VEGETABLE FATS AND OILS

VEGETABLE FATS AND OILS

Their Chemistry, Production, and Utilization for Edible, Medicinal and Technical Purposes

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SECOND EDITION

American Chemical Society
Monograph Series

REINHOLD PUBLISHING CORPORATION
330 WEST FORTY-SECOND ST., NEW YORK, U. S. A.
1943

Printed in the United States of America by
THE HADDON CRAFTSMEN, INC., SCRANTON, PA.

GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie, Moissan's Traité de Chimie Minérale Générale, Friend's and Mellor's Textbooks of Inorganic Chemistry and Heilbron's Dictionary of Organic Compounds, it often takes a great deal of

time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

Preface to First Edition

An attempt has been made to bring within the compass of one comparatively small volume as much information as possible in regard to the vegetable fats and oils. Those requiring other or more detailed information will find the available references under each subject treated.

After much consideration, it was decided to divide the fats and oils into three classes: the first, commonly known as the non-drying class, to contain those products having iodine numbers up to 100; the second, or semi-drying class, to contain those having iodine numbers from 100 to 130; and the third, or drying class of oils, to contain those with an iodine number of 130 or more. Naturally, as this is an arbitrary classification, there is some overlapping of the groups and in the allocation of these borderline products, the limits set above for the range of the iodine numbers of the classes will be slightly extended. Whenever feasible, the fats or oils from plants of the same family will be grouped together.

For convenience, there have been prepared both an alphabetically arranged table of the plant families under which the species are listed and a botanical index which contains in alphabetical order the species mentioned in this work.

Although the methods in common use for the extraction of fats and oils are discussed in the first chapter, further attention is paid to methods of expression under the production of individual products such as cottonseed, linseed and olive oils. Under cottonseed oil, caustic soda refining, bleaching, deodorization, hydrogenation, the preparation and distillation of fatty acids recovered from refinery soap stock are discussed. It may be noted that these methods are applicable as such or with slight modification to the treatment of a large number of fats and oils.

It will be observed that the chapter on methods, with few exceptions, contains but one standard procedure for each determination or test. Nearly all the methods have been critically examined in the author's laboratory.

The characteristics given for the various fats and oils have not been placed in the usual open space blocked tables as commonly used in many other works, in order to conserve both space and expense. Little usage, however, is required to become entirely accustomed to the form in which they are presented.

Acknowledgment is hereby made in connection with the preparation of this volume, of the use of information found in various works, journals, and other publications dealing with the subjects treated.

Washington, D. C. G. S. JAMIESON

Preface to Second Edition

The arrangement of the subject matter in the present volume has not changed from that used in the previous edition. In a few cases, it was found desirable to rewrite the descriptive matter either wholly or in part. However, in all cases, an effort has been made to bring the information given up to date. A considerable number of fats and oils have been described in addition to those appearing in the first edition. To the chapter on methods have been added several other procedures, including that for the determination of the diene value. Attention is called also to the new directions given for determining the thiocyanogen value. In view of the inquiries received from time to time regarding the quantity and character of oil in seeds from ornamental (besides some other) trees and plants, data on a number of these seeds and oils will be found in the appendix.

I am much indebted to W. G. Rose and L. Zeleny for the descriptions of several analytical procedures, and to E. M. Nelson for the paragraphs on vitamins.

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Washington, D. C.
August, 1943

Abbreviations of Characteristics

B. Pt.	Boiling point
Sp. g.	Specific gravity.
Sp. ht.	Specific heat.
N_D^o	Refractive index.
Sap. V.	Saponification value.
Iod. No.	Iodine number or value.
Acid V.	Acid value.
Acetyl V.	Acetyl value or number.
R. M. V.	Reichert-Meissl value.
Pol. No.	Polenske number or value.
Unsap.	Unsaponifiable matter.
Unsat.	Unsaturated.
Crismer V.	Crismer value.
M. Pt.	Melting point.
SCN V.	Thiocyanogen value or number.
Sol. Pt.	Solidification point.
Kirchner V.	Kirchner value.
OH	Hydroxyl value.
$[\alpha]_D$	Specific rotation.

Contents

PAGE

General Introduction 5

Preface to First Edition 7

Preface to Second Edition 9

Abbreviations of Characteristics 10

Chapter I. Fats and Oils 13

Chapter II. Non-drying Fats and Oils 30

Chapter III. Semi-drying Oils 171

Chapter IV. Drying Oils 253

Chapter V. The Fatty Acids 336

Chapter VI. Methods 371

Appendix I Various Other Seed Oils 469

Appendix II Tables 473

Index to Botanical Names 495

Subject Index 499

Chapter I

Fats and Oils

Introduction

Fats and oils not only are an essential part of the diet of men and animals, but they play an important rôle in many industries. Consequently, the life and progress of a nation depend in no small measure on its supply of these products. They are used as such or are manufactured into edible, medicinal and technical products. The demand for fats and oils increases with the population and through the discovery of new uses for these substances.

Although it is well known that the quantity of fats and oils obtainable from land and marine animals is clearly limited, such is not the case with those of vegetable origin, and this is particularly true when the possibilities of the tropics are taken into consideration. Even now the production of oil seed crops in many temperate and subtropical regions is far below the maximum; moreover, this will be raised through plant breeding, which will result in certain cases in raising the oil content of the seeds, and improved agricultural methods will increase the yield of seeds per acre. Active study along these lines is in progress in many countries and some notable results have already been obtained. Furthermore, the better utilization of the available fats and oils is dependent to a large extent upon having a more intimate knowledge of their composition.

The attention of those who are connected with industries using oleaginous products is called to the importance of comprehending their constitution to the fullest extent possible. In view of this, an effort has been made to present, whenever available, the most recent information regarding the constituents of both crude and refined products.

Use of the Terms "Fats and Oils." It is desirable to make certain at this time that the uninitiated understand these terms, especially as considerable confusion exists in regard to their use. The distinction between them is merely a physical one, the oils being liquid and the fats solid. However, an oil in one country may be a solid fat in another because of differences in temperature. The common or trade name given in the country of origin is often retained elsewhere; coconut and palm oils may be mentioned as examples. In several cases products have been named simply on account of their physical condition, long before their chemical nature was understood; examples are sperm oil, which is a liquid wax, and Japan and myrtle waxes, both

of which are fats. As the term *oil* is commonly applied to various classes of substances in no way related, the terms *fats, fixed* or *fatty oils* are used to designate those substances consisting essentially of mixtures of glycerides, and the term *fat* frequently includes both fats and oils.

Their Distribution, Formation, Utilization by Plants, and Composition

Fats and oils are widely distributed both in the animal and vegetable kingdoms where they are found in varying quantities in organisms consisting of a single cell, as well as in those most highly developed. In plants, they are found chiefly in the spores, seeds, and fruits, but they occur also in the leaves, roots and other vegetative organs. The function of these substances in the leaves has not yet been determined, but those in the spores, seeds and some tubers constitute a food reserve to be drawn upon during germination and the early life of the plant. In the early stages of germination the total fat present undergoes little diminution, but following this period it rapidly diminishes. During the latter stage, the fat contains a considerable proportion of free fatty acids. Also it has been observed that the iodine number is lower than that of the fat in the original condition. S. Ivanov [*Jahrb. wiss Bot.*, **50**, 375 (1912)] believes that the more unsaturated fatty acids are utilized first by the plant. Policard and Mangenot [*Compt. rend.*, **177**, 346 (1923)] have shown that the fat before germination is homogeneously distributed throughout the seed or germ, as the case may be; but as germination proceeds, it appears as an infinite number of drops suspended in the dytoplasm. Rhine [*Botan. Gaz.*, **82**, 154 (1926)] states that during germination the fat is not transported as such but is first converted into carbohydrates before being transported into the plant.

In spite of many investigations, much remains to be determined in regard to the synthesis of fats in nature. It is now generally agreed that they are formed from carbohydrates. It is noteworthy that the fatty acids found in fats contain an even number of carbon atoms. There is considerable evidence that the fatty acids are produced first and that at a later stage they are combined, through the agency of lipase, with glycerin to form the triglycerides [Ivanov, *Ber. deut. Bot. Ges.*, **29**, 595 (1911); Dunlap and Gilbert, *J. Amer. Chem. Soc.*, **33**, 1787 (1911); Welter, *Z. angew. Chem.*, **24**, 385 (1911)]. Also, it is believed that the glycerin is formed from carbohydrates. In the early stages of development, seeds and fruits contain notable quantities of free fatty acids, but these practically disappear when maturity is reached. The cause of this delay in the formation of triglycerides is not yet known, but has been the subject of considerable speculation.

For information on the various theories that have been proposed from time to time on fat formation in animals and plants, Leathe's and Raper's work entitled "The Fats" (Longmans, Green and Co., 1925) should be consulted.

From the investigations that have been made, it appears that the

fat stored in fruits and seeds is not transported from other parts of the plant, but is formed where found.

In general, there appears to be some relation between the composition of fats and conditions of the environment in which they are found. In this respect both animals and plants more or less adapt themselves to the surrounding conditions. In the case of plants, this has been shown by the studies of Pigulevsky and of S. Ivanov. The fats, with a few exceptions from tropical plants, are characterized by containing notable percentages of saturated acids, whereas those from plants growing under colder climatic conditions contain large proportions of unsaturated acids. Consequently, drying and semi-drying oils are of more frequent occurrence in plants of temperate climates than in those found in the tropics. On the other hand those of the non-drying class predominate in tropical regions. [The Taxonomic and Climatic Distribution of Oils, Fats and Waxes, by J. B. McNair, *Am. J. Bot.*, **16**, 832-41 (1929)].

S. Ivanov, who has been studying the effect of climate upon the composition of vegetable fats over a considerable period of years, with particular reference to those belonging to the drying class, has formulated the following rules:

1. Plants which contain fats having acids with two and three double bonds are relatively more sensitive to variations of climate than plants, the fat of which contains only acids with one double bond.

2. The climate of southern lands favors the formation of oleic acid, whereas that of northern lands favors the formation of linolenic acid in the fats.

3. The variability of the iodine number depends upon the climate, and is more striking in the case of those fats which contain the larger quantity of acids with two and three double bonds. For example, investigations indicate that the further north flaxseed and soybeans are grown, the higher is the iodine number of their fats. For further information consult S. Ivanov, *Chem. Absts.*, **21**, 3382 (1927), **24**, 1885 (1930); *Chem. Umschau*, **36**, 401 (1929).

For some time it has been recognized that the seed fats from plants belonging to the same or closely allied botanical orders often contain the same fatty acids. Members of certain botanical families (or smaller divisions) yield fats in which a given acid or acids predominate. Examples are lauric acid in the kernel fats of the *Palmae*, myristic acid in those of the *Myristicae*, erucic acid in those of the *Cruciferae*, petroselinic acid in those of the *Umbelliferae*, and the chaulmoogric group of acids in the fats of the *Flacourtiaceae*. With the larger botanical families, the similarity in the composition of the fats is more or less confined to those of a tribal group or even a genus.

With the application of modern methods for the investigation of fats, including those developed by Hilditch and co-workers by which it is possible to determine the component glycerides of a fat, a more intimate insight is being obtained not only in regard to the character and quantity of the fatty acids present but also as to how they are

combined to form glycerides. Hilditch [*Proc. Roy. Soc. London*, **B 103**, 111 (1928)] has found a striking similarity of the mixtures of glycerides composing the seed fats from closely related plants.

From the component glyceride studies that have been made, Collin and Hilditch [*Biochem. J.*, **23**, 1273 (1929)] stated that from the data at hand, there is a pronounced tendency to an even distribution of the fatty acids throughout the glycerides of the seed fats. On the other hand the glycerides of fats from parts of the plant other than the seed, like those of the animal fats, are built upon more heterogeneous lines. Also, it is interesting to note that both these investigations, as well as those on record which are based upon the isolation of the glycerides by fractional crystallization, have indicated that simple triglycerides occur in only a very few fats.

For additional information the "Chemical Constitution of Natural Fats" by T. P. Hilditch (Chapman and Hall, London, 1940) should be consulted. Also attention is called to the symposium on the molecular structure of fats and oils [*Chem. Reviews*, **29**, 199-438 (1941)].

In addition to the glycerides, which constitute by far the major portion of the fats, they contain small percentages of sterols as such, or as esters, phosphatides, such as lecithins and cephalins, pigment compounds, and vitamins. As obtained by expression or solvent extraction, they may contain more or less resins and essential oils, as well as small quantities of waxes, and more or less of vegetable extractives such as pentosans, proteoses, peptones, etc. As the triglycerides of fats are colorless and practically tasteless, any color the fat may possess is due to pigments such as carotene, xanthophyll, chlorophyll, etc., or to resins, and any noticeable flavor is generally due to the presence of more or less essential oil.

Extraction and Refining

Vegetable fats and oils are chiefly obtained by expression or by means of solvents. Some oil is separated by the centrifuge and by boiling the oleaginous products with water. A method of recovering vegetable oils by a bacterial process has been proposed by J. W. Beckman [*Ind. Eng. Chem.*, **22**, 117 (1930)].

In the United States, most of the vegetable oils are obtained by expression. In recent years a number of sizable solvent extraction plants have been established and used chiefly for the extraction of oil from soybeans. Solvent extraction, however, has been used for many years in Europe, and since 1914 large quantities of edible fats and oils have been obtained by this means. For those not familiar with Europe, it should be mentioned that the tonnage of products expressed there is still very large. In Africa and Asia nearly all the fats and oils produced are obtained by expression.

Depending upon the nature of the oleaginous products, the methods used in preparing them for extraction by any method naturally vary, but the first step in any case is to remove as completely as possible all kinds of foreign matter. Foreign matter is not only likely to unduly

wear or injure the machinery, but it may seriously reduce the quality of the oil and the cake or meal. With small seeds such as those of flax it is important also to remove the weed seeds carefully. Oil of good quality can only be obtained from clean sound fruits, nuts, and seeds when extracted in a clean mill.

Dust, sand, and the larger pieces of foreign matter are separated mechanically by sieves; then the seeds or nuts are passed over magnets to remove any remaining pieces of iron. The next step in the case of nuts and many of the larger seeds is that of decortication and separation of the kernels from the shells. The preparation of olives, palm fruits and cottonseed for the extraction of the oil is described under the individual oil. Decorticating machines or "hullers" are set so as to crack the larger sized seeds, and after removing the kernels, it is customary to pass the unbroken smaller seeds through a second machine adjusted to crack them. The kernels are separated from the broken shells by means of shaker sieves, frequently aided by a suction or air blast system.

In the case of palm nuts and various fruit pits, after cracking, the kernels are commonly separated by flotation, using a solution of brine or calcium chloride of such a gravity that the shells float and the kernels sink. However, in recent years, equipment has been designed for the mechanical separation of these kernels, which is a decided improvement over the older method which necessitated the subsequent washing and drying of the kernels after removal from the flotation tank or vat.

The third step in the preparation or milling is that of crushing or rolling in order to make the product suitable for the extraction of the oil. Unless care is given to this, satisfactory recovery of the oil cannot be expected. With copra and the larger nuts, a preliminary crushing is made, either by means of reducing rolls or other types of crushing machines. Then the product is passed between the finishing rolls. These rolls are also used for crushing the small oil seeds. Constant attention should be given in order that the rolls may be kept in proper alignment and that their surfaces are kept in proper condition. Also attention should be given to feeding the rolls so that the kernels or seeds are evenly distributed throughout their width. Neglect of any of these points results in an excessive use of power and a more or less unsatisfactory condition of the crushed product.

Correct milling is essential for efficiency in extraction of the oil either by expression or solvents. The particular physical character of the product has to be taken into consideration in determining how it should be milled so as to give the best results, and usually this can be decided only through experience. With products of high oil content, it is important to mill them so as not to separate any oil, because this interferes with the subsequent extraction process. For extraction with solvents, the meal is usually not crushed quite so fine as when the oil is to be expressed.

