had the following properties:

Specific Gravity at 15°/15°	0.901
Optical Rotation	−10° 34′
Refractive Index at 20°	1.4710
Acid Number	6.8
Ester Content, Calculated as Geranyl Tiglate	27.0%
Formate Content, Calculated as Geranyl Formate	12.7%
Total Alcohol Content, Calculated as Geraniol	70.3%
Citronellol Content	32.9%
Ketone Content, Calculated as Isomenthone (Stillman-Reed Method)	8.7%
Solubility at 20°	Soluble in 2 vol. of 70% alcohol and more

OIL OF GERANIUM ITALIAN

The literature on essential oils contains numerous references to oil of geranium produced in Italy (Sicily and Calabria), but no practical purpose would be served by quoting data on the many experimental lots examined by various authors. Suffice it here to give a general account of the present state of Italy's geranium oil industry.

According to La Face,[81] the geranium plantations started in Italy prior to

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[80] "Die Ätherischen Öle," 3d Ed., Vol. II, 898.

[81] The author is greatly indebted to Dr. Francesco La Face, Director of the Stazione Sperimentale per l'Industria delle essenze e dei derivati dagli agrumi, Reggio Calabria, for the recent information contained in this monograph (private correspondence).

World War II have generally diminished in productivity, but plantings established more recently promise an increase in the production of the oil within a few years.

Before World War II there existed in Italy two centers of geranium cultivation: one in Calabria (Reccella Ionica), of only about 10 hectares in extent, and yielding 250 to 300 kg. of oil per year; the other in Sicily (Fiumefreddo), of about 12 hectares, yielding 300 to 350 kg. of oil per year. The old plantings in Calabria have now been reduced to about 6 hectares, those in Sicily to about 4 hectares, producing altogether 200 kg. of oil per year. However, new plantations have recently been started in Sicily (Province of Syracuse). These will cover about 15 hectares. New plantings in Calabria (Province of Catanzaro) will be of about the same extent.

The plant cultivated in Sicily and Calabria for the production of geranium oil is *Pelargonium roseum* Willd. In Sicily it is planted on volcanic soil, in the area around Fiumefreddo, or on somewhat compact soil of calcareous-marly nature. In Calabria it is grown on loose alluvial soil of siliceous origin or of calcareous nature.

Cultivation of geranium is begun by the preparation (in the summer) of well protected nursery beds, in which are planted slips, 25 to 30 cm. long, taken from strong parent plants, and containing three nodes. Six months after planting the slips have developed a sufficiently strong root system to permit transplantation to their permanent location, after the soil has been plowed 50 cm. deep. In the first year of growth the planting should be weeded 2 or 3 times during the summer, and watered regularly. In the fall the field is fertilized, for the first time, with phosphates, ammonium sulfate, and potassium sulfate. In the spring of the following year (April–May) the plants can be cut for the first time. The second harvest takes place in August, the third in October.

The plant material is distilled with live steam in stills holding 200 to 300 kg. of herb. The yield of oil depends upon the time of the harvest and the condition (woodiness) of the stalks and branches. Yields of oil varying from 0.08 to 0.11 per cent have been observed (in exceptional cases the yield has been as low as 0.05 per cent, or as high as 0.13 per cent). The average yield of oil, calculated on three harvests per year, amounts to 0.09 per cent.

La Face[82] has reported the following values for Calabrian and Sicilian geranium oils:

Specific Gravity at 15°	0.8866 to 0.9075
Optical Rotation at 15°	−6° 12′ to −12° 36′
Acid Number	2.1 to 6.2
Ester Content, Calculated as Geranyl Tiglate	20.40 to 29.88%
Total Alcohol Content, Calculated as Geraniol	57.01 to 68.40%

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[82] *Ibid.*

Free Alcohol Content, Calculated as Geraniol	41.08 to 54.15%
Citronellol Content	26.45 to 39.60%

The odor of the Italian geranium oils is fine and rose-like; it resembles that of the Algerian oils.

Oil of Geranium Egyptian

About 1930 small quantities of geranium oil were produced, more or less on an experimental basis, by a French grower (the late Charles Garnier) on his plantations in El Shubra, near Cairo. The plants had originally been imported from the Grasse region in Southern France.

Two oils, analyzed by Naves,[83] had these properties:

	I	*II*
Specific Gravity at 15°/15°	0.8976	0.8972
Optical Rotation	−15° 40′	−11° 30′
Refractive Index at 20°	1.4686	1.4673
Acid Number	2.4	1.96
Ester Number	84	61.9
Ester Content, Calculated as Geranyl Tiglate	35.4%	26.5%
Ester Number after Acetylation	215.6	216.6
Total Alcohol Content, Calculated as Geraniol	66.3%	68.8%
Free Alcohol Content	43.1%	50.8%
Apparent Citronellol Content	49.9%	47.3%

Remarkable was the high citronellol content of these two oils. Their odor resembled that of the Algerian type.

Two other oils, also examined by Naves, and originating from the same producer, had a high specific gravity (0.9060 and 0.9068), a relatively low optical rotation (−8° 5′ and −9° 0′), and a high citronellol content (46.3 and 48.5 per cent).

An oil produced by the late Charles Garnier and analyzed by the author had similar properties:

Specific Gravity at 15°	0.906
Optical Rotation	−8° 16′
Acid Number	8.4
Ester Content, Calculated as Geranyl Tiglate	22.7%
Total Alcohol Content, Calculated as Geraniol	70.8%

When incorporated into soap stock, the oil proved to be of outstanding strength.

Oil of Geranium Congo

Introduction and Producing Regions.—According to Goethals,[84] geranium has been grown in southern Ituri since 1932, and in eastern Kivu since 1933.

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[83] *Parfums France* **12** (1934), 176.

[84] *Bull. Classe Sci. Acad. Roy. Belg.* [5], **25** (1939), 91.

(Both districts lie in the eastern part of the Congo.) The plant was introduced into the Belgian Congo when the raising of coffee became unprofitable in the early 1930's, and local planters turned to the cultivation of other crops, among them essential oil bearing plants. At first, results were not encouraging, but by 1939 six planters in the two districts were growing geranium and distilling the oil in commercial quantities. In 1946 the Belgian Congo produced about 4 metric tons of geranium oil, of which approximately 2.3 tons came from Kivu. In 1948 there were three regular commercial essential oil distilleries in operation, but most planters operated their own field stills. It should be emphasized that geranium does not constitute a primary crop in the Belgian Congo; it is a subsidiary crop, intended to safeguard the planters against any sudden collapse in the price of their Arabica coffee.