The next step is the extraction of the oil. Solvent extraction will

be discussed later. The oil may be expressed either cold or hot, or by a combination of both methods. Many mills make a cold pressing, then a second one hot, but in the United States in the case of oil seeds, it is customary to make a single hot pressing. For hot pressing, the meal is heated for a half hour or longer at a temperature a little above that of boiling water in a "cooker" by steam heat. In the cooker, the moisture of the meal may be reduced by allowing it to evaporate, or be increased by adding steam in order to get the meal in a suitable condition for pressing. It is very important that the meal should be evenly cooked and that it be neither too dry nor too wet. Between eight and nine per cent of moisture in the cooked meal gives good press room results. The cooker, whether of batch or stack type, should be of such a size that a charge is sufficient to fill the battery of presses it serves; otherwise the press room cannot be efficiently operated. After the charge is cooked, it is delivered as needed to the cake former and the cakes are loaded into the presses, of either open box or cage type. In pressing, the best results are obtained when the pressure is very slowly increased, after the oil begins to run, until the maximum is reached. This gives the oil an opportunity to drain, which would not be the case if at this stage the pressure were raised rapidly. In the United States, the presses are allowed to drain for 20 or 30 minutes, then unloaded. Presses, like other equipment, require attention. Sometimes, one or more in a battery will be found that fail to function as well as the others because they do not exert sufficient pressure. From time to time the working pressure of each press should be checked.

The oil from the presses is allowed to drain by gravity into the settling tanks for the purpose of separating the press foots. All settling tanks should have conical bottoms and be so located that they can readily be cleaned. Unfortunately, the tanks are often badly placed.

As soon as the press foots have settled, the oil should be withdrawn from them and transferred to storage tanks. In a comparatively short time, oil left in contact with the settling begins to deteriorate, thereby increasing the refining loss. It is of no little importance that a mill should have a sufficient number of settling tanks of ample capacity to handle the daily production of oil, so that the settling of the press foots can be properly conducted. At some mills, the oil after a brief settling is filtered through filter presses, usually after the addition of a filter aid.

The customary practice at many coconut oil mills is to express part of the oil from the copra with the expellers. Then the press cake is ground, cooked, and given a final pressing in hydraulic presses. Anderson Expellers are used in expressing many kinds of oils in the United States and elsewhere. The newer type differs from the previous ones in that it operates best when the moisture content of the product to be pressed is first reduced to between one and two per cent. It is very efficient, leaving in most cases between four and five per cent of oil in the press cake.

In the United States, expeller-made cottonseed oil is still designated as "cold pressed" to distinguish it from the so-called "hydraulic oil." The only apparent difference between these oils is that, upon refining, the former requires much longer agitation with the caustic soda solution before it is heated. Those not familiar with expellers should understand that the term "cold pressed" apparently originated from the fact that the crushed seed or meals, as the case may be, were not cooked before pressing. However, the friction of the seed or meals against the barrel of the expeller heats both the oil and the cake. After the expeller has been in operation for about two hours, the oil and cake issue hot. In many cases, the oil from the expellers is filtered directly after pressing and is put into storage tanks.

Solvent Extraction. As previously mentioned, the preparation of the product to be extracted is of no little importance, because upon this the success of the process depends. For efficient extraction it is obviously necessary that the solvent must have access to the oil-bearing cells. The physical character of the raw product has to be considered. Fibrous products, for example, can usually be ground finer than those which yield compact, slimy masses. The presence of an excess of very fine material reduces the efficiency of the extraction by retarding the flow of solvent, and it also increases the difficulty of removing the last of the solvent from the extracted meal by steaming.

Quite a number (20 or more) of solvents have been proposed for the commercial extraction of fats and oils. Among these may be mentioned the specially prepared solvent extraction gasoline or benzine, benzene (benzol) and various chlorinated products such as di- and trichloroethylene. Carbon bisulfide has been extensively used for extracting the residual oil from olive press cake. Gasoline, on account of its cheapness and because it extracts less coloring matter and other non-oil constituents than most if not all other solvents, is in more general use, particularly for the extraction of oils intended for edible purposes, in which it is essential that all traces of the solvent be removed. The gasoline (benzine) employed for solvent extraction usually distills completely within a range of 20° C. Depending somewhat upon the type of the plant and also upon its location (temperate or tropical regions) the solvent used may distill from 60° to 80°, 80° to 100°, or 90° to 110° C. In comparing the costs, the density of the solvent should be given consideration, as a given weight of meal requires a definite volume of solvent for the recovery of the oil, and in contrast to gasoline most of the other solvents are much heavier than water. Although highly inflammable, gasoline is not subject to spontaneous combustion and there is practically no danger in its use in properly designed and operated extraction plants. On the other hand, the chlorinated solvents burn with difficulty. Carbon tetrachloride is not a satisfactory solvent because it undergoes some hydrolysis, resulting in the corrosion of the equipment. Di- and trichloroethylene are very stable solvents, but it is exceedingly important that they should under no circumstances be heated in the presence of any free alkali. Failure to observe this pre-

caution has resulted in several explosions (*Chem. Age,* **32,** 264) which were believed due to the formation of chloroacetylene by the action of caustic soda during the distillation of the solvent. Trichloroethylene, which is known in Europe as "Westrosol," has a density of 1.47 and distills at 87° C., whereas dichloroethylene at 20° C. has a density of 1.257 and boils at 83.5° C. [*Oil, Paint and Drug Reptr.,* **110,** No. 23, 38A (1926)].

For ready reference, the following table of fat and oil solvents has been compiled:

SOLVENTS[1]

Name	Formula	M. W.	Sp.G.	B.Pt.	Sp.Ht.
Acetone	C_3H_6O	58.1	0.796 at 15° C.	57° C.	0.47 cal.
Benzene	C_6H_6	78.05	0.878 at 20	80.2	0.436
Carbon tetrachloride	CCl_4	153.8	1.583 at 25	76.7	
Carbon disulfide	CS_2	76.13	1.2927 at 0	46	
Chloroform	$CHCl_3$	119.38	1.526 at 0	61.2	
Dichloroethylene	$C_2H_4Cl_2$	98.95	1.257 at 20	83–4	0.305
Trichloroethylene	C_2HCl_3	131.4	1.460 at 25	87	
n-Pentane	C_5H_{12}	72.1	0.625 at 17	37	
n-Hexane	C_6H_{14}	86.1	0.662 at 17	71	0.527
n-Heptane	C_7H_{16}	100.13	0.681 at 23	98.4	0.504
n-Octane	C_8H_{18}	114.14	0.717 at 0	125.5	0.505
n-Nonane	C_9H_{20}	128.16	0.732 at 0	149.5	
n-Decane	$C_{10}H_{22}$	142.18	0.748 at 0	173	
Benzine[2]			0.68 to 0.72 at 15	70 to 90	

[1] Commercial solvents usually have slightly different distilling temperatures from the chemically pure compounds.
[2] Consists chiefly of hexane and heptane.

Attention is called to the following references:

"Die Losungsmittel der Fett. Öle, Wachse und Harze," by H. Wolff (Wissenschaftiche Verlaggesellschaft, Stuttgart, 1922).

"Solvents" by T. H. Durrans (Chapman and Hall, London, 1930). Deals chiefly with cellulose-lacquer solvents. Solvent power, action and balance as well as inflammability, toxicity, etc., are discussed.

"Ethylene Glycol: Its uses and properties," G. Curme and C. O. Young, *Chem. Met. Eng.* **28,** 169 (1923); F. C. Fuller, *Ind. Eng. Chem.,* **16,** 624 (1924).

"Glycol Ethers and Their Use in the Lacquer Industry," J. G. Davidson, *Ind. Eng. Chem.,* **18,** 669 (1926).

"Commercial Solvents For Solvent Extraction," L. C. Whiton, *Oil and Fat Ind.,* **3,** 336 (1926).

"Toxicity of Industrial Organic Solvents" (Report No. 80 of Industrial Health Research Board, England), Chem. Publishing Co., New York, 1938.

"Industrial Solvents," I. Mellan, Reinhold Publishing Corporation, New York, 1939.

"Extraction Naphthas: General Chemical Composition," A. E. MacGee, *Oil and Soap,* **14,** 324 (1937). "An Historical Outline," *ibid.,* 322.

"Properties of Flammable Liquids, Gases and Solids," Associated Factory Mutual Fire Insurance Companies, *Ind. Eng. Chem.,* **32,** 880 (1940).

Many types of batch or discontinuous extractors have been designed and a number of them have been extensively used, particularly in Europe, during the past 25 years, for the extraction of oil from seeds and press cakes of various kinds. During recent years, several successful types of continuous extractors have been made. The different systems of these extractors vary chiefly in the equipment used for the

transportation of the oleaginous material through the extractor. In all of them, the solvent flows counter-current to the movement of the product being extracted. The meal, in thin layers, is mechanically brought into contact with the sprayed solvent until the oil content of the meal has been reduced to about one per cent. Then the meal is conveyed from the extractor into a heated system where all the residual solvent is removed. After separation of the finely divided meal, the solvent containing the oil is largely recovered by distillation at ordinary pressure, and the remainder of it is removed from the oil under greatly reduced pressure. Another distinct type of continuous extractor has been devised in which the seeds are comminuted in the solvent in a series of separate operations between each of which the crushed product is pressed.

Batch extractors consist of a vertical or horizontal steel cylinder or tank which may or may not be equipped with agitators. In cases where the use of agitators has failed to facilitate the extraction of the oil, they are used only to assist with the discharge of extracted meal. With any type of extractor it is very important that all connections be kept gas-tight and also that ample condensing equipment be provided; otherwise excessive loss of solvent will occur. In a well-designed and properly operated plant, the loss of solvent should not exceed 3 gallons per ton of material treated, and some plants keep their solvent loss down to about 2 gallons.

After the charging of an extractor, the meal is treated with two or more portions of solvent from other units which contain some oil, and finally given a wash with fresh solvent. Depending upon the character of the raw material and the quantity of oil it contains, the number of treatments with solvent usually vary from three to six in order to reduce the oil content of the meal to about one per cent. When the solvent becomes sufficiently charged with oil, it is transferred to the still in which the larger part of the solvent is removed, the remainder being separated from the oil in the second or "finishing still" with the aid of steam. Although stills of various types are used for recovery of solvent, the modern continuous ones are to be preferred. With any type, attention should be paid to the elimination, insofar as is possible, of fine meal from the oil-laden solvent before transferring it to the still to avoid undue interruptions of the distillation of solvent in order to clean the still.

After extraction of the oil, the residual meal in the extractor is steamed until all the remaining solvent is removed. If the meal is heated and dry steam is used, the meal requires no further drying. Unless this is done, it is necessary to dry the meal sufficiently, after steaming, to prevent subsequent spoilage. Meal should not contain over eight per cent of moisture. Long steaming, particularly in the presence of moisture, impairs the color and reduces the quality of the meal. The following references may be of interest:

"A Mathematical Study of Solvent Extraction," L. F. Hawley, *J. Ind. Eng. Chem.*, **9**, 866 (1917).

"Solvent Extraction of Vegetable Oils," G. H. Pichard, *Cotton Oil Press*, **5**, No. 2, 119 (1921).

"Practical Considerations of Vegetable Oil Extraction," E. W. Albrecht, *Chem. Zeit.*, **46**, 1034 (1922); *J. Soc. Chem. Ind.*, **42**, 22A (1923).

"Modern Edible Oil Manufacture by Extraction With Subsequent Refining," Albrecht, *Seifensieder Ztg.*, **50**, 65 (1923); *Chem. Abst.*, **17**, 1726 (1923).

"Oil Extraction in Theory and Practice," L. C. Whiton, *Oil and Fat Ind.*, **3**, 219 (1926).

"A New Plant for Fat Extraction By Solvents," Simon and Hinchley, *J. Soc. Chem. Ind.*, **45**, 252T (1926).

"Extraction Experiences in Foreign Lands," B. Hassel, *Oil and Fat Ind.*, **4**, 163 (1927).

"Recent Developments Relating to Oil Extraction by the Solvent Process," E. W. Schmidt, *Oil, Pt. Chem. Rev.*, **96**, No. 23, 9 (1934).

"Alcohol Extraction of Fatty Oils," M. Sato, T. Inaba, and K. Kitagawa, *J. Soc. Chem. Ind., Japan*, **37**, 718 (1934).

"Low Boiling Hydrocarbons as Oil Extraction Media," H. Rosenthal and H. P. Trevithick, *Oil and Soap*, **11**, 133 (1934).

"Modern Oil Milling," L. H. Downs, *Oil Col. Trd. J.*, **95**, 715 (1939).

"Continuous (Solvent) Extraction and Equipment," K. H. Hildebrandt, *Fette u. Seifen*, **46**, 350 (1939).

"Continuous Hanso-Mühle Equipment and Operation," A. Schmidt, *Fette u. Seifen*, **46**, 464 (1939).

As up-to-date details on the structural features of oil-mill machinery and accessories are to be obtained from the current catalogs of manufacturers and dealers, the names of which are listed with addresses in business directories, no attempt has been made to discuss them here. When necessary, oil-mill architects and engineers who specialize in the design and erection of complete plants for the extraction of fats and oils by pressure and solvents as well as refineries, may be consulted or employed. Without doubt, more attention should be given than has been the case in the past to the design and construction of seed houses and silos or seed tanks as well as to the actual storage of the seed; this would largely reduce losses incurred through seed deterioration which results in a lower quality of the oil, cake or meal. Such losses can be reduced to a minimum provided well ventilated and dry storage facilities are available and that wet seeds are sufficiently dried before going into storage.

Refining of Vegetable Oils. The most important method and the one most commonly used is known as the "caustic soda process" which, depending upon circumstances, may or may not be followed by bleaching with earth or activated carbon, and deodorization. Caustic soda refining is an art that can be acquired only through experience gained in a refinery and no description, however detailed it may be, can take the place of actual experience. A description of refining is given under cottonseed oil; this method is applicable with or without modification to the treatment of a great many other fats and oils. Also refining is referred to under certain other oils, notably linseed and coconut.

Attention is called to the following references:

"Continuous Oil Refining," P. D. Boone, *Soap*, **14**, No. 9, 257 (1938), deals with acid refining of soap oils.

"A Comparison of Prevailing Neutralization Methods in the Oil Industry," L. H. Manderstam, *Oil Col. Trdes. J.*, **98**, 795 (1940).

"Special Methods For Refining Oils," R. G. Dressler, *Oil and Soaps,* **17,** 124 (1940).

"Continuous Refining of Vegetable Oils," E. M. James, *Proc. Inst. Food Technologists,* 224 (1941), *Chem. Absts.,* **36,** 922 (1941).

"The Centrifuge: Its Application in the Oil and Fat Refining Industry," D. G. Gillies, *Oil and Col. Trades J.,* **99,** 242 (1941).

Nutritive Value

The writer continues to be frequently questioned with reference to the nutritive value and digestibility of commercial edible animal and vegetable fats. Frequently, comparative information is desired, such as for example, whether refined seed oils (corn, cottonseed, etc.) have a nutritive value equal to that of olive oil, or whether vegetable fats are better than those of animal origin for use in cooking.

The edible fats, such as lard, olive, cottonseed, corn, peanut, sesame, soybean, etc., have been found to be almost completely assimilated as shown by the extensive investigations of C. F. Langworthy and A. D. Holmes [*U. S. Dept. Agric. Bulls.* **505** and **781**; *Ind. Eng. Chem.,* **15,** 276 (1923)], who experimented with over 20 animal and about 40 different vegetable fats on human subjects. As was to be expected, hydrogenated fats with melting points of 50° C. or higher, were only partially assimilated. However, when those products are fed in admixture with soft or liquid fats, they are readily digestible.

The fats are chiefly utilized by man in the production of bodily energy or heat and to some extent they are deposited in the body as reserve materials. From a calorific standpoint, all the edible commercial fats are practically identical, except that butter and margarin, which contain 10 per cent of water, and often more, give slightly lower values. The heat of combustion of edible animal and vegetable fats ranges from 9473 to 9500 calories or 17,051 to 17,100 B.t.u.

Generally speaking, vegetable oils are not regarded as important sources of vitamins essential to man. Obviously only the fat-soluble vitamins need to be considered. Most vegetable oils contain small and unimportant quantities of the carotenes, which are precursors of vitamin A, but palm oil is a notable exception. This oil is reported to contain from 48 to 158 International units of vitamin A per gram (Circular 638 USDA, May 1942).

Several vegetable oils have been reported to contain vitamin D, but a critical examination of the literature indicates that coconut oil is the only one containing demonstrable quantities. Vitamin D is produced from ergosterol when this compound is exposed to ultraviolet rays. Coconut oil probably acquires some vitamin D potency when copra is exposed to the sun during the drying process. Excessive exposure to ultraviolet ray also causes the destruction of vitamin D so that coconut oil must be regarded as a variable and uncertain source of this vitamin.

Methods for the determination of vitamin E have not been perfected to the extent that reliable information has been obtained with respect to its distribution. The biological method of assay is tedious and not very accurate. More recently chemical methods for the determination

of tocopherols, which are the compounds that have vitamin E activity, have been developed, but their reliability remains to be demonstrated. Most vegetable oils which have been examined have been found to have some vitamin E activity. Wheat germ oil has long been regarded as the richest natural source of this vitamin. Quackenbush, Gottleib and Steenbock report the following tocopherol contents of vegetable oils [*Ind. Eng. Chem.*, **33**, 1276 (1941)]:

Wheat germ	0.31 –0.38%
Soybean	0.12 –0.21
Corn	0.119
Cottonseed	0.110
Olive	0.025
Coconut (hydrogenated)	0.003

These values appear to be in fairly good agreement with other reports. Since this vitamin will not withstand drastic treatment with alkali, it must be expected that the refining process will have an important influence on the vitamin E content of these oils.

Vitamin K, a substance necessary for the production of prothrombin, which in turn functions in the clotting of the blood, has been found to be present in some vegetable oils. Methods for the determination of this vitamin have not been perfected to the point where it has been possible to obtain reliable data on many oils. Hempseed, soybean and probably many other vegetable oils contain this vitamin. Oil refining processes may have a destructive effect on it.

Rancidity: Stabilization

Fats which have developed an objectionable odor and taste upon standing are said to be rancid. Rancidity is usually the result of chemical changes brought about by the action of oxygen on the fat, but in some cases it is apparently caused by the action of enzymes formed by the fungi with which the fat has become inoculated. The development and progress of rancidity through the action of oxygen are accelerated by light, heat, and certain metals such as copper, zinc, etc., which act as catalysts, whereas that due to enzymic action may take place in the absence of both light and air. In either case the reactions involved are complex and as yet but little understood. The products formed as a result of rancidification of fats consist of a mixture of aldehydes, ketones, lactones, oxy and hydroxy acids, and other acids of smaller molecular weight than those originally present, as well as alcohols, carbon dioxide and moisture. Some of the products that have been isolated and identified are azelaic acid, azelaic, pelargonic and heptylic aldehydes, as well as the acids from acetic to nonylic and their aldehydes.

It is now generally accepted that autoxidation is the primary cause of the onset of rancidity. The first stage in the spontaneous oxidation of fats is probably the formation of peroxides at the ethnoid linkages of the unsaturated acids. These, or other loosely bound oxygen com-

pounds of the unsaturated acids, in the presence of moisture are believed to give ethylene oxide derivatives and hydrogen peroxide, which causes the formation of the odoriferous aldehydes and ketones. It is evident that much remains to be determined in connection with the complicated mechanism of the various reactions which take place and the compounds formed during the development of rancidity, in spite of the fact that for years many investigators have been engaged upon this problem.

Owing to the situation that many still connect and confuse the acidity of fats with rancidity, it should be emphasized that the presence of free fatty acids either in small or large quantities is no indication whatsoever of rancidity, or that such a product may necessarily become rancid. Rancid fats may contain very small or large quantities of free fatty acids. The odoriferous constituents found in rancid fats are apparently derived chiefly from oleic acid in cases where rancidity is caused by the spontaneous oxidation of fats.

It has been stated that the more saturated acids a fat contains, the less likely it is to become rancid, and cocoa butter is usually mentioned as an example. However, some fats of this character are exceptions to this observation, such as Chinese vegetable tallow. On the other hand, cold-pressed almond and sesame oils which consist chiefly of glycerides of unsaturated acids do not readily become rancid.

When fats become rancid, the iodine number decreases, while the specific gravity, Reichert-Meissl, Polenske and acid values as well as the unsaponifiable matter, all more or less increase. The measure of these changes is not an indication of rancidity. A number of tests have been proposed for the detection of rancidity, particularly for those cases in which it is not readily detected by organoleptic methods. A test for incipient rancidity is of no little value, for example, to the cracker or biscuit baker and the salad-dressing manufacturer. Of the tests that have been suggested, that of Kreis is in most common use. This test, which is described elsewhere, is based upon shaking the sample with concentrated hydrochloric acid, then shaking again after the addition of an ethereal solution of phloroglucin; the acid layer which separates upon standing becomes pink or red. The extensive investigation of W. C. Powick [*J. Agric. Research*, **26**, 323-362 (1923)] on compounds present in rancid fats, has indicated that epihydrin aldehyde was the compound which reacted with phloroglucin in the Kreis test to give the characteristic colors. Evidence was given that this aldehyde did not exist in the free condition until the fat was in contact with the concentrated hydrochloric acid. It was also indicated that the aldehyde was probably formed from oleic acid.

The use of the peroxide or active oxygen test suggested by C. Lea [*Proc. Royal Soc. London* **B108**, 175 (1931)] has been modified and extended by D. H. Wheeler [*Oil and Soap*, **9**, 89 (1932)] and subsequent investigators, A. E. King, H. L. Roschen, and W. H. Irwin [*Oil and Soap*, **10**, 105, 129 (1933)], V. C. Stebnitz and H. H. Sommer [*ibid.*, **12**, 201 (1935)] into the form of an accelerated test for determining the stability or keeping quality of a fat or oil. For details con-

cerning the method and the apparatus used the original articles must be consulted.

Stabilization of Fats.—For some years, considerable attention has been given to finding substances which would inhibit or retard the development of rancidity. Many of those substances which have been found most effective for this purpose, owing to their toxic character, can be used only for the treatment of fats and oils intended for technical purposes. However, some substances have been discovered which can be added to edible products for improving their keeping qualities. Most of the useful preservatives are covered by patents.

Aromatic amines, non-hydroxy aromatic derivatives, quinol, pyrogallol, gum guaiac, glucamine derivatives, maleic acid, cereal flours, and some other substances have been suggested for use as stabilizing agents. Attention is called to the following references:

"Inhibiting Agents in The Oxidation of Unsaturated Organic Compounds," O. M. Smith and R. E. Wood, *Ind. Eng. Chem.*, **18**, 691 (1926).

"Negative Catalysis of Auto Oxidation," C. Mourice and C. Dufraisse, *J. Soc. Chem. Ind.*, **47**, 819 (1928).

"Effect of Various Compounds on Rate of Development of Rancidity," W. J. and L. M. Husa, *J. Am. Pharm. Assocn.*, **17**, 243 (1928).

"Preservation of Fats," G. W. Fiero, *Am. J. Pharm.*, **102**, 146 (1930).

"The Influence of Air, Light and Metals on the Development of Rancidity," J. A. Emery and R. R. Henley, *Ind. Eng. Chem.*, **14**, 937 (1922).

"Quantitative Aspects of Kreis Test," G. E. Holm and G. R. Greenbank, *Ind. Eng. Chem.*, **15**, 1051 (1923).

"The Cause and Prevention of Rancidity," R. H. Kerr and D. G. Sorber, *Cotton Oil Press*, **5**, No. 3, 45 (1921).

"The Occurrence of Azelaic Acid as a Product of the Spontaneous Oxidation of Fats," B. H. Nicolet, *Ind. Eng. Chem.*, **8**, 416 (1916).

"Rancidification of Fats," A. Tschisch and A. Barben, *Chem. Umschau*, **31**, 141 (1924).

"Rancidity Due to Formation of Aldehydes and Ketones From Glycerol," A. Schmid, Schweiz, *Apoth. Zeit.*, **62**, 409 (1924).

"Susceptibility of Fats to Autoxidation," G. E. Holm, G. R. Greenbank, and E. F. Deysher, *Ind. Eng. Chem.*, **19**, 156 (1927).

"Tests For The Incipient Rancidity of Fats," W. L. Davis, *J. Soc. Chem. Ind.*, **47**, 185T (1928).

"A Photochemical Method For Measuring Susceptibility of Fats and Oils to Oxidation," G. R. Greenbank and G. E. Holm, *Ind. Eng. Chem.*, **22**, 9 (1930).

"Antioxidants and the Autoxidation of Fats," H. A. Mattil, *J. Biol. Chem.*, **90**, 141 (1931).

"Studies on the Nature of Antioxygens Present in Natural Fats. I. Separation of Fatty Derivatives from Antioxygens by Distillation," T. P. Hilditch and J. J. Sleighthol, *J. Soc. Chem. Ind.*, **51**, 39T (1932).

"Carotene As a Natural Anti-Oxidant," R. C. Newton, *Oil and Soap*, **9**, 247 (1932).

"Chemistry of Ketone Rancidity of Fats. I. A New Analytical Method," K. Täufel and H. Thaler, *Chem. Ztg.*, **56**, 265 (1932).

"Auto-oxidation," N. A. Milas, *Chem. Rev.*, **10**, 295-364 (1932).

"Studies on the Nature of Antioxygens Present in Natural Fats. II. Some Further Observations on the Removal of Antioxygens from Olive and Linseed Oils," A. Banks and T. P. Hilditch, *J. Soc. Chem. Ind.*, **51**, 411T (1932).

"Stability of Fats and Oils, Applications of the Methylene Blue Test," H. D. Royce, *Ind. Eng. Chem. (Anal. Ed.)*, **5**, 244 (1933).

"The Action of Micro-organisms on Fats," L. B. Jensen, *Oil and Soap*, **10**, 23 (1933).

"Photochemical Studies of Rancidity: Antioxidants vs. Green Light Protection," M. R. Coe and J. A. LeClerc, *Oil and Soap*, **12**, 231 (1935).

"New Light on Rancidity," G. A. Wieshahn, *Food Ind.*, **7**, 222, 275 (1935).

"Recent Research on Antioxidants," *Chem. Trde. J.*, **97**, 1933 (1935). An instructive review.

"Antioxidants and the Autoxidation of Fats," H. S. Olcott and H. A. Mattill, *J. Am. Chem. Soc.*, **58**, 1627 (1936).

"Photochemical Studies of Rancidity: Induction Period of Protected and Non-protected Oils," M. R. Coe, *Oil and Soap*, **13**, 197 (1936).

"Antioxidants and the Preservation of Edible Fats," C. H. Lea, *J. Soc. Chem. Ind.*, **55**, 293T (1936).

"The Effect of Various Adsorptive Mediums upon Rancidity and the Kreis Test," J. P. Harris and W. A. Welch, *Oil and Soap*, **14**, 3 (1937).

"The Spoilage of Fats and Oils. The Kreis Reaction and Its Carrier," R. New, *Chem. Ztg.*, **73**, 733 (1937).

"Oat Flour As an Antioxidant," F. N. Peters and S. Musher, *Ind. Eng. Chem.*, **29**, 146 (1937).

"Nature of Antioxygens Present in Natural Fats. III. Occurrence of Anti-oxygenic Compounds in Extracted Soybean Oilcake," T. G. Green and T. P. Hilditch, *J. Soc. Chem. Ind.*, **56**, 23T (1937).

"The Chemistry of the Spoiling of Fats. III. The Influence of Substances which Accompany Fats," F. Kiermeier and K. Täufel, *Fette u. Seifen*, **45**, 487 (1938).

"Rancidity in Edible Fats," C. H. Lea, Special Report 46, Food Investigations, Dept. Sci. and Ind. Res., Great Britain, 1938. Published in book form by Chemical Publishing Co., New York, 1939.

"Photochemical Studies of Rancidity: The Mechanism of Rancidification," M. R. Coe, *Oil and Soap*, **15**, 230 (1938). Cites 34 references.

"Studies on the Nature of Antioxygens Present in Natural Fats. IV. The Proportions and Properties of Antioxygenic Compounds in Various Seed Cakes," T. P. Hilditch and S. Paul, *J. Soc. Chem. Ind.*, **58**, 21 (1939).

"Antioxidants and the Autoxidation of Fats," F. E. Deatherage and H. A. Mattill, *Ind. Eng. Chem.*, **31**, 1425 (1939).

"Photochemical Studies of Rancidity: A Note on the Possibility of Using 'Chlorophyll Values' as Means of Estimating the Stability of an Oil or Fat," M. R. Coe, *Oil and Soap*, **16**, 146 (1939).

"The Mechanism of the Autoxidation of Fats," H. A. Matill, *Oil and Soap*, **18**, 73 (1941).

"Antioxidants For Edible Fats and Oils," H. S. Allcott, *ibid.*, 77.

"Methods of Measuring the Rate and Extent of Oxidation of Fats," F. C. Vibrans *ibid.*, 109.

"Photochemical Studies of Rancidity." The Chlorophyll Value in Relation to Autoxidation, M. R. Coe, *Oil and Soap*, **18**, 227 (1941).

"Factors Which Increase the Rate of Oxidation of Fats and Oils with Special Reference to the Role of Light, M. R. Coe, *ibid.*, 241.

Emulsions. Margarine.

Emulsions. In view of the extensive use made of emulsified fats for edible, pharmaceutical, and technical purposes, the subject will be very briefly discussed. References will be given for those not familiar with them and those who wish additional and more detailed information.

An emulsion may be defined as a system which consists of two liquid phases, one being in the form of globules dispersed in the other, which is known as the continuous phase. Emulsions may be divided into two classes. One is the so-called "dilute simple" oil-in-water emulsion and the other is the concentrated, more complex class embracing both oil-in-water and water-in-oil types. These contain an emulsifying agent or agents which are added to facilitate the formation of the emulsion as well as to render it more stable. It is this second class of emulsions that is of industrial importance.

The type of emulsion obtained depends largely in most cases upon the character of the agent used. Water-soluble colloids tend to give

the oil-in-water type and oil-soluble colloids tend to give the water-in-oil type of emulsion. Milk is an example of an oil-in-water emulsion, whereas butter is of the water-in-oil type. Butter substitutes or margarines, depending upon the method of manufacture, may be water-in-oil or oil-in-water types.

Some of the more important emulsifying agents are soaps, acacia (gum arabic), egg yolk and white, saponins, sulfonated oils, lecithins, proteins, algin, alginates, ethanolamines, and bentonite. These agents not only facilitate the emulsification but protect the droplets of the dispersed phase from uniting.

Formerly, emulsions were prepared only in batches, but now continuous processes are receiving attention. In order to obtain more uniform as well as smaller globules of the dispersed phase so as to increase the stability of the finished product, use is made of equipment known as homogenizers and colloidal mills, of both of which there are several types.

The general procedure for the preparation of emulsions is to add the emulsification agent, depending upon its character, either to the water or the oil, and agitate the two liquids at the proper temperature, by mechanical means until the emulsion is formed. It is customary to add the constituents together gradually during the agitation. The rate of agitation, time, and temperature not only vary for different types of emulsion equipment, but also depend upon the substances to be emulsified and also upon the character of the emulsifying agent used. This being the situation, it is obvious that each emulsion problem must be handled as a special case. Under some circumstances, for example, excessive or too rapid agitation in certain cases may cause a disintegration or breaking of the emulsion formed at first.

Special attention is called to the following references:

"The Theory of Emulsions and Their Technical Treatment" (contains an extensive bibliography), by W. Clayton, J. and A. Churchill, London, 1936.