As has been pointed out above, there are several varieties of *Pelargonium* that differ in the chemical composition of their essential oils, rather than in morphological characteristics. The geranium plants were originally imported into the Belgian Congo from Grasse (A. M.), France, either directly or indirectly. According to private information,[85] two types of rose-geranium were introduced, viz., *Pelargonium capitatum* Ait. and *P. radula* l'Hérit. var. *rosodora*. The former produces an oil of rather unpleasant odor, whereas the latter yields an oil with a pronounced rose-like odor. The present producing regions in the Belgian Congo are in the provinces of Kivu, Ituri, and Ruanda-Urundi, at altitudes ranging from 1,750 to 2,000 m. In Ituri the geranium is often planted among coffee trees. The plant grows well in many regions provided the climate is not too hot and particularly not too humid. Cultivation experiments carried out several years ago in truly equatorial sections of the Belgian Congo (Eala, Kisantu) failed because of the torrential rains during the hot season. Although the geranium plant is very sensitive to cold weather, it nevertheless is relatively long-lived in the Congo, and can be grown for several years. After the third year the yield diminishes, and after the fifth or sixth year the planting should be discontinued. Geranium is not very exacting in regard to the physical condition and chemical composition of the soil. It thrives in sandy as well as in clayey and moist soils. The best results, however, are obtained in fertile, fresh, sandy-clayish soils containing sufficient lime.

Cultivation and Harvest.—The plant is multiplied by terminal cuttings of strong stalks (not too woody), about 25 cm. long, each slip containing at least one eye. The cuttings are planted in a shaded nursery and watered. For this purpose they should be placed into the furrows in a slanting position, the upper end protruding from the soil. After one or two months in the nursery, the young plants are set out in the field, in rows 80 cm. apart,

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[85] Supplied by the Ministère des Colonies, Bruxelles, Office des Produits Agricoles de Costermansville, Institut National pour l'Etude Agronomique du Congo Belge, Yangambi. All through the courtesy of Mr. Gerard J. Danco, New York.

with a spacing of 25 to 40 cm. between the plants in the rows. The spacing depends upon the fertility of the soil and the amount of manure applied. The soil should be plowed as deeply as possible, and dressed. After each harvest the field should be hoed (or plowed) to remove all weeds. Immediately before or at the beginning of the flowering period, and preferably during dry weather, the plants are cut with pruning shears, care being taken to retain one shoot on each tuft. On the average there are two harvests per year; in the region of Ituri, for instance, the harvests take place in April–May and in August–September.

Distillation and Yield of Oil.—The larger distilleries are equipped with batteries of steam stills, each battery comprising three stills of 500 to 600 lb. capacity each. Steam pressure varies from 1.2 to 1.5 kg. per sq. cm. Other stills are of the tilting type, and of 1 to 3 cbm. capacity. The field stills hold 100 to 150 kg. of fresh plant material. Distillation of one charge requires from 1 to 3 hr.

Under normal conditions of growth it is possible to obtain about 10 kg. of oil per hectare in the first year, 30 kg. each in the second and third, 25 kg. in the fourth, and 15 to 20 kg. each in the fifth and sixth years. After the sixth year the planting becomes unprofitable.

The yield of oil, calculated upon fresh plant material, varies from 0.100 to 0.125 per cent. It is higher in the dry season than in the wet season.

Physicochemical Properties.—Goethals [86] reported the following physicochemical properties for geranium oil from the Belgian Congo (15 samples):

Specific Gravity at 15°/15°	0.8947 to 0.9041
Optical Rotation at 20°	−10° 12′ to −13° 42′
Refractive Index at 20°	1.4673 to 1.4730
Acid Number	2.8 to 6.7
Ester Number	48.5 to 68
Ester Content	20.4 to 28.65%
Ester Number after Acetylation	201 to 230
Total Alcohol Content	65.09 to 76.44%
Citronellol Content	34.3 to 47.6%

From an investigation of these oils Goethals drew the following conclusions:

1. The citronellol content of the oil is strongly influenced by the season, being 35 to 37 per cent in the rainy season, and 42 to 45 per cent in the dry season.

2. The Ituri oils differ from the Kivu oils in having a slightly higher specific gravity and refractive index.

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[86] *Bull. Classe Sci. Acad. Roy. Belg.* [5], **25** (1939), 91.

Shipments of commercial geranium oils from the Congo received by Fritzsche Brothers, Inc., New York, had properties varying within these limits:

Specific Gravity at 15°/15°	0.897 to 0.903
Optical Rotation	−8° 0′ to −13° 46′
Refractive Index at 20°	1.4698 to 1.4726
Acid Number	4.9 to 13.0
Ester Content, Calculated as Geranyl Tiglate	15.9 to 24.5%
Total Alcohol Content, Calculated as Geraniol	63.0 to 72.6%
Formate Content, Calculated as Geranyl Formate	6.7 to 13.0%
Solubility	Soluble in 2 vol. of 70% alcohol, cloudy in 10 vol.

Three samples of commercial geranium oils from the Belgian Congo examined in 1949 by the same firm exhibited the following properties:

	I	*II*	*III*
Specific Gravity at 15°/15°	0.898	0.897	0.897
Optical Rotation	−8° 47′	−9° 6′	−9° 12′
Refractive Index at 20°	1.4714	1.4717	1.4717
Acid Number	5.6	21.5	23.3
Ester Content, Calculated as Geranyl Tiglate	17.0%	13.8%	13.3%
Formate Content, Calculated as Geranyl Formate	7.8%	0.9%	0.9%
Total Alcohol Content, Calculated as Geraniol	75.5%	79.0%	80.5%
Solubility	Soluble in 2 to 6 vol. of 70% alcohol; not clearly soluble in 6 to 7 vol. of 70% alcohol		

Except for the high acid number and the low formate content of samples II and III (which may have been caused by the age of these two oils), the properties of the three oils were normal. However, their odor was quite different from that of the geranium oils from Réunion Island and Algeria. It is possible that the Congo oils are distilled from plants that have hybridized, or developed into distinct local varieties since their introduction to the Congo (cf. the monograph on "East African Geranium Oils").