"Modern Emulsifying Agents," S. R. Trotman, *Chem. Trade J.*, **85**, 77 (1929).

"Emulsions in Theory and Practice," J. E. Rutzar, *Oil and Fat Ind.*, **7**, 61 (1930).

"Bentonite (Stable emulsions)," Woodman and Taylor, *J. Soc. Chem. Ind.*, **48**, 121T (1929).

"Emulsion Using Triethanolamine," A. L. Wilson, *Ind. Eng. Chem.*, **1930**, 22, 143 (1930); *cf.* R. B. Trusslar, *Oil and Fat Ind.*, **5**, 338 (1928).

"Emulsifiers For Oils, Fats and Waxes," H. A. Gardner, *Pt. and Var. Mfgrs'. Assoc. Cir.*, **323**, (1928).

"The Estimation of the Efficiency and Dispersive Power of Emulsifying Agents," R. C. Smith, *J. Soc. Chem. Ind.*, **46**, 345T (1927).

"Tecknik der Emulsion," by Otto Lange (Julius Springer, Berlin, **1929**, 391 pages).

"Emulsions and Foams," Berkman and Egloff, New York, Reinhold Publishing Corp., 1941.

"What Makes a Good Emulsion?" H. Bennett, *Chem. Markets*, **27**, 483 (1930).

Margarine: Its Manufacture, etc. Although vegetable fats and oils are important constituents in most types of margarines (and this important industry is continually expanding both in America and Europe) the treatment of this subject will be confined to giving the following selected references for those not familiar with the literature:

"Cottonseed Oil in Margarine," *Cotton Oil Press,* **4,** No. 10, 29 (1921).
"Oleomargarine: A Useful and Economical Substitute For Butter," J. P. Street, *The Modern Hospital,* **8,** 195 (1917).
"Margarine, The Equal of Dairy Butter," L. H. Ashe, *Cotton Oil Mag.,* **35,** Aug. No. 40 (1920).
"Present Status of Margarine in Nutrition," C. Funk, *Nat. Provisioner,* **66,** No. 22, 20 (1922).
"The Manufacture of Margarine," P. S. Arup, *Food Manuf.,* **3,** 544 (1928); **4,** 29 (1929).
"Modern Manufacture of Margarine," H. W. Vahlteich, *Food Industries,* **1,** 436 (1929).
"Margarine," Wm. Clayton, Longmans, Green Co., **1921.**
"Margarine," G. Lebbin, M. Janecke, Leipsig, **1926.**
"Die Fabrikation der Margarine," P. Pollastschek, Vol. 4, Monographien aus dem Gebiete der Fett-Chemie, Stuttgart, **1929.**
"Margarine as a Butter Substitute," Katherine Snodgrass, **1931,** Food Research Institute, Stanford University, Cal.
"Recent Improvements in Margarine Manufacture," *Oil Col., Trd. J.,* **81,** 1138 (1932).
"Technical Study of the Margarine Industry," *Intern'l Rev. Agric. (Rome),* **26,** 11 (1935).
"Some Recent Developments in the Manufacture of Margarine," A. A. Robinson, *Oil and Soap,* **15,** 203 (1938).

Chapter II

Non-drying Fats and Oils

Seed Oil of Condor or Corail Tree (*Adenanthera pavonia*). The seed and oil of this Indian tree have been investigated by S. M. Mudbidri, P. R. Ayyar, and H. E. Watson, *J. Indian Inst. Sci.*, **11A**, 173 (1928); *Brit. Chem. Absts.*, B, **1929**, 218. The kernels, which amount to about 50 per cent of the seed investigated, contained 28 per cent of oil which gave the following characteristics: Sp. g. at 15.5° C. 0.9168; $N_D^{60°}$ 1.4570; Sap. V. 181.1; Iod. No. 87.9; Acetyl V. 3.4; R.M.V. 1.22; Pol. No. 24; Unsap. 1.4%; Acid V. 0.6; Titer, 58.4°. The fatty acids contained 36 per cent of saturated acids. The composition of the fatty acids was as follows: Myristic 0.4, palmitic 9.0, stearic 1.1, lignoceric 25.5, oleic 49.3, and linoleic acid 14.7 per cent. The very large quantity of lignoceric acid present in this oil is noteworty and it would, if available, constitute the best source for getting this acid in quantity for experimental purposes.

Acorn (Oak) Oils. W. D. Hutchins [*Oil and Soap*, **14**, 148 (1937)] examined the expressed crude and refined oil from acorns of the pin oak, *Quercus palustris*, of the *Fagaceae*. The Farmers' Oil Mill at Newberry, South Carolina, expressed the oil. The acorns as collected contained 24 per cent of moisture and 13.4 of oil. Characteristics of the crude oil were as follows: Sap. V. 192.9; Iod. No. (Wijs) 99.4; Acetyl V. (André-Cook) 6.9; Unsap. 1.11% which gave an Iod. No. (Wijs) of 120.9. Refined oil: Sp. g. at 25/25° C. 0.9158; $N_D^{40°}$ 1.4647; Sap. V. 193.2; Iod. No. (Wijs) 97.2; SCN V. 73.7; Unsap. 0.45%; Acid V. 0.06; Sat. acids 14.5%; Crismer Test 70.3°; Acetyl V. 3.6; Titer 25.9°; Flash Pt. 320° C.; Fire Pt. 360° C. The refined oil could be used for edible purposes.

C. J. Monarco and E. V. Lynn [*J. Am. Pharm. Assoc.*, **26**, 433 (1937)] reported the following characteristics for oil from the acorns of the red oak, *Quercus ruba*: Sap. V. 195.3; Iod. No. 100.1; R.M.V. 0.2; Pol. No. 0.8; Unsap. 0.9%.

S. V. Puntamekar and S. Kkishna [*J. Ind. Chem. Soc.*, **11**, 721 (1934)] determined the characteristics of the oils from the north India oaks, *Quercus incana*, *Q. dilatata*, and *Q. ilex*. The range of the characteristics for these three oils is as follows: Sp. g. at 25° C. 0.9079 to 0.9084; $N_D^{30°}$ 1.4576 to 1.4588; Sap. V. 188 to 192.2; Iod. No. (Hanus) 81.5 to 90.3; Unsap. 0.8 to 2.3%.

Allanblackia Seed Fats or Butter. These fats are obtained from

the seeds of several species of African trees belonging to the *Guttiferae* family.

The so-called Kagné butter is obtained from the seeds of *Allanblackia oleiferae* which is found in tropical East Africa, Congo, and Cameroon. The kernels contain about 60 per cent of fat which has been examined by Pieraerts and Adriaens [*Mat. grasses,* **21,** 8510 (1929)], with the following results: Sp. g. at 100° C. 0.8977; $N_D^{65°}$ 1.4471; Sap. V. 197.9; Iod. No. 42.3; Unsap. 1.60%; Acetyl V. 19.9; Titer 56.5° to 58° C.; M. Pt. 38 to 40° C.; Crismer V. 71.5° (1 vol. fat+2 vol. alc. 99.4%). The insoluble fatty acids consist of 52 to 54 per cent of saturated acid and 45.5 to 48 per cent of unsaturated acids.

The fat is used locally for edible and other purposes.

The kernels from the seeds of *A. stulhmanii,* native to East Africa, contain about 54 per cent of fat which has been examined by Kraus and Disselhorst [*Chem. Rev. Fett Harz-Ind.,* **16,** 200 (1909)] with the following results: Sp. g. at 17.5° C. 0.8736; $N_D^{50°}$ 1.4503; Sap. V. 188.6; Iod. No. 37.5; M. Pt. 43 to 46° C.; Titer 57.5°.

T. P. Hilditch and S. A. Saletore [*J. Soc. Chem. Ind.,* **50,** 468T (1932)] received a portion of a sizable sample of seeds which were sent to the Imperial Institute from the East African Agricultural Research station at Amani, Tanganyika. The kernels, which amounted to 80 per cent of the seed, contained about 62 per cent of fat. It gave a saponification equivalent of 293.2, an iodine number of 39.4, and contained 0.55 per cent of unsaponifiable matter. The fat melted at 40.6°. The mixed fatty acids contained the following percentages of constituents: palmitic 3.1, stearic 52.6, oleic 44.1, and linoleic 0.2. It was found that the fully saturated glycerides in the fat did not exceed 1.5 per cent, and that the mono-oleo-distearins probably constituted over 65 per cent, the remainder being largely dioleo-monosaturated glycerides, on the assumption that triolein probably was not present in any notable quantity.

This yellow fat is used locally for edible and other purposes.

The kernels from the seeds of *A. floribunda* found on the Gold Coast of Africa contain about 70 per cent of a hard, almost white, fat which has been examined at the Imperial Institute [*Bull. Imp. Inst.,* **20,** 463 (1922)] with the following results: $N_D^{40°}$ 1.4553; Sap. V. 190.8; Iod. No. 44.2; Unsap. 0.4%; M. Pt. 38.6° C.; Titer 57.6°. The fat is stated to be edible.

Pieraerts and Adriaens [*Mat. grasses,* **21,** 8539 (1929)] examined the seeds and fat of the *Allanblachia floribunda* of the Belgian Congo. These kernels contain from 60 to 63 per cent of fat which gave the following characteristics: Sap. V. 197 to 200.7; Iod. No. 39.2 to 41.6; M. Pt. 37° to 40° C.

M. L. Meara and Y. A. H. Zaky [*J. Soc. Chem. Ind.,* **59,** 25 (1940)] investigated the fatty acids and glycerides of the seed fat of *A. floribunda.* The fat gave an iodine number of 35.4 and a saponification equivalent of 297.7. The mixed fatty acids contained the following percentages of constituents: Palmitic 2.88, stearic 56.78, arachidic 0.23, oleic 39.12,

linoleic 0.41, and unsaponifiable 0.58. Percentages of component glycerides: about 76 of oleo-distearin, 15 of stearo-diolein, and 5 of oleo-palmitostearin.

They investigated nuts and fat from *A. parviflora* (*loc. cit.*). The nuts contained 64.5 per cent of kernel and 35.5 of shell. The extracted fat gave an iodine number of 37.2, a saponification equivalent of 295.3, and an acid value of 2.8. The mixed fatty acids contained the following percentages of constituents: Myristic 1.45, palmitic 2.29, stearic 52.05, arachidic 0.26, and oleic acid 43.95. Glycerides: about 60 of oleodistearin, 26 to 29 of stearodiolein, and 6 to 9 per cent of oleo-palmitostearin. Also, there may be as much as 3.9 per cent of oleo-myristostearin present in the fat.

Almond Oil. This oil is obtained from the kernels of the bitter and sweet almond (*Prunus amygdalus*). The bulk of the oil of commerce is expressed from the bitter almond. Almonds are grown in the Canary Islands, California, France, Morocco, Iran, Portugal, Spain, Sicily, Syria and on a smaller scale elsewhere. Bitter almonds contain from about 40 to 56 per cent of oil and sweet almonds from about 47 to 61 per cent. There is apparently no difference between the oils from these two varieties. In the United States the oil is marketed under the name of "sweet almond oil," thus distinguishing the fatty oil from the essential or volatile oil of bitter almond which is obtained from the bitter almond press cake. The fixed or fatty oil of almond, contrary to former statements, has excellent keeping qualities. The oil varies from almost colorless to a pale yellow and has a slight but pleasant nutty taste. It is used largely in the manufacture of certain pharmaceutical preparations.

Characteristics and Composition. The usual range of characteristics is as follows: Sp. g. at 15° C. 0.9175 to 0.9199; N_D° at 20° C. 1.4705; at 40° C. 1.4624 to 1.4643; Iod. No. 95 to 102; Sap. V. 183 to 196; Sol. Pt. 9° to 12° C.; R.M.V. 0 to 0.35; Pol. No. 0.2 to 0.8.

Heiduscka and Wisemann [*Chem. Absts.*, **24**, 2907 (1930)] examined commercial almond oil with an iodine number 99.6 and saponification value 188.8 with the following results: Oleic acid 77, linoleic acid 19.9 and palmitic acid 3.1 per cent. W. A. Bush and E. A. Lasher [*Ind. Eng. Chem.*, **33**, 1275 (1941)] determined the more important characteristics of oils expressed from 5 different varieties of almonds. The iodine numbers (Hanus) ranged from 102 to 105.7.

B. G. Gunde and T. P. Hilditch [*J. Soc. Chem. Ind.*, **59**, 47 (1940)] in connection with their investigation of the unsaturated glycerides of non-drying oils, reported that the mixed fatty acids from a sample of almond oil contained the following percentages of constituents: Myristic 1.2, palmitic 4.5, oleic 77.0, and linoleic 17.3. In round numbers the percentages of glycerides were as follows: Myristo-dioleins 3, palmito-dioleins 14, linoleo-dioleins 52, and triolein 31. However, a small quantity of oleodilinolein may also be present.

Adulteration. Almond oil is not subject now to adulteration with the common commercial vegetable oils which could be readily detected,

but frequently apricot kernel oil is mixed with it and sometimes complete substitution is made. On account of the similarity of the two oils, care and experience are required in drawing conclusions with the color test described below for the detection of apricot oil. Occasionally, peach kernel oil is also used to adulterate almond oil.

Examination. Determine the acid value (which in the case of oil of good quality will be under 4), the iodine and saponification values, and compare the results with figures already given. It should be observed that the iodine number of pure almond oil is only rarely above 100, while those of apricot or peach oils usually range from 101 to 110.

Make the Bieber Color Test as follows:

Reagent. Mix together in an Erlenmeyer flask equal weights of fuming nitric acid, concentrated sulfuric acid, and water. As this mixture must be freshly prepared, make only a sufficient quantity for the tests to be made at one time.

Test. To 5 cc. of the sample to be tested in a test tube, add 1 cc. of the reagent, mix thoroughly, allow it to stand for several minutes, and note the development of color. Almond oil gives no color, apricot kernel oil gives a pink color, and peach oil, after the mixture has stood for some time, gives a faint pink color. Freshly prepared oils give stronger colors than old samples. On account of this difference and the fact that oils from different sources also show a considerable variation in the intensity of the color, the test cannot be used for even an approximation of the quantity of apricot oil present in admixture with almond oil. This test becomes uncertain unless the sample examined contains about 50 per cent or more of apricot oil. Other tests have been proposed but they are considered even less useful than that of Bieber. However, more recently Pritzker and Jungkunz [*Analyst*, **53**, 102 (1928)] have studied the test devised by Kreis [*Analyst*, **27**, 330 (1902)] and conclude that with this test it is possible to detect as little as 5 per cent of apricot kernel oil in admixture with almond oil. The test is made as follows: To 5 cc. of the oil in a test tube, add 5 cc. of nitric acid sp. g. 1.40, shake and add 5 cc. of a 0.1 per cent ether solution of phloroglucinol. Shake thoroughly and note the color. Apricot kernel oil gives a magenta color. The test is not reliable for the detection of peach oil.

Andiroba or Crabwood Oil. This oil is sometimes known as *Carapa, touloucouna* and *tulucuna*. The oil is obtained from the seeds of various species of *Carapa,* belonging to the natural order of *Meliaceae*. These trees are found in South America, West Africa, and the West Indies. From a botanical standpoint, much confusion exists in regard to the species. *C. guianenis* (*guianenis*), *C. touloucouna* and *C. procera* appear to be but one species, but it is possible that *C. surinamenis* and *C. moluccensis* are only varieties of *C. procera* and not distinct species.

The seeds, which weigh about 15 grams, consist of about 75 per cent of kernels and about 25 per cent of shells. The kernels contain from 55 to 60 per cent of oil which is usually semi-solid. The characteristics are as follows: Sp. g. at 15.5° C. 0.927 to 0.933; $N_D^{40°}$ 1.4593 to 1.4623; Sap. V. 195 to 198; Iod. No. 58 to 76; Unsap. 0.6 to 2%; R.M.V. 2.5 to 3.5; Pol. No. 3, Kirchner V. 2.1; Titer 35° to 37°. Bolton and Hewer [*Analyst,* **42**, 35 (1917)] found the oil to be slightly optically active.

T. F. de Amorin [*Revista Chim. Ind.* (*Brazil*), **8**, 214 (1939)] examined the oil with the following results: $N_D^{40°}$ 1.4648; Sap. V. 197.3; Iod. No. (Hübl) 65.8; R.M.V. 0.19; Pol. No. 0.4; Unsap., 1.0%.

The following percentages of acids were found in the oil: Myristic 17.9, palmitic 12.4, oleic 58.4, and linoleic 4.9.

Both the seeds and the oil have an intensely bitter taste and are reported to be poisonous. In Brazil, the Guianas, and West Africa, the oil is used as an illuminant, for making soap, and as an ointment to protect the natives from attacks by insects.

The oil from *Carapa grandiflora* was expressed and examined by Lewkowitsch, [*Analyst,* **33,** 184 (1908)]. The kernels of this species contained 30.2 per cent of oil which remains solid at ordinary temperatures. Characteristics: Sp. g. at 40° C. 0.9171 to 0.9215; Sap. V. 198 to 202; Iod. No. 73 to 84, R.M.V. 3.8; Unsap. 1.6 to 3.7%; M. Pt. 23° to 30° C.; Titer 35° to 39°.

The cold-pressed oil in a 100 mm. tube gave a rotation of 2° 4′ to the left.

The oil like that of other species of *Carapa* is bitter and inedible.

Apeiba (Burillo Seed) Oil. This oil is obtained from the seeds of the tree *Apeiba tibourbou,* native to Central America, particularly common in Nicaragua. Lewkowitsch examined the oil and obtained the following results: Sp. g. at 15° C, 0.9275; Sap. V. 234.8; Iod. No. 77; R.M.V. 7.75; Pol. No. 27.2; Unsap. 1.28%. The high iodine number distinguishes this oil from those of the palm kernel group.

No mention is made as to the possible uses of this oil or to the possibilities of preparing it on a commercial scale.

Atta (Owala Bean) Oil. This oil is found in the seeds of the *Pentaclethra macrophylla* of the *Leguminosae,* which grows in East and West Africa. The large flat beans contain from 31 to 38 per cent of oil; the kernels 39 to 51 per cent.

The characteristics are as follows: Sp. g. at 15° C. 0.916; Sap. V. 181 to 182; Iod. No. (Wijs) 100.5, (Hübl) 94.4; $N_D^{40°}$ 1.4637 to 1.4644; Unsap. 0.3 to 1.4%; M. Pt. 18° to 24° C.; Sol. Pt. 10° to 16°; Titer 52° to 53°. Margaillon, Dupuis, and Rosello [*Chem. Absts.,* **23,** 1295 (1929)] reported the following: Sp. g. at 40° C. 0.902; $N_D^{40°}$ 1.4682; Sap. V. 181; Iod. No. 98.9; M. Pt. 24° C.; R. M. V. 1.27; Resin 0.5%; Acid V. 3.7. The kernels from which this oil was extracted analyzed as follows: moisture 8.5, oil 41, protein 25, fiber 5, ash 2.1 and carbohydrates 18 per cent.

In spite of the high titer, the oil is stated to yield a rather soft soap. Bolton and Hewer [*Analyst,* **42,** 43 (1917)], who have also examined this oil, stated there is little doubt that it is edible. They called attention to the fact that often along with these beans is the very poisonous calabar or ordeal bean (*Physostigma venenosum*) as well as other beans.

Pracaxy Oil. This oil is obtained from the beans or seeds of *Pentaclethra filamentosa* which is common in Brazil. Bolton and Hewer [*Analyst,* **42,** 43 (1917)] found the following characteristics: $N_D^{40°}$ 1.4590 to 1.4613; Sap. V. 175 to 180; Iod. No. (Wijs) 67 to 70; Sol. Pt. 12° to 14°; Titer 54° to 55°. Margaillon, Dupuis, and Rosello [*Chem. Abstrs.,* **23,** 1925 (1929)] found the following: $N_D^{40°}$ 1.4561;

Sap. V. 182; Iod. No. 67.3; R.M.V. 1.2; Acetyl V. 54.2; Acid V. 3.6; M. Pt. 28° C.; Resin 0.7%. They examined the kernels with the following results: Moisture 10.6, ash 1.4, fat and resin 48.3, proteins 14.4, carbohydrates 22, and fiber 4.2 per cent.

Avocado Oil. This oil is located in the fleshy portion of the avocado fruit (also known in the United States as Alligator Pear) from the tree *Persea americana* which is cultivated in many tropical and subtropical regions including California and Florida. In parts of Central America, Mexico and the West Indies, avocados have been cultivated for centuries, and as in the case of many other cultivated fruits, the horticultural varieties of the avocado may be placed in several distinct groups; three of these are the Guatemalan, West Indian, and Mexican, which are now recognized by most investigators.

The fruits, which weigh from several ounces up to three pounds, contain a single large seed that contains only 1 or 2 per cent of oil. The seed amounts to from about 8 to about 26 per cent of the fruit. The oil content of the fleshy portion ranges from 8 to about 30 per cent.

An extensive investigation on the composition of California avocados during growth has been made by C. G. Church and E. M. Chace (*U. S. Dept. Agr. Bull.*, **1073** of 1922).

According to W. Popenoe (*U. S. Dept. Agr. Bull.*, **743** of 1919) the native method in Guatemala for obtaining the oil consists in heating the crushed flesh of the avocado until a large portion of the water (juice) has been evaporated, then pressing the residue in bags between two heavy stones. The oil is said to be used locally as a pomade and for the treatment of burns. Soap is made by mixing the crushed flesh with other oils or fats and the mixture is saponified with alkali. This soap is recommended for washing the hair. Mr. Popenoe states that the soap is manufactured commercially in Guatemala, but it appears questionable whether all brands on the market actually contain avocado pulp. The quantity of oil prepared appears to be very small.

In California, avocado oil is expressed on a small commercial scale from the fruit broken into several pieces after the removal of the large seeds, which had been dehydrated at 130° F. in an oven containing an atmosphere of nitrogen. The resulting press cake can be fed to livestock or returned to the soil. The oil is used chiefly by cosmetic manufacturers. In Hawaii, where some of the oil is produced, it is used to some extent for making salad dressings.

The oil obtained by expression and by extraction of the Feurte variety of avocado was green and had a mild, pleasant flavor. These avocados and their proteins were examined by D. B. Jones and C. E. F. Gersdorff, *J. Biol. Chem.*, **81**, 533 (1929). The fruit contained 71 per cent of water, 20 of oil and 0.38 of nitrogen, which is equivalent to 2.37 per cent of crude proteins. Three distinct types of proteins were separated and investigated. The oil separated prior to the extraction of the proteins was examined by Jamieson, Baughman, and Hann [*Oil and Fat Ind.*, **5**, 202 (1928)] with the following results: Sp. g. at

25° C. 0.9132; $N_D^{20°}$ 1.4700; Sap. V. 192.6; Iod. No. (Hanus) 94.4; Unsap. 1.6%; Acetyl V. 9.2; Acid V. 2.8; R.M.V. 1.7; Pol. No. 0.2; Sat. acids 7.2 and unsaturated acids 84.3 per cent. The oil was found to contain 74 per cent of oleic, 10.3 of linoleic, 0.05 of myristic, 6.62 of palmitic, 0.53 of stearic and a trace of arachidic acid.

L. S. Malowan [*Seifensieder Ztg.*, **64**, 908 (1937)] found that the oils extracted from avocados grown in Panama gave saponification values from 186 to 196 and iodine numbers from 71 to 77. C. N. Valdivia [*Bol. Soc. Quim., Peru*, **5**, 207 (1939); *Chem. Absts.*, **34**, 3937 (1940)] reported saponification values from 185 to 197.7 and iodine numbers from 70.6 to 76.4, and solidification points from 7 to 9° C. The presence of vitamins A, D, and E in the oil was shown.

Attention is called to the following references:

Avocado Oil in Cosmetics, R. N. Ball and R. F. Eaton, *Drug Cosmetic Ind.*, **33**, 535 (1933). A note on Avocado Pear Oil, A. L. Bacharach and E. L. Smith, *Analyst*, **63**, 811 (1938). Chemical Composition of Avocado Fruits, A. R. C. Haas, *J. Agric. Res.*, **54**, 669 (1937). The Sulphuric Acid Digestion Oil Method for Avocados, H. P. Traub *et al.*, *Proc. Amer. Soc. Hort. Sci.*, **36**, 429 (1939).

Bacury Kernel Oil. This oil is obtained from the seeds of the fruit of *Platonia insignis* which grows in tropical South America. The fruit, which is about as large as an ordinary apple, contains five or six flattened ovoid seeds surrounded by pulp. The seeds are soft, covered by a thin brown skin and pitted all over with small resin ducts. The pulp is reported to be eaten by the natives of Brazil. When extracted, the oil is dark brown and firm in consistency. The seeds contain about 70 per cent of oil. Bolton and Hewer [*Analyst*, **47**, 282 (1922)] examined the oil with the following results: Sap. V. 191.8; Iod. No. 63.3; Unsap. 4.2%; M. Pt. 51.7° C.; $N_D^{40°}$ 1.4659.

The authors state that the oil might be used for making candles and soap.

Baobab Oil. This oil, which is also known as Fony or Reniala oil, is found in the seeds of the fruit of the large trees, *Adansonia digitata, A. grandidieri, A. madagascarienis,* etc., common to many parts of Africa. The size of the seeds, the percentage of kernels, and their oil content show a wide variation with the different species. The seeds of *A. digitata* weigh about 0.4, *A. madagascarienis* 0.9, and *A. grandidieri* somewhat over a gram. Depending upon the variety, the seeds have thick or thin tough shells. The percentage of kernels of these three varieties, according to Bontoux, varies from about 40 to 67. The oil content of the whole seed ranges from 12 to 43 per cent; the kernels from 31 to 63.5. The seeds of *A. digitata* (12 to 13 per cent) contain much less oil than the others. They yield a liquid oil while that of the others is semi-solid. Various observers have reported the following characteristics:

A. digitata.—Sp. g. at 15° C. 0.915; Sap. V. 190 to 192; Iod. No. 76 to 78; Sol. Pt. +3° to −3° C.; Titer 32° to 34°.

A. grandidieri.—Sp. g. at 15° C. 0.919; Sap. V. 190 to 193; Iod. No.

57 to 66; M. Pt. 21° to 25° C.; Sol. Pt. 11° to 13° C.; Titer 43° to 44.5°.

A. madagascarienis.—Sp. g. at 15° C. 0.9198; $N_D^{40°}$ 1.4600; Sap. V. 190.5; Iod. No. 67.5; M. Pt. 22° C.; Sol. Pt. 12° C.; Titer 44°.

The expressed oils have a golden yellow color and a pleasant nutty taste. They give a much more intense Halphen test than cottonseed oil.

Baobab oil is not yet a commercial product, but it is said to be prepared for local use in some parts of Africa. It is suitable for edible purposes and soap making. Belland [*J. Pharm. Chem.*, **20**, 529 (1904)] suggests that the solid varieties could be used as a substitute for coconut oil, but this appears doubtful to the writer on account of their lack of similarity to the latter oil.

Batiputa or Bati Oil. This oil is located in the fleshy part of the small red (and yellow) fruits of *Ouratea* (*Gomphia*) *parviflora,* a member of the *Ochnaceae.* These shrubs, which grow from 7 to about 15 feet high, are abundant in certain parts of the Brazilian States of Parahyba, Pernambuco and Rio Grande de Norte. The ripe fruits contain 10 to 12 per cent oil. The characteristics of the oil reported by various investigators are as follows: Sap. V. 192, 197, 202 and 212; Iod. No. 51, 56, 58 and 70; Crismer V. 70.0° and 77.3°; M. P. 19° 30° and 30-2° C; $N_D^{15°}$ 1.4615 and at 40° 1.4631.

The soft fruits are easily injured and soon after this has occurred, a notable quantity of free fatty acids is liberated by the action of enzymes on the oil.

The problems involved in the production of an edible oil from this fruit on a commercial scale are discussed by Jayme Sta. Rosa in "Gordura de Bati" (18 pages), Instituto Nacional de Tecnologia, Rio de Janeiro, 1939.

Bayberry Tallow (Myrtle Wax). The tallow covers the outside of the berries of various species of Myrica growing in North America, South America and South Africa. These shrubs are found for the most part along the seacoast. Along the Atlantic coast are found *M. cerifa* and *M. carolinensis.* The berries contain 15 to 20 per cent of their weight of tallow. The berries are boiled with water and the molten tallow is removed by skimming or after it has solidified. The crude product is remelted in clean water to purify it further. It is prepared in North America, Mexico, and Africa, and used along with other substances in the manufacture of candles. In Europe it is used for making soap.

The characteristics are as follows: Sp. g. at 15° C. 0.995, at 99° C. 0.878; $N_D^{80°}$ 1.4363; Sap. V. 205 to 212; Iod. No. 1 to 4; R.M.V. 0.5; M. Pt. 40° to 46° C.; Titer 46° C.; Unsap. 2.5%. The so-called Cape Berry Wax [*Bull. Imp. Inst.*, **4**, 300 (1906)] gave characterictics within the range of those noted above from South Africa. The tallow has a greenish color but on exposure to the air and light, the outer portions become bleached. The composition of the fat has not until recently been investigated, but W. R. Smith and B. Wade [*J. Am. Chem. Soc.*,

25, 629 (1903)] confirmed Chittenden and Smith in that the fat contains a large quantity of palmitin.

Jamieson, McKinney and Gertler examined the fat from bayberries of *Myrica mexicana* collected in Salvador, C. A. The berries contained 28.3 per cent of fat which gave an iodine number (Hanus) 1.2 and a saponification value 216.7. It was found to contain the following percentages of fatty acids: Oleic 1.3, myristic 58.0, palmitic 35.6 and a trace of stearic acid. The unsaponifiable matter amounted to 0.85 per cent.

Bay Tree Seed Fat. This fat is found in the seeds from the California Bay tree *Umbellularia Californica,* a member of the Lauraceae. The tree, which ranges in height from 30 to 80 feet, is planted for ornamental and shade purposes in California and Oregon. Its fruits are small drupes which are purple at maturity.

C. R. Noller, I. J. Millner, and J. J. Gorden [*J. Am. Chem. Soc.,* **55,** 1227 (1933)] who investigated the extracted fat, reported that the kernels contained 58.5 per cent. The fat gave the following characteristics: Sap. V. 275.1; Iod. No. 5.7; Unsap. 2.1 per cent; M. Pt. 29 to 30° C.

The approximate percentage composition of the mixed acids from the fat was found to be as follows: Caprylic 1.0, capric 37.0, and lauric 62.0.

The authors stated that although the iodine number of the methyl esters of the fatty acids indicated the presence of about 6 per cent of oleic acid, the saponification equivalents of the highest fractions (distilled) gave no indication of any acid having a higher molecular weight than lauric acid.

The oil undoubtedly contains some oleic or other unsaturated acids.

Ben (Moringa) Seed Oil. This oil is obtained from the seeds of the tree *Moringa oleifera* belonging to the *Moringaceae,* which contains but two other species. This tree, which is indigenous to Arabia, India and Syria, was introduced many years ago into many tropical and semi-tropical regions, including Central and South America and the West Indies. Early records state that in 1784 the tree was established in the vicinity of Kingston, Jamaica, by Hinton East. The tree is found widely distributed in the Philippines. In India and elsewhere, it has long been known as the horse-radish tree on account of the flavor of the roots. The soft white wood of the tree, when freshly cut, has the same odor and taste.

The tree, which reaches a height of about 30 feet, is a rapid grower even in poor soil and it is reported to be little affected by considerable periods of drought. The fruits are three-angled, or cornered, nine-ribbed slender pods which vary from 15 to 30 centimeters in length. Each pod contains about 20 seeds which are three-angled and winged on the angles. The seeds vary in weight from 0.3 to 0.5 grams, and, depending upon their source, contain from about 25 to 34 per cent of oil.