Chemical Composition.—Investigating the chemical composition of a geranium oil produced in the Kivu section of the Belgian Congo, Goethals[87] reported the presence of the following constituents:

44.1%	Citronellol
16.5%	Formates (as citronellyl formate)
8.42%	Isomenthone and menthone
77.2%	Total alcohols

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[87] *Natuurw. Tijdschr.* **23** (1941), 81; **24** (1942), 15. *Chem. Abstracts* **37** (1943), 6410.

60.2%	Free alcohols
44.7%	Primary and secondary free alcohols
15.5%	Tertiary free alcohols

The terpene mixture consisted chiefly of terpenes containing conjugated double bonds. The linaloöl obtained from this oil exhibited a very slight optical rotation. Geranyl formate was present only in small amounts. Next to the formates, the tiglates were the most important esters. The high boiling esters consisted chiefly of geranyl esters. Phenylethyl alcohol occurred in the oil only as an ester, probably as the tiglate.

Rosenthal[88] identified 3-hexen-1-ol in a geranium oil from the Belgian Congo.

It should be mentioned that in some cases geranium oils with very abnormal properties have been produced (perhaps experimentally) in the Belgian Congo. Most likely they were distilled from *Pelargonium* species other than *graveolens*. For example, Goethals[89] reported upon an oil distilled from *P. capitatum* that deviated appreciably from oils previously obtained; it contained about 75 per cent of *l*-isomenthone (α_{D}^{20} −94° 18′).

The Congo geranium oil cannot replace the Réunion or Algerian oils in all established formulas, because its odor differs materially from that of the others. The Congo oil became known in the United States particularly during World War II, when the Réunion and Algerian oils were not readily available. On the other hand, production in the Belgian Congo could probably be substantially increased (if demand should warrant such expansion), since natural conditions are favorable.

Future Outlook.—In 1947 the exports of geranium oil from the Belgian Congo had come almost to a standstill, but in 1948 an improvement could be noted. The principal obstacles were lack of uniformity in the lots offered on the world market and the small quantities actually offered by the producers in the Congo. The government of the colony is at present making serious efforts to remedy the situation by a number of planned measures, among them:

1. A systematic study of the distillation apparatus used by the various producers.
2. Efforts to prepare larger and uniform lots of better quality than offered before by the exporters.
3. Unification of the producers, perhaps in the form of a cooperative.
4. Abandonment of the older, unproductive plantings by the growers.
5. Abolishment of any export duties on essential oils.

[88] *Deut. Parfümerieztg.* **27,** No. 14 (1941), 153.
[89] *Natuurw. Tijdschr.* **24** (1942), 15.

Oil of Geranium North American

In the United States geranium oil has never been produced on a commercial scale, although this would appear to be feasible, provided harvesting of the plant material could be mechanized. Some years ago, Sievers, Lowman and Marshall[90] carried out experiments, growing and distilling *Pelargonium odoratissimum* L. in Texas, Florida, and several sections of California. The work of these officials of the U. S. Department of Agriculture will be briefly reviewed here.

The first experiments were undertaken in February of 1924 with rooted cuttings from Washington, which were planted near National City, San Jose, and Los Gatos in northern California. When irrigated, the plants grew to a height of 2 to 3 ft. by November–December. However, a cold wave destroyed the plantings in December, and the experiment was abandoned.

During March, 1925, another start was made in Torrey Pines near La Jolla, southern California. In this generally frost-free region the plants never suffered any damage from cold weather, although the temperature dropped at one time as low as 27° F. The experiments were continued for six years. The rainfall in the region of La Jolla from fall to spring is only 3 to 27.6 in., measured over a period of seventy years, or 9.6 in. on the average. This, however, did not seem to affect the plants, because during the winter the plants make no progress and, even if irrigated, remain practically dormant. The experimental plants thus had no difficulty maintaining themselves.

They were set out in March, became quickly established, grew rapidly, and in August were in full bloom. After the first year the blooming took place in spring and early summer, with only scattered flowers left later in the season. The crop should, therefore, be harvested and distilled in early summer, when the plants attain their heaviest and bushiest growth. This probably results from a somewhat dormant stage during the winter. Late and abundant spring rains are very helpful and make irrigation unnecessary. Irrigation increased the yield of herb and essential oil substantially. The combined effect of irrigation and fertilization (with ammonium sulfate) was an increase of 64 per cent in the amount of herb, and 97 per cent in the yield of oil. Irrigation, however, was found to play a much greater role in this respect than fertilization.

The greatest obstacle in the way of successful production of geranium oil in the United States is the cutting of the plant material, which is carried out abroad by hand, as the stalks are very woody. A mower of the usual type could, therefore, not be used. Moreover, the plants are easily pulled out of

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[90] *Am. Perfumer* **26** (1932), 683.

the ground by a dragging sickle bar or rake, and for this reason the ordinary haymaking machinery is unsuited for harvesting the geranium crop. However, with some modification a haymower can probably be used. A shorter and stronger sickle bar with the knife operated at a uniform speed should be quite satisfactory. Since it is very difficult to collect and gather up the cut material except with pitchforks, some means of transferring this material to the space between the rows must be provided. The sickle bar should be carried at the farther end on a wheel and so equipped that the bar can be raised or lowered and moved forward without any dragging effect. A sheet metal platform with a 5 or 6 in. edge attached to the bar and so shaped that the outlet extends behind the mower into the space between the rows would make it possible to rake off the cut material into bunches. A modern clover buncher has the essential features required for handling the cut material. With such a machine as described, it should be possible to cut even the heavy, woody stalks of the first year's growth. The growing of geranium on a large scale in the United States is largely dependent upon the success of such a machine.