The usual range of characteristics of the oil is as follows: Sp. g. at 15.5° C. 0.913 to 0.919; $N_D^{40°}$ 1.4653 to 1.4668; Sap. V. 186 to 187.7;

Iod. No. 67.7 to 72.2; Acid V. 0.9 to 2.3; Unsap. 0.9%; Titer 32 to 38° C.

G. S. Jamieson [*Oil and Soap*, **16**, 173 (1939)] examined the oil expressed from a 34-pound sample of seeds received from the National Agricultural Service of the Republic of Haiti. The seeds consisted of 26.2 per cent of shell and 73.8 of kernel. The kernels contained 5.1 per cent of moisture and 37.7 of oil. (Seeds from Nicaragua were found to contain 70.7 per cent of kernels. The latter contained 49.2 per cent of oil and 5.4 of moisture.) The bright yellow oil had a slight, pleasant taste. The characteristics of the oil were as follows: $N_D^{25°}$ 1.4651; Sap. V. 186.4; Iod. No. (Hanus) 68.0; Acid V. 0.74; Unsap. 1.5%; Sat. acids 22.38; Unsat. acids 71.82. The oil contained the following percentages of acids: Oleic 68.9, linoleic 3.8, myristic 1.5, palmitic 3.6, stearic 10.8, behenic 6.3, and lignoceric 0.13.

In India and elsewhere, the oil is used as a cosmetic, for cooking, and as an enfleurage. Many years ago in Jamaica it was used to lubricate delicate machinery, including watches.

The press cake, or meal, which has a bitter taste, could be used as a fertilizer material.

Oil from Moringa aptera seed from Egypt [*Bull. Imp. Inst.*, **28**, 276 (1936)] gave the following characteristics: Sp. g. at 15° C. 0.9151; $N_D^{40°}$ 1.461; Sap. V. 188.2; Iod. No. (Wijs) 71.2; Acid V. 05; Titer 28.1° C.

The kernels contained 50 per cent of oil. The extracted meal, which contained 48.6 per cent of proteins, had a bitter taste.

Bey Bean Butter. This fat is found in the seeds of various species of *Baillonella* growing in West Africa, and common in certain parts of Liberia. The seeds, which resemble those of the tree *Madhuca toxisperma* (see Djave butter) but slightly smaller, also yield a somewhat similar fat. The seeds consist of 13 per cent of shells and 87 of kernels. The kernels contain when fully matured about 63 per cent of fat for which Bolton and Hewer [*Analyst*, **47**, 282 (1922)] report the following characteristics: $N_D^{40°}$ 1.4605; Sap. V. 180.3; Iod. No. 60.7; Unsap. 6.2%; M. Pt. 33° to 44° C. The fat could be used for making soap, but it will be observed that it contains a notable quantity of unsaponifiable substances.

Borneo Tallow. This product, which is known also in the trade as "Green Butter" and "Tengkawang" Fat or Tallow, is obtained from the seeds of a number of trees belonging to the *Dipterocarpaceae*, found in Borneo, Java, Malaya, Philippines, Straits Settlements, and Sumatra. According to A. J. Bal [*Intern. Review of Agric.*, **25**, 7178 (1934)] in the native dialects there are 80 names given to these so-called tengkawang trees. The characteristics which enable the native to distinguish varieties and species are the flowers and fruits.

The more important species appear to be the *Shorea aptera, S. gysbertsiana, S. seminis, S. stenoptera, Hopea aspera,* and *Pentacme siamensis.* Of these, the *S. stenoptera* is probably the most important [*Bull. Imp. Inst.*, **19**, 140 (1921)] from a commercial standpoint.

The kernels from the seeds of this species, depending upon their source, contain from 45 to over 60 per cent of fat. It may be mentioned that these trees produce characteristic winged fruits which differ from each other chiefly in their size.

The seeds usually are exported under the name of the place of origin, together with the color and the size, such as Large and Small Sarawak Illipé, Large Black or Brown Pontianak Illipé, and Small Pontianak Illipé nuts or kernels. These names may also be applied to the tallow, to indicate its source. These should not be confused with the Illipé nuts and tallow from India which are obtained from the species of *Madhuca* (Bassia) of the *Sapotaceae.*

The natives in certain parts of Borneo and Malaya have in rather recent years planted these trees for the production of seed chiefly for the export trade. A. J. Bal (*loc. cit.*) states that in Malaya, the seeds are planted in nurseries and when sufficiently large, the trees are transplanted, whereas in Borneo, the Dajaks usually scatter the seed where they wish the trees to grow. In favorable situations, the trees begin to bear when 10 to 12 years old.

It is probable that the larger part of the seeds collected are from the trees growing wild. It is reported that the yield of seed is very uncertain and this is due to unfavorable weather during the blossoming period.

The seeds are collected by the natives, after they fall from the trees. In some localities, quantities of the seed fall into the sea, where, because of tidal influences, they accumulate in inlets or coves along the shore, so that they can easily be gathered.

In various localities the seeds are subjected to some heat and smoke before the extraction of the kernels. Such kernels, however, are stated to be more liable to damage by borers and consequently less in demand than those from the seeds which have been submerged in running water for about six weeks in order to soften the tough shells so that the kernels can be readily removed. After the removal of the kernels, they are placed in direct sunlight until dry. This causes many of them to split into two or more triangular segments. The smoke treatment results in producing what is known in trade as "brown" kernels, whereas those from the water treatment are "black" kernels. Those not required for local production of fat are exported. The natives use the fat for cooking and other purposes. It can be used for making candles and soap. Some thousands of tons of kernels are annually exported to Europe where the fat is expressed or extracted. The press cake or meal is used as a cattle food. Its protein content ranges from 10 to 13 per cent.

Borneo tallow is a hard, brittle solid that resembles cacao butter in many respects. When freshly prepared it is usually more or less yellowish green, hence the name "Green Butter," but it bleaches upon standing. That produced by modern methods has a slight odor suggestive of cacao butter and with little taste, while the native product is

not only very crude but has an unpleasant odor and taste. In Europe, it is used largely as a substitute for cacao butter.

The usual range of the characteristics is as follows: Sp. g. at 100°/15° 0.852 to 0.860; $N_D^{40°}$ 1.4561 to 1.4573; Sap. V. 189 to 200; Iod. No. 29 to 38; Unsap. 0.4 to 2%; R.M.V. 0.1 to 0.5; Pol. No. 0.3 to 0.4; M. Pt. 34° to 39° C.; Titer 51° to 53°.

These characteristics are well within the range for those given by cacao butter; consequently they afford no means for distinguishing between the two fats. The method of Bywaters, Maggs and Pool [*Analyst,* **52,** 324 (1927)] for its estimation in mixtures is given under cacao butter.

Hilditch and Priestman [*J. Soc. Chem. Ind.,* **49,** 197T (1930)] have studied the fat from the *Shorea stenoptera* and found that the mixed fatty acids consisted of 1.5 myristic, 21.5 palmitic, 39 stearic and 38 per cent of oleic acid. The fat contained 4.5 per cent of fully saturated and 95.5 of saturated-unsaturated glycerides. It consisted approximately of 82 of mono-oleo, 18 of dioleosaturated glycerides and 9 per cent of triolein.

W. J. Bushell and T. P. Hilditch [*J. Soc. Chem. Ind.,* **57,** 44 (1938)] have made an extensive examination of a sample of Borneo tallow which contained about 4 per cent less palmitic acid and 4 per cent more of stearic acid than the sample previously investigated (*loc. cit.*). The neutralized sample had a saponification equivalent of 294.5, an iodine number of 33.2, and contained 1.1 per cent of unsaponifiable matter. The approximate percentages of components in the fat are as follows: oleodistearin 40, oleopalmitostearin 31, stearodiolein 13, palmitodiolein 3, oleodipalmitin 8, and fully glycerides 5 (mainly palmitostearins). It was found that the tallow follows very closely the even distribution of the fatty acids among the glycerides, which is a characteristic of seed fats.

An extensive investigation of the fat from the seeds of *Shorea robusta* has been made by T. P. Hilditch and Y. A. H. Zaky [*J. Soc. Chem. Ind.,* **61,** 34 (1942)]. They found that the kernels contained only 14.2 per cent of fat having an iodine number of 41.2.

Cacao Butter. Cacao butter is obtained from the seeds, which are commonly known as beans, of the fruit from the tree *Theobroma cacao* indigenous to the Amazon Valley, but now extensively cultivated in most tropical countries. The beans contain from 50 to 57 per cent of a pale yellowish fat which melts between 30° and 34° C.

Cacao butter is largely a by-product from the manufacture of beverage cacao, which is made by pressing decorticated, roasted and crushed cacao beans [*Chem. Age,* **32,** 85 (1924)]. The press cake when ground and bolted constitutes cocoa. Increasingly large quantities of cacao butter are also now being pressed or extracted with volatile solvents from unroasted beans.

Although the chief use of cacao butter is the manufacture of confectionary, it is also an important ingredient of several pharmaceutical preparations.

Characteristics. The usual range of the characteristics is as follows: Sp. g. at 60° C., 0.8823 to 0.8830, at 50° C., 0.8921, at 25° C., 0.973, at 15° C., 0.990 to 0.998; $N_D^{40°}$ 1.4565 to 1.4570; Sap. V. 192 to 198; Iod. No. 32 to 40; SCN V. 35 to 37; R.M.V. 0.3 to 1.0; Pol. No. 0.5; Acid V. 1 to 4; Unsap. 0.3 to 0.8 per cent; Titer 48 to 50° C.

Composition. Although from time to time attempts have been made to determine the composition of cacao butter, only the more recent investigations will be considered; these deal with the glyceride structure of the fat. Attention is called to the investigations of Hilditch and Lea [*J. Chem. Soc.*, **1927**, 3106], Lea [*J. Soc. Chem. Ind.*, **48**, 41T (1929)], and Hilditch and Stainsby [*J. Soc. Chem. Ind.*, **55**, 95T (1936)]. As a result of these investigations, they suggested that cacao butter contained in round numbers the following percentages of glycerides: oleopalmitostearin 52, oleodistearin 19, stearodiolein 12, palmitodiolein 9, oleodipalmitin 6, and palmitostearins (saturated) 2. The very small quantity of linoleic acid present is included in the oleoglycerides. It was concluded that β-oleodipalmitin and β-oleodistearins are probably the isomerides of these types mainly present, and the trebly mixed glyceride must be largely β-palmito-oleo-stearin. Both α- and β-stearodiolein may also be present.

The mixed fatty acids from the 1935 sample of the fat contained the following percentages of constituents: palmitic 24.4, stearic 35.4, oleic 38.1, and linoleic 2.1. The 1927 sample: palmitic 24.4, stearic 34.5, oleic 39.1, and linoleic 2.0.

The composition of the fats from the cacao seed shells, cotyledons and germs have been investigated by K. H. Bauer and L. Seber [*Fette u. Seifen*, **45**, 293 and 342 (1938)]. They found that the extracted cacao butter contained 1.5 per cent of unsaponifiable matter, whereas the expressed product, as is well known, contains a much smaller quantity (0.3 to 0.8 per cent).

Properties. Cacao butter when fresh is a pale yellow brittle solid, but upon standing exposed to the light it gradually bleaches. It has an agreeable characteristic cacao odor and taste. When desired, it can be bleached and deodorized. This product is noted for its fine keeping qualities, but when exposed to air and bright sunlight it will turn rancid. Cacao butter from different localities as now prepared is very uniform in composition, as shown by the small range in the characteristics.

Adulterants. These include the so-called "chocolate fats," which are coconut and palm kernel oil stearins, Borneo tallow, Bassia (Illipé) fats, tallow oleo-stearin, paraffin wax, and hydrogenated oils. The detection of skillful adulteration is difficult, and often cannot be accomplished by any one test, but a careful examination by all the tests suggested will usually give information as to the nature of the adulterants, if present.

Examination of Cacao Butter. The sample should be melted and thoroughly mixed so that the portions taken for analysis will be uniform in composition. Then determine the iodine number, saponification

value, unsaponifiable matter, Reichert-Meissl value, Polenske number, acid value, and melting point. The melting point is determined by drawing the melted sample into open capillary tubes; after closing the lower end of the tubes with a small flame they are allowed to stand in a refrigerator for a day or longer before taking the melting point; otherwise an abnormally low melting point will be obtained.

The presence of stearins of the coconut group of oils will be revealed by the high values for the Reichert-Meissl and Polenske determinations. Bassia (Illipé) fat (Iod. No. 54 to 68) would raise the iodine number of cacao butter.

Paraffin would be found in the unsaponifiable matter. Likewise, the presence of the shea butter (with unsaponifiable ranging from 3 to 11 per cent) would raise that of cacao butter above the normal quantity. The presence of vegetable oil stearins and hydrogenated oils lowers the specific gravity below that for pure cacao butter. The Villavecchia test will indicate the presence of hydrogenated sesame oil or its stearine.

As the characteristics of Borneo tallow (Green Butter) are very similar to those of cacao butter, the only procedure by which it can be detected is that first proposed by M. Prichard [*Compt. rend.*, **176**, 1224 (1923)] and further studied by Bywaters, Maggs and Pool [*Analyst*, **52**, 324 (1927)] and is based on the determination of the turbidity temperature. The method is as follows:

Fill a 6 x 1 inch test tube half full of the melted sample. Insert a thermometer calibrated in tenths of a degree through the center of a cork which fits the test tube, so that the bottom of the thermometer is 0.75 inch from the bottom. Then insert the test tube through a cork provided with a short glass inlet tube, which fits a liter filter flask. Connect the inlet tube with a long coil of metal tubing which is placed in a water bath, maintained at 18° C. Connect the filter flask to the water pump or vacuum system and regulate the flow of air through the flask so as to cause a fall in temperature of the melted sample at the rate of 0.5 degree per minute. Note the temperature at which the first sign of turbidity reaches the center of the bulb. Repeat the test twice and take the average of the three determinations. The average turbidity temperature for cacao butter is 21.4°, while that for Borneo tallow is 30.8°.

The Acetone-Carbon Tetrachloride Test for the Detection of Hydrogenated Oils, Tallow, Oleostearin or Paraffin. Weigh 5 grams of the melted sample which has been previously filtered through a dry paper in an oven heated to 110° C. and transfer it to a test tube containing 5 cc. of a mixture of equal volumes of acetone and carbon tetrachloride. Shake until the sample is dissolved. Place the test tube in an ice-water bath for about 30 minutes. At the same time make a blank test using a sample of pure cacao butter. A white flocculent precipitate will appear if the sample contains any of the above-mentioned substances. Sometimes the ice bath is so cold that the cacao butter separates and this will be indicated by the control test with the pure cacao butter. In such cases, remove the test tubes from the ice bath and allow them to remain at room temperature for a time. Any solidified cacao butter will soon dissolve, but precipitates due to the above-mentioned adulterants require a much longer time for solution. This method can be used as a sorting test, the results of which should be confirmed by making the critical temperature of dissolution test.

Critical Temperature of Dissolution in Acetic Acid. For the determination, insert a thermometer calibrated to 0.1° into a cork that fits a 6 x 0.75 inch test tube, so that the bulb of the thermometer will be entirely submerged by the addition of 10 cc. of liquid to the test tube. Insert this test tube through a cork placed in a 4 x 1.25 inch test tube which should contain enough glycerin to bring its surface slightly above that of the 10 cc. mark on the inner test tube, which

should extend almost to the bottom of the larger tube. Cut a groove through the edge of the larger cork to equalize the pressure when the glycerin is heated.

Melt the sample and filter about 10 grams through a small folded filter into a small flask to remove any moisture, the filtration being made in an oven heated to about 110° C. Allow the sample to cool to about 40° C., then weigh 5 grams of the sample and 5 grams of glacial acetic acid (99.5 per cent) into the smaller test tube. Insert the cork, holding the thermometer, and place the tube in the glycerin bath. Heat and shake the apparatus frequently until the sample is completely dissolved in the acetic acid. While the test tube remains in the glycerin bath, allow the solution to cool with constant shaking until the first sign of turbidity appears; then quickly note the temperature. Make a similar test using cacao butter of known purity.

As free fatty acids lower the turbidity temperature, a correction is made for the acid value of the sample under examination as well as of the pure cacao butter. If the strength of the glacial acetic acid is such that the turbidity temperature of the pure cacao butter is approximately 90° C., one unit of acid value will cause a reduction of 1.4 degrees in the critical temperature of dissolution. If the turbidity temperature is approximately 100° C., one unit of acid value will cause a reduction of 1.2°. For intermediate temperatures, the reduction is proportional.

Determine the acid value in the usual manner using 5-gram portions of the sample being tested and the pure cacao butter. Multiply the acid value by the correction factor and add the results respectively to the observed turbidity temperatures to obtain the true value for the critical temperature of dissolution. In the case of the sample under examination a temperature lower than 2° C. for that found for pure cacao butter, adulteration with coconut, palm kernel oils, or their stearins, as well as the stearins of peanut, cottonseed and other oils is indicated.

A large number of analysts have used this method for some years and have found it satisfactory in connection with the examination of commercial cacao butters.

The following references may be of interest:

"Cultivation and Preparation of Cocoa," *Bull. Imp. Inst.*, **18**, 36 (1920).

"Detection and Estimation of Ellipé Butter Used as a Substitute For Cacao Butter," Tate and Pooley, *Analyst*, **41**, 229 (1921).

"Adulteration of Cacao Butter," Prichard, *Analyst*, **48**, 556 (1923).

"The Setting of Cacao Butter with Special Reference to Development of Bloom on Chocolate," R. Whymper and A. Bradley, *J. Soc. Chem. Ind.*, **44**, 77T and 143T (1925).

"Detection and Determination of Coconut Oil and Milk Fat in Cacao Butter," Kuhlmann and Grossfeld, *Z. angew. Chem.*, **39**, 24 (1926).

"Detection of Coconut Oil in Cacao Butter and Chocolate," Duffy, *Brit. Chem. Abts.*—B, **1926**, 552.

"Cacao Butter Substitutes and Their Detection," Knapp, Moss and Melley, *Analyst*, **52**, 452 (1927).

"Feeding Cocoa Meal to Hogs," R. D. Alpin, *Vt. Sta. Bull.*, **1927**, 271.

"Effect of Feeding Cocoa Meal to Milking Cows," Alpin and Ellinberger, *Vt. Exp. Sta. Bull.* **272.**

"The Estimation of Milk Fat in Milk Chocolate by Means of a Modified Xylene Number," C. A. Greenleaf, *J. Assoc., Offic. Agr. Chem.*, **10**, 396 (1927).

"Distinction Between Expressed and Extracted Cacao Butter," Anfrecht, *Brit. Chem. Absts.*—B, **1929**, 141.

"Detection of Coconut Fat in Cacao Butter and Cacao Products," F. Hartel, *Chem. Absts.*, **22**, 1195 (1928).

"Detection of Adulterants in Cacao Butter and Chocolate," Colombier and Chaize, *Brit. Chem. Absts.*—B, **1928**, 385.

Cupu Seed Oil. This oil is obtained from the seeds of the tree *Theobroma grandiflora* of the *Sterculiaceae*, a native of the upper Amazon and in the province of Para, Brazil. The flat, roughly ovate seeds weigh about 2 grams and contain over 48 per cent of oil.

According to Bray and Islip [*Analyst,* **46,** 325 (1921)] the oil examined by them had the following characteristics: Sp. g. 100°/15° C. 0.8522; $N_D^{40°}$ 1.4560; Iod. No. (Hull) 44.8; Sap. V. 188; R.M.V. 0.08; Pol. No. 0.12; Unsap. 0.91%; M. Pt. 32° C.; Titer 48° C.; Acid V. 44. Bolton and Hewer [*Analyst,* **47,** 282 (1922)] obtained similar results, except that complete fusion takes place at 45.50.

The product extracted with petroleum ether was almost white, of rather soft consistency and almost tasteless and odorless. It is stated that it could probably be used for edible purposes.

Lupu Seed Oil. This oil is from the seeds of *Theobroma bicolor.* The seeds consist of 25 per cent of shell and 75 of kernel, which contains about 60 per cent of oil, from which Bolton and Hewer report the following characteristics: $N_D^{40°}$ 1.4565; Sap. V. 189; Iod. No. 44.4; Unsap. 0.9%; M. Pt. 40° C.; Sol. Pt. 26°.

The cupu and lupu fats are said to be similar to those of cacao but somewhat softer.

Calophyllum Oil. This oil is found in the seeds of the fruits of the large evergreen tree *Calophyllum inophyllum,* which belongs to the *Guttiferae* family. The tree is found in India, East Africa, East Indies, and Polynesia. The oil is known by various names, some of which are as follows: Dilo, Domba, Laurel nut, Indian or Alexandrian laurel, Pinnay, and Poonseed. The globular green fruits, which are an inch or slightly more in diameter, gradually turn brown and become wrinkled. The shell of the fruit, which is ⅛ to ¼ of an inch thick, is woody on the outside, spongy in the middle, and has a thin, highly polished inner skin. The shells amount to from 47 to 57 per cent and the kernels from 43 to 52 per cent of the fruit. The kernels weigh from 2 to 2.5 g. Their oil and resin content appears to range from 50 to 73 per cent. Both the extracted and expressed oils are dark green, viscous liquids. The crude oil has a disagreeable aromatic odor and taste. Owing to the presence of toxic, non-fatty constituents, it is not used for edible purposes. In various places it is used as an illuminant, for medicinal purposes and for making soaps. The natives have long used the oil for the treatment of skin diseases and rheumatism. The refined oil, or the ethyl esters of the fatty acids, have been intramuscularly injected to relieve the pains of leper patients at the Sungei Buloh leper colony. The range of the characteristics which have been reported by various investigators from 1888 to 1930 are as follows: Sp. g. at 15° C. 0.9415 to 0.9452; $N_D^{15°}$ 1.4699 to 1.4772; Sap. V. 191 to 202; Iod. No. 82 to 98. Unsap. 0.25 to 1.4%; Acid V. 27 to 78; R.M.V. 0.13 to 0.50. The quantity of resinous substances in the oil varied from about 10 to over 30 per cent.

D. R. Dhingra and T. P. Hilditch [*J. Soc. Chem. Ind.,* **50,** 9T (1931)] examined a sample of the crude oil received from the Forest Research Institute, Dehra Dun. It gave an iodine number of 92, an acid value of 47.2 and a saponification equivalent of 286.6. The percentage composition of the mixed fat acids freed from resinous consti-

tuents was as follows: oleic 49.7, linoleic 23.8; palmitic 16.8, and stearic 9.7.

Soliven [*Phil. Agr.*, **13**, 65 (1924)], who examined a Philippine oil, stated that the fatty oil fraction contained the following percentage of acids as glycerides: oleic 31.5, linoleic 39.7, palmitic 13.3 and stearic acid 14.5. In this case the original sample of oil contained 32 per cent of resin.

K. W. R. Glasgow [*J. Soc. Chem. Ind.*, **51**, 172T (1932)] reported that kernels received from one of the Fiji Islands contained 58 per cent of oil. The ether-extracted oil, which was of an amber color, gave a saponification value of 200.9, an iodine number of 81.7, and an acid value of 68.

The percentages of constituents in the mixed acids were as follows: resin acids 9.7, oleic 48.0, linoleic 14.3, erucic 3, palmitic 14.1 and stearic 11.0. Although some analytical evidence was given, it should be noted that erucic acid was not separated in a pure condition, nor was it hydrogenated for identification purposes.

C. D. V. Georgi [*Malayan J. Agric.*, **24**, 3 (1936)], who had occasion to prepare a considerable quantity of the refined oil for experimental use in the alleviation of pain at the Sungei Buloh Leper Colony, describes the tree, fruits, and the preparation of the crude (and refined) oil from Malayan seeds. The characteristics of the crude oil were as follows: Sp. g. at 15.5° C. 0.9411; $N_D^{20°}$ 1.4814; Sap. V. 184.2; Iod. No. (Wijs) 98.2; Acid V. 35.0. Refined oil: Sp. g. at 15.5° C. 0.9276, $N_D^{20°}$ 1.4753; Sap. V. 188.2; Iod. No. (Wijs) 90.0; Acid V. 1.8.

From the investigations made, it will be observed that the oil from different sources varies greatly in composition both in respect to the proportion of resin and of fatty acids.

Cashew Nut Oil. This oil is found in the kernels of the nuts from the tree *Anacardium occidentale* of the *Anacardiaceae* family, which is indigenous to Central and South America. The tree is extensively cultivated in western India, Portuguese East Africa, Tanganyika and Kenya. The tree is also grown in the Philippines, Madagascar, and other tropical regions. Large quantities of the African nuts are exported to India where these and the locally produced nuts, prior to the separation of the kernels, are processed for the recovery of the so-called cashew shell oil. This tree bears a yellow pear-shaped fruit with a kidney-shaped seed (nut) attached to one end. Both the fruit and the kernel of the seed are eaten raw or roasted. The shell, which amounts to about 30 to 40 per cent of the seed, yields a dark viscous liquid (cashew nut shell oil) that, according to Joseph and Sudborough [*Chem. Absts.*, **17**, 1897 (1923)], contains a phenolic compound called "Cardol" ($C_{32}H_{52}O_4$) and an acid $C_{22}H_{32}O_3$, which has been named anacardic acid. This oil had an iodine number of 296, an acid value of 107, a saponification value of 119, and a density at 26° C. of 1.0131. The shells contain about 20 per cent of this so-called oil. This poisonous product is extracted locally and used for protecting books, etc., from

the ravages of white ants. Various patents have been issued covering the extraction of the shell oil, and the equipment used; others describe methods for the manufacture of various products from this oil for use in protective coatings. Attention is called to "Cashew Nut Shell Liquid" by M. T. Harvey and S. Caplan, *Ind. Eng. Chem.*, **32**, 1306 (1940). Also see pages 74 to 101, Vol. 1 (1941) Protective and Decorative Coatings, J. J. Mattiello, Editor, John Wiley and Sons, New York.

The kernels, which weigh from 1 to 2 grams, contain from 38 to 46 per cent of a pale yellow oil. It has been examined by Niederstadt, Bolton and Jesson [*Analyst*, **40**, 3 (1915)]; C. D. V. Georgi [*Malayan Agri. J.*, **10**, 301 (1922)]; Patel, Sudborough, and Cruz [*Phil. J. Sci.*, **23**, 337 (1923); *Abstract, Analyst*, **49**, 39 (1924)]. The range of the characteristics reported is as follows: Sp. g. at 15° C. 0.911 to 0.918; at 26° C. 0.9105, $N_D^{40°}$ 1.4623 to 1.4633, at 30° C. 1.4665; Sap. V. 187 to 195; Iod. No. 79 to 85; Unsap. 0.4 to 1.5%; R.M.V. 1.6; Pol. No. 0.25; Acid V. 1.4 to 1.6; Titer 28° to 30°.

Patel, Sudborough, and Watson (*loc. cit.*) found that the fatty acids from the sample of the oil which they examined consisted of 73.8 oleic, 7.7 linoleic, 6.4 palmitic, 11.2 stearic and 0.5 per cent of lignoceric acid, whereas West and Cruz reported that their oil contained 16.52 per cent of saturated acids consisting chiefly of stearic acid, and the unsaturated fraction which amounted to 76.9 per cent of the oil contained only oleic acid. This fraction after bromination gave no petroleum ether-insoluble tetrabromide and its bromine content corresponded to the dibromide of oleic acid, which showed that this Philippine oil contained very little, if any, linoleic acid.

As the available supply of cashew kernels is used for edible purposes, there is little likelihood of the oil being expressed on a commercial scale, but when properly prepared, it has a fine mild flavor and can be used for edible purposes.

Castor Oil. Castor oil is obtained from the seeds of the plant, *Ricinus communis*, found in most tropical and subtropical regions, where it grows wild and is also cultivated. The castor plant varies greatly in size (6 to 35 ft.), in the color of the stems, as well as in the size and color markings of the more or less mottled seed. These marked variations are due to the existence of several varieties and to some extent by differences in climate and soils. The oil content of the seed ranges from 35 to 55 per cent, the average being about 44 or 45. The seed contains from 70 to 80 per cent of kernels. A bushel of seeds weighs about 46 lbs. and a cubic foot of them, about 37 lbs. The seeds range in weight from 0.1 to 1.3 grams.

The seed and oil of commerce come chiefly from India, China, Manchuria, Mexico, and Brazil. India and Brazil are the largest producers of the seed. During the nineteenth century large quantities of seed, popularly known as "castor beans," were produced in the United States, chiefly in Illinois, Kansas, Missouri and Oklahoma. In response

to the demand for aircraft lubricants, several thousand tons of the seed were produced in the southern states in 1918-19.

Castor oil is obtained by expression and solvent extraction. It is customary in the United States to press the cleaned, unheated seed in cage hydraulic presses. The press cake is then ground and the residual oil is obtained by solvent extraction. After removal of the solvent, this oil is graded as No. 3, whereas that obtained by expression is known as No. 1. The extracted meal, which is very poisonous, is used as a fertilizer material.

The expressed oil is heated under diminished pressure until the moisture is removed. When desirable the warm oil is agitated a short time with 2 to 4 per cent of fuller's earth along with 0.2 to 1 per cent of activated carbon and filtered. It is customary to deodorize the medicinal oil with the aid of super-heated steam, in a vacuum deodorizer.

Grades. The trade determines the quality of the oil by its color, clearness and acidity. No. 1 is low in acidity, brilliantly clear and nearly colorless. No. 3 varies in color from yellow to dark brown or dark green. The trade no longer recognizes any grade as No. 2.

Hydrogenated Castor Oil. The oil can be hardened in the usual manner. The hydrogenated oil, which has an iodine number of 18, melts at 81° and that with an iodine number of 2 melts at about 86° C. Highly hydrogenated castor oil evolves hydrogen when heated from 150° to about 280° C., according to A. Brocket [*J. Soc. Chem. Ind.*, **42**, 317A (1923)]. Thomas and Dickert [*Analyst*, **46**, 139 (1921)] separated a new hydroxy stearic acid with a melting point of 83° C. from the hydrogenated oil. Bömer [*J. Soc. Chem. Ind.*, **42**, 1232A (1923)] isolated the following glycerides: Trihydroxystearin, M. Pt. 89.4° C.; stearodihydroxystearin, M. Pt. 75° C.; and distearohydroxystearin, M. Pt. 69.5°.

Castor oil is distinguished from most other oils by its high specfic gravity, acetyl value and viscosity, its solubility in alcohol and its slight solubility in large quantities of petroleum ether, gasoline, kerosene, and the higher-boiling petroleum distillates. It dissolves in its own volume of petroleum ether. The oil dissolves at ordinary temperatures in glacial acetic acid while other oils, with the exception of croton, dissolve only in the heated acid. Its acetyl value is higher than that of any other known fatty oil. The oil does not "dry" on exposure to the air, but the specific gravity increases while the iodine and acid values undergo little or no change. The oil has excellent keeping qualities. When heated and blown with air, the specific gravity increases and the iodine value decreases. Although the oil does not dissolve to any extent in mineral lubricating oil, it will dissolve readily if another fatty oil, such as rape, is added. When about 10 per cent of the weight of castor oil has been removed by distillation at ordinary pressure, the undistilled portion is miscible in all proportions of mineral oils. This product has little solubility in alcohol. A product with similar properties is obtained when the oil is heated from 260° to 300° C. for about 10 hours under a pressure of 4 to 6 atmospheres (Eng. Pat. 24935, 1905).