Summarizing their experimental work, Sievers, Lowman and Marshall[91] arrived at the conclusion that geranium (*Pelargonium odoratissimum* L.) cannot be successfully grown in regions where freezing temperatures occur even occasionally. Moderate frost will not destroy the roots and will do little or no serious damage, but cold waves with temperatures considerably below freezing will kill much of the herb and thus reduce the returns from the crop. In Texas and most sections of Florida the frost hazard is probably too great to justify any large investment in this crop. In the more tropical parts of Florida conditions should be generally favorable, but no experiments have been made in such regions to demonstrate this. In the coastal districts of southern California favorable temperatures prevail but irrigation will be necessary in summer and sometimes in winter, when the rather limited rainfall is not properly distributed.

Geranium may be easily propagated from slips. These can be rooted in sand and then transplanted, or under favorable conditions the slips may be planted directly in the field without previous rooting. In Florida the success of the latter method depends upon the rainfall, but in irrigated districts in California it has been shown to be feasible with a resulting reduction in propagating costs. The plants can be maintained in good productive condition for at least five or six years if properly cared for. In Florida two crops a year, one in June and one in October, may reasonably be expected, provided the plants are not too severely damaged by frost, especially in late winter, and provided also that growing weather in late summer and fall is

[91] *Ibid.*

normal. Under irrigation in the southern coastal district of California the indications are that three crops may be obtained annually if fertilizer and water are used to the best advantage.

It has been demonstrated that the plant responds well to nitrogenous fertilizer, the amount of herb produced being greatly increased by its application. If the bushy, leafy character of the plants is maintained by frequent cutting, the use of such fertilizer should very materially increase the yield of oil from a unit area by stimulating growth, although it apparently does not noticeably affect the percentage yield of oil.

The yield of oil obtained from the plant depends on the proportion of leaf surface present. Heavy, woody stems contain practically no oil, and their presence therefore merely adds to the cost of harvesting and distilling. Percentage yields ranging from 0.03 to 0.10 have been obtained in California and similar yields were also secured in Florida. To translate percentage yields into acre yields, it is necessary to take into consideration the amount of herb produced. The maximum acre yield of oil produced in California from a single cutting under irrigation was about 17 lb. It is estimated that with proper use of water and fertilizer the annual yield of oil under California conditions will approximate about 25 lb. per acre.

The small areas that have been under cultivation have not provided a satisfactory basis for estimating the cost of production. It is evident, however, that geranium will not yield large returns and that the crop can probably be best grown on large areas on which labor-saving practices can be used to advantage.

The oils produced by Sievers, Lowman and Marshall were judged to be of excellent quality by experts in the perfume and essential oil industry of the United States.

In a later publication, Lowman[92] reported the physicochemical properties of the oils produced in the experiments described above. Unfortunately most of the oils were analyzed several years after they had been produced. In the interim the properties had undoubtedly undergone substantial changes. (Cf. the section on "Physicochemical Properties of Algerian Geranium Oil.") Suffice it, therefore, to quote here only the properties of those California geranium oils which were produced in 1932 and 1933 and analyzed in 1933.

Specific Gravity at 15°	0.8893 to 0.8957
Optical Rotation	−7° 50′ to −9° 6′
Refractive Index at 20°	1.4612 to 1.4630
Acid Number	3.5 to 9.0
Ester Content, Calculated as Geranyl Tiglate	25.92 to 36.03%
Total Alcohol Content, Calculated as Geraniol	59.33 to 66.12%
Free Alcohol Content, Calculated as Geraniol	37.27 to 47.55%
Combined Alcohol Content	16.91 to 23.50%

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[92] *Ibid.* **28** (1933), **185.**

The solubility of the oils in 70 per cent alcohol in most cases was poor.

According to Naves,[93] the values reported by Lowman are not reliable, because the method of calculating the free alcohol and total alcohol content employed by Lowman is wrong.

OIL OF GERANIUM RUSSIAN

Development.—At the time of this writing (1949) little, if any, information is available about the actual state of geranium oil production in the Soviet Union. The short account given below has been made up from scattered notes which have appeared in essential oil literature within the past few years.

So far as we can judge, prior to World War II much work was done in the U.S.S.R. on the development of a geranium oil industry. However, the invasion of southern Russia by German forces, and postwar reconstruction efforts have probably upset this program.

According to a report by Viltchinsky,[94] geranium was not cultivated in Czarist Russia; it was first propagated about 1920 from a single plant (*Pelargonium roseum* Willd.) found near Sukhum, and then cultivated, as an annual, on an ever-increasing scale along the coast of the Black Sea, in the Caucasus, on the Crimean Peninsula and in some of the central Asiatic republics. Despite the great attention which was given to the new industry by various government organizations, many difficulties—lack of experience and scientific data, shortage of trained workers, unfamiliarity with methods of storage of the cuttings during the winter months, etc.—had to be overcome, and since 1929 geranium has been grown in the temperate and more humid regions of Abkhasia as well as Batum, Sochi, the Crimea, and in the central Asiatic republics. Originally the yield of plant material per hectare, as well as the yield of oil, was very low, but much progress has lately been made. The yield of oil has been increased, while the cost of production has been lowered. Fertilizers are now applied, methods of crop rotation have been introduced, and cultivation partly mechanized. In 1932 geranium plantations in the regions mentioned above totaled about 900 hectares.

According to later reports,[95] the Soviet Union produced about 15 metric tons of geranium oil in 1934, and 20 tons in 1936. Of the latter quantity 11.9 tons came from Abkhasia, which region produced 13.3 tons in 1937.[96] A substantial part of this quantity seems to have been consumed in the Soviet Union, but a part was exported.

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[93] *Parfums France* **12** (1934), 179.

[94] *Perfumery Essential Oil Record* **25** (1934), 210.

[95] *Ibid.* **28** (1937), 385.

[96] *Chem. Ind.* **61** (1938), 251; through *Ber. Schimmel & Co.* (1939), 35.

Physicochemical Properties.—The odor of the Russian geranium oils which the author had occasion to examine was not as strong as that of the Réunion or Algerian oils. However, it was stronger and more rose-like than the odor of the East African (mawah) oils.

Two batches of Russian geranium oil analyzed by Fritzsche Brothers, Inc., New York, had these properties:

	I	*II*
Specific Gravity at 15°/15°	0.981	0.981
Optical Rotation	−12° 20′	−12° 56′
Refractive Index at 20°	1.4671	1.4669
Acid Number	2.8	4.2
Ester Content, Calculated as Geranyl Tiglate	25.2%	28.1%
Total Alcohol Content, Calculated as Geraniol	68%	68.3%
Ketone Content, Calculated as Isomenthone (Hydroxylamine Hydrochloride Method)	9%	10.2%
Solubility	Soluble in 2.5 vol. of 70% alcohol; turbid with more	Soluble in 2.5 vol. of 70% alcohol; turbid in 4 to 4.5 vol. and more; separation of paraffin

Rutovski and Makarova-Semlyanskaya[97] examined a Russian geranium oil distilled in the Caucasus (probably from *Geranium* [*Pelargonium?*] *roseum*), which exhibited the following properties:

Specific Gravity at 20°/20°	0.9038
Optical Rotation	−9° 40′
Refractive Index at 20°	1.4617
Acid Number	9
Ester Number	56.6
Ester Number after Acetylation	191.5

Chemical Composition.—The oil investigated by these authors contained:

1.5%	Terpenes
7.4%	Linaloöl
1.2%	Geraniol
64.2%	Citronellol
4.6%	Menthone
1.4%	A Compound(?) b. 125°–148°
	A Sesquiterpene Alcohol(?)
	Tiglic, butyric, and acetic acids, and an acid(?) b. 180°–225°

According to a trade news report,[98] a serious effort has been made, in recent years, to establish a new industry—the cultivation of essential oil-

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[97] *Riechstoff Ind.* 4 (1929), 193.

[98] *Chemist Druggist,* April (1949), 479.

yielding plants in the Georgian Republic of the Soviet Union, which enjoys a subtropical climate and has a rich soil. One of the principal perfume sources to be developed is *Pelargonium* from which many tons of oil are now produced annually. In 1947 at least seven million cuttings were prepared, and energetic steps are now being taken to increase cultivation. The Sukhum zonal experiment station has developed a new variety yielding three times as much oil as the rose geranium hitherto employed. Experimental crops have given very satisfactory results, and it is planned to have from 700 to 800 hectares under this crop by the end of five years.

Oil of Geranium East African

(Oil of Mawah)

Development.—The story of the introduction, development, and cultivation of several types of geranium (*Pelargonium*) in the highlands of East Africa (Kenya and Tanganyika) should be of considerable interest to the prospective essential oil producer. It demonstrates that, despite the investment of much capital and labor, and notwithstanding the expenditure of great effort, enthusiasm, and determination on the part of agricultural experts, it is not always possible to raise aromatic plants commercially in certain parts of the world, or to compete successfully with other, old-established producing regions. Factors, unforeseen when the new venture is initiated, are liable to crop up in the course of development, and failure against high hopes and great expectations may result. The only safe procedure for the beginner is to carry out systematic, carefully controlled experiments on small but sufficiently large lots *over a number of years,* and to distill experimental batches of plant material in order to study yield and quality of the oil thoroughly. He ought also to make sure that the trade will be interested in, and actually accept, his oils as something new, or as a replacement for an old-established type of oil. Quality, yield, and cost of the new oil will be the factors determining the success or failure of the planned enterprise. All too often prospective growers have set out with large plantings, but, unfamiliar with the intricacies of the essential oil trade, have ended up in failure and large losses, which might have been avoided by careful, systematic experimentation. The story of the geranium oil industry in Kenya and Tanganyika affords a typical example.

To begin with, it should be pointed out that there are two types of East African geranium oil, viz., the so-called mawah oil, and the real geranium oil—the latter not yet having attained any commercial importance. They represent two distinctly evolved separate types, although in literature they are often confused, probably because in the early days of East Africa's geranium oil industry the two types had not evolved sufficiently to permit any clear differentiation, all oils then simply being offered as "East African geranium oil."

The original intention was to produce, in the highlands of Kenya Colony, a geranium oil of a quality similar to that of the Algerian and the Réunion, and at a price that would be stable and not, like the Réunion oil, be liable to fluctuation from year to year. This seemed feasible if a very large acreage around a centrally located, efficient distillery of large capacity could be planted.

Pelargonium graveolens, imported from the Grasse region of Southern France and from Algeria and Réunion Island, was planted over an extended area. This type yielded a true geranium oil, but suffered badly from the effects of the high altitude, rarefied air (exposure to ultraviolet rays during the hot, cloudless days), very cool nights, and particularly the extreme dryness prevailing in the highlands of Kenya Colony up to 9,000 ft. above sea level. The plants developed excessive woody stalk, and insufficient leaf material, with the result that the yield of oil was only one-third to one-half of that derived from mawah plants (see below). The low yield of oil has also been attributed to the too rapid expansion of the plantations which may have weakened the plants themselves to the point of degeneration. At any rate, the failure of the venture demonstrates that conclusions based upon small-scale experimentation should not be prematurely applied to large-scale production of essential oils. Experience over a period of years should always precede actual commercial production.

Oil of Mawah.—Simultaneously with the above-described development,[99] which was started by Messrs. J. L. Greene and J. Verchère de Reffye near Njoro, Kenya Colony, in 1926, went that of the so-called mawah oil.

The term mawah or manah is derived from the Swaheli word, "maua," the plural of "ua" = flower. Beckley[100] concludes that mawah is a hybrid of *Pelargonium graveolens* and *P. radula*. The latter has also been classified as *P. roseum* Willd. non Ait., but in the opinion of Beckley the name *P. roseum* is simply a garden term for both *P. graveolens* and *P. radula*. According to Greene,[101] mawah is probably *P. radula* var. *quercifolium*.

Mawah plants growing in the gardens of Kenya Colony were first singled out as a potential source for commercial geranium oil in 1926. In the same year they were multiplied for this purpose near Njoro. The plant had probably been introduced into Kenya by Dutch immigrants from South Africa, where many *Pelargonium* species grow wild. Dutch settlers there

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[99] For details see an article by the author, "Perfume Oils of Kenya," *Soap & Sanitary Chemicals* **15** (January, February, 1939).

[100] *Perfumery Essential Oil Record* **28** (1937), 235. Beckley's paper contains interesting details pertaining to the taxonomy of *Pelargonium* in general, and about hybrids from which East African geranium oils were produced experimentally.

[101] Recent private communication of Mr. J. L. Greene, Sanya Juu, Moshi, Tanganyika.

grew the plants around their houses, and used the tops as brooms in their homes as they impart a refreshing, pleasant scent to a room.

Mawah turned out to be a much hardier plant than the other geranium types imported from Southern France, Algeria, and Réunion Island. It flourished even in the high altitudes of Njoro, and resisted the generally dry climate, the excessive heat of the day, the radiation of the sun in the rarefied air, and the very cool nights common in that part of Africa. (Even the white man retains his vitality in the invigorating climate of Kenya's highlands.) The yield of oil derived from mawah has varied from 0.1 to 0.15 per cent, which compares well with that obtained in Algeria and Réunion from geranium plants.

Encouraged by these facts, enterprising planters cultivated a large acreage of mawah near Njoro and constructed an efficient distillery, equipped with steam stills of 1-ton capacity, near the fields. Roads were laid out, permitting easy haulage of the harvested plant material to the distillery. All the work—cultivating, harvesting and distilling—was carried out by low-priced native labor, under the supervision of one or two Europeans.

For propagation, cuttings were prepared during the rainy season, rooted in nurseries, and after a few months, in fair weather, planted by hand in fields previously prepared. Rows were laid out 2 yd. apart, this distance permitting cultivation with a vineyard disk harrow.

The time of harvesting depends upon the rains, which vary in intensity and date of arrival. The first crop can usually be gathered one year after the plants have been set out into the fields. A fully developed planting is cut once every year, but under the most favorable weather conditions a second crop (or at least a partial crop) can be obtained. The plants are harvested when fully grown and in flower. This stage of maturity can be attained in any month of the year except March. All cutting is done by hand, with scissors, by native boys and girls. The average planting lasts for five years, at the end of which time it has to be renewed, with proper crop rotation.

The cut plant material is distilled within 48 hr. of harvesting. During this period, the stalk and leaf material becomes sufficiently soft to be packed into the stills quite tightly. Storing has no effect upon the yield of oil, which ranges from 0.10 to 0.15 per cent. Distillation of one charge lasts 4 hr. The steam is generated in a separate steam boiler.

The production of mawah oil thus has been well organized. In 1937, when the author visited Kenya Colony, there were 1,500 acres planted with mawah. Of the substantial quantities of oil produced every year, 5 or 6 tons were exported to the United States, the remainder to Europe.

The entire venture had practically everything in its favor: plenty of low-priced land for expansion, low-priced labor, efficient management, etc. But the trade did not readily accept the oil, because its quality differed substantially from that of the Réunion and Algerian geranium oils. Mawah oil, therefore, had to be offered at a price lower than that of geranium oil. In this connection, it should be kept in mind that the idea of producing geranium (or a similar) oil in Kenya Colony was conceived in the late "twenties," when overproduction and a world-wide economic depression had lowered the prices of cereals to unprofitable levels. It was hoped geranium oil might yield better returns. When this proved not to be the case, the interest of the producers in mawah oil diminished. Moreover, one of the chief sponsors of the venture, Mr. R. L. Hansard, died early in 1939. World War II brought about an urgent demand for food products in the British Empire, prices of cereals rose, and the land devoted for about ten years to the growing of aromatic plants in Njoro was partly planted with more vital crops. Today only about 600 acres are planted with mawah in Njoro, producing about 2 tons of oil annually.

Physicochemical Properties of Mawah Oil.—The odor of mawah oil resembles that of geranium oil, but is somewhat coarser, for which reason the oil has been used for the scenting of soaps. For a time mawah oil was employed as a "stretcher" of the more expensive geranium oil, but this practice did not work out too well. The essential oil trade has therefore been reluctant to adopt the oil.

Naves[102] reported the following properties of mawah oils examined from 1927 to 1934 in the laboratories of Établissements Antoine Chiris, Grasse (A. M.), France:

Specific Gravity at 15°/15°	0.8854 to 0.8964
Optical Rotation at 20°	$-15° 0'$ to $-19° 10'$
Refractive Index at 20°	1.4685 to 1.4734
Acid Number	Up to 6.3
Ester Number	16.4 to 22.4
Ester Content, Calculated as Geranyl Tiglate	6.9 to 9.4%
Ester Number after Acetylation	209.1 to 224
Total Alcohol Content, Calculated as Geraniol	67.9 to 72.4%
Free Alcohol Content, Calculated as Geraniol	62.2 to 64.8%
Citronellol Content	15.5 to 21.4%
Solubility	Soluble in 1 to 4 vol. of 70% alcohol

Three samples of mawah oil analyzed by Schimmel & Co.[103] had these values:

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[102] *Parfums France* **12** (1934), 177.
[103] *Ber. Schimmel & Co.* (1931), 32; (1932), 33; (1939), 36.

	1931	*1932*	*1939*
Specific Gravity at 15°	0.8908	0.8929	0.8926
Optical Rotation	−15° 42′	−18° 53′	−15° 45′
Refractive Index at 20°	1.47003	1.46934	1.47131
Acid Number	4.1	4.7	4.8
Ester Number	22.4	18.7	19.6
Ester Content, Calculated as Geranyl Tiglate	9.4%	7.9%	8.0%
Ester Number after Acetylation	212.8	209.1	201.6
Total Alcohol Content, Calculated as Geraniol	69.6%	68.2%	65.3%
Solubility in 70% Alcohol	In 1.9 vol. and more	In 1.9 vol. and more	In 1.5 vol. and more

For the properties of other samples the reader is referred to the literature.[104]

Shipments of mawah oils, and samples procured by the author during a visit to Njoro in 1937, on analysis in the New York laboratories of Fritzsche Brothers, Inc., exhibited properties varying within the following limits:

Specific Gravity at 15°/15°	0.892 to 0.895
Optical Rotation	−15° 15′ to −17° 35′
Refractive Index at 20°	1.4692 to 1.4703
Acid Number	2.8 to 5.6
Ester Content, Calculated as Geranyl Tiglate	6.3 to 8.4%
Total Alcohol Content, Calculated as Geraniol	64.8 to 67.2%
Formate Content, Calculated as Geranyl Formate	Up to 0.5%
Ketone Content, Calculated as Isomenthone (Hydroxylamine Hydrochloride Method)	18.1 to 21.2%
Solubility at 20°	Soluble in 2 vol. and more of 70% alcohol

Chemical Composition of Mawah Oil.—Glichitch and Muller [105] examined geranium oils from British East Africa and arrived at the conclusion that they seem to fall into two classes:

(a) Oils high in geraniol and menthone, but low in citronellol.
(b) Oils high in citronellol, but practically free from geraniol.

The oils falling under type (a) are the mawah oils. Glichitch and Muller found mawah oil to have the following composition (details of the analysis are given in the original literature):

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[104] Cf. *Chemist Druggist* **107** (1927), 97. Anonymous, *Perfumery Essential Oil Record* **25** (1934), 278; V. A. Beckley, *ibid.* **28** (1937), 235.

[105] *Parfums France* **5** (1927), 361. Cf. Naves, *ibid.* **12** (1934), 177.

4%	Terpenes
20%	*l*-Menthone
50%	Geraniol
10%	*d*-Citronellol
5%	Linaloöl, isopulegol and citral
5%	A laevorotatory sesquiterpene (or mixture of sesquiterpenes)
1.5%	Tiglic acid
0.75%	Fatty acids (heptylic acid?)
0.75%	*d*-Citronellic acid
3%	Undetected and losses

Interesting is the fact that Glichitch and Muller detected dextrorotatory citronellol (+3° 45′) in mawah oil, as well as in the African geranium oils which these authors classified as group (b) (see above). The low ester content of these oils is also characteristic.

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It would serve no practical purpose to describe here the numerous varieties of *Pelargonium* experimented with in Kenya and Tanganyika, most of which have never been identified morphologically, or to record the analytical data observed on samples of oil distilled from these varieties. The reader interested in the details of this very confused subject is referred to a number of papers and discussions which appeared in trade magazines between 1929 and 1939, when there was much interest in the development of an essential oil industry in the British colonies.[106]

Two samples of geranium oil offered in 1948 from Arusha (Tanganyika), as distilled from *Pelargonium graveolens* (I) and from a *Pelargonium* hybrid (II), were analyzed in the New York laboratories of Fritzsche Brothers, Inc. These oils had the following properties:

	I	*II*
Specific Gravity at 15°	0.892	0.890
Optical Rotation	−9° 27′	−33° 22′
Refractive Index at 20°	1.4693	1.4572
Acid Number	7.8	3.8
Formate Content	0%	0%
Ester Content, Calculated as Geranyl Tiglate	7.5%	6.3%
Total Alcohol Content, Calculated as Geraniol	76.2%	51.2%
Free Alcohol Content, Calculated as Geraniol	71.2%	47.7%
Citronellol Content (by Hot Formylation)	30.7%	53.0%
Ketone Content, Calculated as Isomenthone (Hydroxylamine Hydrochloride Method)	16.8%	40.3%
Solubility in 70% Alcohol	Soluble in 2 vol.	

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[106] Glichitch and Muller, *Parfums France* **5** (1927), 361. Anonymous, *Perfumery Essential Oil Record* **25** (1934), 278; Bovill, *ibid.*, 385. Anonymous, *Bull. Imp. Inst.* **32** (1934), 196, 198, 202, 203. V. A. Beckley, *Perfumery Essential Oil Record* **28** (1937), 235; R. L. Hansard, *ibid.*, 321.

It is interesting that neither of the two oils contained any formate. Their ester content, calculated as geranyl tiglate, was low. The oil distilled from the hybrid (II) exhibited a high optical rotation, a high ketone content, and a low total geraniol content. Its odor was very minty. The other oil had a good geranium odor, which, however, differed from that of the Réunion, Algerian, Moroccan, French, and Spanish oils.

Before closing the discussion of the East African geranium oils, it should be mentioned that the experimental work on the production of geranium oil in Kenya and Tanganyika is being continued. According to the latest reports [107] received by the author, the Kenya Department of Agriculture, under the able guidance of Mr. V. A. Beckley, has recently succeeded in selecting and acclimatizing some very remarkable species producing an oil equal, if not superior, in quality to the geranium oils generally known on the world markets.

When general economic conditions become more normal, Kenya and Tanganyika may well develop into an important and valuable source of different types of geranium oil.

OIL OF GERANIUM MACRORRHIZUM
(Bulgarian Geranium Oil)

Geranium macrorrhizum L. (*G. lugubre* Salisb. or *Robertium macrorrhizum* Picard, commonly called "Bigroot" Geranium) grows wild as a low shrub in certain parts of France and Italy (Maritime Alps and Apennines), and in the Balkan countries. The plant has become naturalized even in some sections of central and northern Europe, where it is grown for ornamental or medical purposes, and for the feeding of bees. In Bulgaria, where the plant is called "Zdravetz," it grows on rocky soil, in altitudes up to about 2,400 m. above sea level. According to Hegi,[108] the plant is highly esteemed as an aphrodisiac in Bulgaria.

The volatile oil distilled from the overground parts of the plant possesses a very pleasant odor reminiscent of clary sage, orris, and particularly of rose. Because of its rose-like odor the oil is occasionally produced in Bulgaria, and sometimes used for the adulteration of rose oil.

Physicochemical Properties.—The distilled oil is semicrystalline at room temperature.

An oil of *Geranium macrorrhizum* procured by the author in Bulgaria had these properties:

Specific Gravity at 25°	0.9515
Optical Rotation	−4° 35′

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[107] Private communication of Mr. J. L. Greene, Sanya Juu, Moshi, Tanganyika.
[108] "Illustrierte Flora von Mitteleuropa," Vol. IV, 3d Part, p. 1708.

Refractive Index at 25°	1.50762
Acid Number	1.9
Ester Number	6.5
Ester Number after Acetylation	35.5
Congealing Point	17° (On cooling the oil separated crystals, and on further cooling assumed a butter-like consistency)
Solubility	Soluble in 5.5 vol. and more of 80% alcohol. Separation of paraffins

An oil examined by Rovesti [109] exhibited the following values:

Specific Gravity at 50°/15°	0.9411
Optical Rotation at 30°	−3° 55′
Refractive Index at 38°	1.5093
Acid Number	0.78
Ester Number	3.53
Ester Number after Acetylation	28.6
Melting Point	28°
Solubility at 18°	Soluble in 1.2 vol. of 90% alcohol

Fifty per cent of the oil consisted of a solid hydrocarbon m. 49°–50° (see below). Rovesti declared this hydrocarbon to be a tricosane $C_{23}H_{48}$ (see below).

Four samples of Bulgarian geranium oil described by Gildemeister and Hoffmann [110] had properties varying within these limits:

Specific Gravity at 40°	0.9431 to 0.9638
Optical Rotation	−5° 45′ to −7° 38′
Refractive Index at 40°	1.50642 to 1.51538
Acid Number	1.2 to 1.5
Ester Number	5.6 to 14.9
Ester Number after Acetylation	33.6 to 35.5
Solubility	Soluble in 90% alcohol; soluble in 6 to 7 vol. of 80% alcohol, but with slight turbidity

About 50 per cent of each oil sample consisted of solid substances which, on recrystallization from dilute alcohol, yielded shiny, hard prisms m. 54°–55°.

One sample of oil was freed, by cooling, from the solid part, and then analyzed as follows:

Specific Gravity at 15°	0.9460
Optical Rotation	−8° 10′
Refractive Index at 20°	1.50698
Ester Number after Acetylation	54.1

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[109] *Notiz. chim. ind.* **2** (1927), 438 (Vallecrosia). Through *Chem. Zentr.* (1927), II, 2360.

[110] "Die Ätherischen Öle," 3d Ed., Vol. II, 906. Cf. *Ber. Schimmel & Co.* (1927), 114.

Solubility	Soluble in 0.5 vol. of 90% alcohol; separation of paraffins in 1.5 and more vol. of 90% alcohol

Two concretes of *Geranium macrorrhizum*, obtained by extraction with petroleum ether and examined by Naves,[111] had these properties:

	I	*II*
Specific Gravity at 55°/55°	0.908	0.9135
Specific Optical Rotation at 20° (in 10% Carbon Tetrachloride Solution)	+8° 40′	+14° 10′
Refractive Index at 55°	1.4859	1.4905
Melting Point	53°	55°
Congealing Point	52°	48°
Acid Number	25.2	30.1
Ester Number	22.4	23.05
Ester Number after Acetylation	62.5	106.75
Ester Number after Cold Formylation	31.85	70.7
Aldehyde or Ketone Content	0.3%	0.5%
Solubility in 3 Volumes of 95% Alcohol	45% soluble	52% soluble

The odor of these concretes was much milder, fuller, and more lasting than that of the distilled oils.

Chemical Composition.—The solid components, which amount to about 50 per cent of the distilled oil, were first investigated by Rovesti (see above), who believed them to consist chiefly of a tricosane $C_{23}H_{48}$. Later, Wienhaus and Scholz[112] established for the solid constituent (m. 54°–55°, d_4^{67} 0.9549, n_D^{50} 1.51610) the empirical formula $C_{16}H_{24}O$, and called the substance "germacrol." This is apparently an oxide. Almost simultaneously Naves[113] arrived at the conclusion that the germacrol present in distilled oil of *Geranium macrorrhizum* possesses the empirical formula $C_{15}H_{22}O$ (m. 56°–56.5°, b_{10} 150°–151°, d_{61}^{61} 0.9711, n_D^{61} 1.51012), and that it is probably identical with the oxide $C_{15}H_{22}O$ identified by Nilov[114] in the oil derived from the fruit of *Smyrnium perfoliatum* L. (fam. *Umbelliferae*).

Examining the concretes of *Geranium macrorrhizum* described above (which exhibit a high fixation value), Naves[115] observed the presence of these compounds:

Geraniol	
Germacrol	(See above)
Mono- and Bicyclic Sesquiterpenes	
A Sesquiterpene Alcohol	
n-Triacontane, $C_{30}H_{62}$	m. 66°
Free Fatty Acids, C_6 to C_8	Small quantities

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[111] *Parfums France* **7** (1929), 310.

[112] *Ber. Schimmel & Co., Jubiläums-Ausgabe* (1929), 280.

[113] *Parfums France* **7** (1929), 304.

[114] *J. Russ. Phys. Chem. Soc.* **60** (1928), 1579. *Chem. Abstracts* **23** (1929), 2249.

[115] *Parfums France* **7** (1929), 304.

Examining the high boiling fractions of oil of *Geranium macrorrhizum*, Pfau and Plattner[116] isolated a mixture of sesquiterpenes b_{10} 120°–123°, n_D^{20} 1.5034, and sesquiterpene alcohols b_{10} 156°–161°, n_D^{20} 1.5141, which on dehydrogenation with sulfur or selenium yielded S-guaiazulene.

In 1949, Naves[117] investigated an oil submitted to him as "Zdravets Oil" from the island of Cyprus, where production of this type of oil had been started in 1947. Naves found that the oil contained 28.1 per cent of ketones (apparently mostly *l*-isomenthone), 36.0 per cent of free alcohols (calculated as $C_{10}H_{18}O$) and 55.2 per cent of total alcohols. A few months later Naves[118] had occasion to examine (partly damaged) plant material from Cyprus and found that the plant, from which the "Oil of Zdravets" was distilled, was not *Geranium macrorrhizum*, but a species of *Pelargonium*.

Use.—Since oil of *Geranium macrorrhizum* is produced only occasionally it is not a regular article of commerce, nor is it used in the perfume, cosmetic, or soap industries. The small lots distilled in Bulgaria are said to be employed sometimes for the adulteration of rose oil.

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[116] *Helv. Chim. Acta* **19** (1936), 858.

[117] *Perfumery Essential Oil Record* **40** (1949), 161.

[118] *Ibid.*, 391.

INDEX

Numbers in *italics* indicate main entries; in the case of a plant species, they indicate references to monographs (or sections of monographs) dealing with the *oil* of the species.

Wherever possible, synonymous names for chemical compounds have been brought together under one main heading, such heading being in each case that employed in Vol. II of this series. Cross references are made from the several synonyms. Thus: in the text, *Eugenol acetate* may be called *Aceteugenol* or *Acetyleugenol.* In this index, the latter two names are cross-referred to *Eugenol acetate.* The researcher interested in tracing the occurrence of any specific chemical compound in the various oils should find this system helpful.