The characteristics of castor oil are usually within the following limits: Sp. g. at 15° C. 0.958 to 0.968; Iod. No. 82 to 90; Sap. V. 177 to 187; Acetyl V. 143 to 150; R.M.V. 0.2 to 0.3, and Unsap. 0.3 to 0.7 per cent. Refractive index at 15° C. 1.4790 to 1.4813, at 25° C. 1.4771, and at 40° C. 1.4659 to 1.4730. The oil is dextrorotary. Lythgoe [*J. Am. Chem. Soc.*, **27**, 888 (1905)] determined the optical rotation of 44 samples of authentic castor oil at 20° C. in a 200-mm. tube and found from +23.4 to 26.1 (Ventzke), which corresponds to the usual polarimetric readings +8° to +9° by other workers. Dening and Renard tested 23 samples of Indian castor oil in the Redwood viscometer and found that the outflow of 50 cc. at 100° F. required from 1160 to 1190 seconds. Atkins [*Anaylst*, **44**, 287 (1919)] found that some Egyptian oils give abnormally low viscosities.

Composition of Castor Oil. Several attempts from time to time have been made by various workers to determine the composition of this oil. The most extensive investigation is that of Eibner and Munzing [*Chem. Absts.*, **19**, 3027 (1925); *J. Soc. Chem. Ind.*, **44**, B679 (1925)]. They found that a sample of the oil contained the following percentages: ricinoleic acid 80, oleic acid 9, linoleic acid 3, stearic and dihydroxystearic acids 3. Ponjutin and Rapoport [*Chem. Umschau*, **37**, 130 (1930)] examined a sample of oil and report the following percentages of constituents: oleic acid 7.0, linoleic acid 3.5, ricinoleic acid 86, stearic acid 0.3, dihydroxystearic acid 1.8, unsaponifiable 1.8. The glycerides are ricinolein, diricinoleostearin, and dioleoricinolein.

H. P. Kaufmann and H. Bornhardt [*Fette u. Seifen*, **46**, 444 (1939)] examined the mixed fatty acids from castor oil and reported the following results: Sap. V. 195.4; Iod. No. (Kaufmann) 85.8; SCN V. 83.0; OH No. (Pyridine method) 165.7. The percentages of constituents were as follows: ricinoleic 87.0, oleic 8.4, linoleic 3.1, dihydroxystearic 0.6, and saturated acids 2.4.

Tests for Castor Oil. H. S. Bailey [*The Cotton Oil Press*, **6**, No. 9, 35 (1923)] found that the petroleum ether solubility test proposed by Frabot [*Ann. chim. anal.*, **22**, 217 (1917)] was particularly suitable for the detection of adulteration of castor oil. The method as described by Bailey is as follows: Shake vigorously 20 cc. of the oil with 80 cc. of petroleum ether (B. Pt. 35° to 70° C) in a graduated glass-stoppered cylinder and place in a water bath at 20° C. until the layers completely separate. The lower layer of castor oil is increased by a certain proportion of the solvent, which in the case of pure castor oil amounts to 11 or 12 cc. Remove and evaporate 50 cc. of the petroleum ether solution and heat the residue at 100° C. until a constant weight is obtained. The weight multiplied by 5 is the Frabot number. Pure castor oil usually gives a number of 7.8 or 7.9 when petroleum ether of a Sp. g. 0.6322 is used. As different petroleum ethers dissolve varying quantities of castor oil and also as the solubility with a given solvent is affected by changes in temperature, it is necessary to run a control test with castor oil of known purity. The presence of other oils is shown by a proportional increase in the Frabot number. Following

these directions it is possible in most cases to detect as little as one per cent of adulteration. Frabot [*Ann. chim. anal.*, **23**, 7 (1918)] gives the volume increase and solubility of castor oil for a large number of petroleum distillates, ranging from petroleum ether 33.2° to heavy kerosene, sp. g. 0.7820. Bailey found that the solubility of the oil in the same solvent varied with the change in temperature about as much as did the solubility in different petroleum ethers at the same temperature, which shows the importance of making a control test along with that of the oil under examination.

The solubility of castor oil in alcohol is greater than that of any oil that might be used as an adulterant. The oil dissolves readily in absolute alcohol. Itallie stated one volume of oil dissolved completely in 2.4 to 2.94 volumes of 90 per cent of alcohol at 20° C. Dowzard [*J. Soc. Chem. Ind.*, **20**, 370 (1901)] found that 3 or 4 volumes of 90 per cent alcohol to one of castor oil were necessary. The well-known Finkener test [*J. Soc. Chem. Ind.*, **6**, 148 (1887)], which consists of shaking 10 cc. of the sample with 50 cc. of alcohol, Sp. g. 0.834, in a stoppered cylinder, is claimed to give a clear solution at 15° C. with pure castor oil, and if only 5 per cent of a foreign oil is present, the solution will be turbid even when warmed to 20° C. Frabot [*Analyst*, **43**, 40 (1918)] modified the Finkener test. He used 5 volumes of 95 per cent alcohol to one of the oil and cooled the mixture to below 20° C., and stated that the solution would remain clear unless a foreign oil was present. Trevithick and Lauro [*The Cotton Oil Press*, **6**, No. 7, 32 (1922)] called attention to the important fact that pure castor oil, which has stood some time after expression, does not dissolve completely in 90 per cent alcohol, although the oils examined when first obtained were completely soluble. These authors state, "While these solubility tests are valuable too much stress should not be laid on them."

H. B. Stocks [*Analyst*, **48**, 590 (1923)] observed that castor oil soap dissociates but little when dissolved in a large quantity of water as compared with soaps made from other commercial vegetable oils and animal fats. He has developed the following method for testing the purity of castor oil: Five grams of the oil is mixed with 40 cc. of 0.5*N* alcoholic potash and heated for a half hour under a reflux condenser to ensure complete saponification. The solution was exactly neutralized to phenolphthalein with *N* hydrochloric acid, transferred to a dish and evaporated to dryness. The soap was dissolved in hot water and washed into a 100-cc. flask, and after cooling, it was diluted to 100 cc. Ten cc. (=0.5 g. of oil) was added to 250 cc. of neutral distilled water, mixed, phenolphthalein added, and titrated with 0.1*N* hydrochloric acid. Castor oil from various sources required from 0.6 to 1.3, cottonseed 7.3 to 7.4, coconut 4.4 to 4.6, palm 8.2 to 8.6, palm kernel 5.2 to 5.3, rape 7.7 to 8.0, linseed 5.5 to 5.6, peanut 9.3 to 9.5, rosin oil 8.5, and tallow 8.7 to 8.8 cc. of the 0.1*N* acid. For other data and information, the original should be consulted. This test is much quicker and simpler than that of Lanes [*J. Soc. Chem. Ind.*, **26**, 597

(1907)], which is based on the insolubility of lead ricinoleate in petroleum ether.

Sometimes castor oil is adulterated with rosin oil, blown oils and other unheated oils. The addition of any of these oils will lower the acetyl value. Rosin oil is readily detected by the increase in the unsaponifiable matter. The addition of fatty oils which have not been blown lowers the specific gravity and the viscosity, in addition to increasing the solubility in petroleum ether as determined by Frabot test. It should be noted that rosin oil (like castor oil) is strongly dextro-rotary in the polarimeter.

Uses. The No. 1 oil is used for medical and technical purposes, and to some extent as a lubricant, but the No. 3 oil is used only for technical purposes in the crude state or after it has been refined. A large quantity is converted into the sulfonated castor oil of commerce, known for many years as Turkey red oil because of its use in dyeing cotton fabrics with alizarine. The production of sulfonated oils requires both skill and experience. Sulfonated castor and other oils are used in the dyeing of fabrics to give clearer and brighter colors, and as an aid in the finishing of cotton, linen, silk and leather. Castor oil is used in the manufacture of some kinds of transparent soap, textile soap, imitation leathers, sticky fly paper, typewriter inks, and lubricants. In regard to the use of castor oil in soap manufacture, N. Spasskii [*Chem. Absts.*, **23**, 725 (1929)] states that this oil increases the lathering power as well as the solubility of the soap in cold water. The addition of 20 per cent of castor oil to the fatty mixture greatly improves the properties of the resulting soap. It was formerly * used for lubricating aircraft motors of the rotary air-cooled type, and in some tropical countries the oil is used for the lubrication of heavy machinery, including locomotives.

Considerable quantities of the oil are used in the manufacture of nitrocellulose baking finishes. The oil is used as a raw material for the preparation of "perfume aromatics" and sebacic acid, an important ingredient for the synthesis of nylon fiber. Large quantities are converted into dehydrated castor oil, which, under various trade names, is sold as a drying oil to the enamel, paint and varnish makers. Blown castor oil is used for grinding lacquer paste colors and for other purposes where a plasticizing oil is required. Hydrogenated castor oil is sulfonated for use in the preparation of ointments.

Dehydrated Castor Oil. It has been known for many years that ricinoleic acid, the chief constituent of castor oil, could be dehydrated by heating it with a suitable catalyst. The hydroxyl group of the acid under these conditions combines with a hydrogen atom from an adjacent group to form water, thereby producing a second double bond. More

* Castor oil was a satisfactory lubricant for aircraft engines some years ago when clearances between moving parts were relatively large and rubbing velocity generally low. Constant reduction of clearances has made the use of such a high-viscosity oil practically impossible, due to its tendency to increase in temperature to a point where it burns out bearings, and to deposit a viscous residue in the engine. Castor oil also attacks metallic surfaces when hot and forms soaps which clog the oil system. Because of these disadvantages mineral oil has almost entirely replaced castor oil for this purpose.

recently, it was found that the same results could be obtained by using the oil, thus converting it into a product having marked drying powers. The dehydration results in changing the ricinoleic acid into 9, 12- and 9, 11-linoleic acids in about the ratio of three to one. The quantity of the conjugated 9, 11-octadecadienoic acid of the commercial products appears to range from 17 to 26 per cent, and the 9, 12-isomer, from 59 to 64 per cent. The commercial dehydrated products are made (patented processes) by heating castor oil from 180 to 280° C. with 0.2 to 0.5 per cent of sulfuric acid, acid sodium sulfate, phosphoric acid, specially prepared tungstic acid after being heated from 225 to 305° C. and phthalic anhydride, using a small enough quantity so as to avoid undesirable ester formation.

The commercial products are marketed under various trade names, some of which are called Castung, Collanoll, Isoline, P.G.D. oil, Synthenol, and Synouryn. They give iodine numbers by the Wijs procedure varying from about 109 to 140. The diene values (a measure of the quantity of linoleic acid with conjugated double bonds and to which the unique drying powers of these products are largely due) for the most part range from 13 to 22 (90.7 for 9, 11-linoleic acid). The composition of nine samples is given, and the analysis of dehydrated castor oil is discussed by G. W. Priest and J. D. von Mikusch [*Ind. Eng. Chem.*, **32**, 1314 (1940)]. Attention is called also to the investigation by W. C. Forbes and H. A. Neville on catalysis and catalytic methods for increasing the unsaturation in long-chain fatty acids of castor oil [*Ind. Eng. Chem.*, **32**, 555 (1940)]. Proposed specifications for dehydrated castor oil are discussed by I. M. Colbeth [*Pt. Oil Chem. Rev.*, **103**, No. 14, 7 (1941)] and F. Scofield [Circ. 621 (1941) of the Nat'l. Pt., Var. Lacquer Association].

Dehydrated castor oil, as such or after suitable bodying (blown and stand oils), particularly since 1937, is being used much more extensively for making enamels, paints, varnishes including overprint and lithographic varnish for the printing industry. The curtailment of the usual tung oil supplies in recent years accounts only in part for the notably increased use made of the product. It should be observed that it serves only as a partial substitute for tung oil. Even when ample supplies of tung oil become available again, dehydrated castor oil will continue to be used in cases where color retention and film flexibility are of importance. On account of its non-yellowing properties, C. W. A. Mundy [*J. Oil and Col. Chem. Soc.*, **24**, 183 (1941)] reported that it was particularly useful in making oil fabric for use in place of window glass.

During 1937, the Munzel Chemical Works at Hausen, Switzerland, were granted a patent (Swiss Pat. 193,931) on a process for making "Trienol" (a synthetic tung oil) from castor oil. The first step is dehydration by a special procedure, which produces conjugated double bonds in the ricinoleic acid. After removal of dihydroxystearic acid, oleic acid, etc. (normal constituents of castor oil) the product, named Dienol, is treated with hypochlorous acid, and finally, to produce

Trienol, with triple-conjugated double bonds. The introduced chlorine and hydroxyl group are eliminated. The characteristics of Trienol are as follows: Sp. g. at 20° C, 0.928; $N_D^{20°}$ 1.5175; Iod. No. 244.5; Sap. V. 190; Acid V. 8.2; Unsap. 0.57%; Heat test 12 miuntes.

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Seed Oil of Ricinus zanzibarinus. The plant which, according to Bloemendaal [*Pharm. Weekblad.* **42**, 70 (1905)], is a native of East Africa was introduced many years ago into South America. It is reported that it is a large producer of fruit when grown in tropical regions.

A. Steger, J. van Loon, and C. Smelt [*J. Soc. Chem. Ind.*, **55**, 41T (1936)] have examined the seed and oil. The large, black, glossy seed which came from Paraguay, consisted of 26 per cent of shell and 74 of kernel. The kernels, which weighed from 0.7 to slightly more than 1 gram, contained 65.1 per cent of oil. The extracted oil gave the following characteristics: $N_D^{20°}$ 1.4788; Iod. No. (Wijs) 88.4; SCN-V. 82; Sap. V. 179.2; Acetyl V. 145; R.M.V. 0.5; Unsap. 0.5%; Sat. acids (Bertram) 0.5%; volatile 4.7%. It will be noted that the oil is somewhat more unsaturated than that from *R. communis* and contains notably less saturated acids, which for the latter oil range from 1.5 to 3.0 per cent. The saturated dihydroxy acids which are present in both oils are not included with the other saturated acids separated by the Bertram method. By other means it was found that the total saturated acids amounted to 1.1 per cent of the fatty acids of the oil under discussion, which also contained 92.3 of reicinoleic and 6.6 of linoleic acid. It remains to be determined whether or not any oleic acid is present in this oil.

Cay-Cay Fat. This fat is obtained from the seeds of the fruit from the tree *Irvingia oliveri* (Simarubaceae), which is found in Annam, Cambodia and Cochin China. The fruit is ovoid or ellipsoidal, the size of a plum. The fibrous mesocarp encloses a nut, the size and shape of an almond. The shell is very hard. The kernels, which amount to about 20 per cent of the nut, contain from 52 to over 70 per cent of fat.

The natives allow the fruits to remain where they fall for about 2 months, during which time the fibrous mesocarp becomes soft. Then the nuts are removed and cracked to obtain the kernels from which the fat is expressed. The difficulty of removing the kernels from the nuts has prevented the preparation of any quantity of the fat for exportation, and even less fat is now obtained than formerly.

Depending upon the quality the fat is nearly white, pink, or greenish yellow. That of the better quality was used for edible purposes and the rest for making candles.

E. Bontoux [*Mat. grasses,* **1,** 1277 (1908)] reported the following characteristics: Sp. g. at 40° C. .9128 to .9130; Sap. V. 235 to 237; Iod. No. 4 to 6.8; R.M.V. 0.6 to 0.75; Unsap. 0.16 to 0.42%; M. Pt. 38° to 39.7°. He found that the fat contained about 5 per cent of oleic acid, 30 to 35 of lauric acid, and 65 to 70 of myristic acid, as triglycerides, but undoubtedly small quantities of palmitic and stearic acids are also present, as in the case of the related dika butter.

Two Other Irvingia Seed Fats. J. Pieraerts [*Bull. Agr. Congo Belg.,* **13,** 460 (1922)] examined the seed fat of *Irvingia smithii* with the following results: Sap. V. 237.3; Iod. No. 2.96; M. Pt. 38°-39° Wijs (*Vetten, Olien en Wassen,* Haarlen, **1906,** 102) reported the following characteristics for the seed fat of *Irvingia malayana:* Sp. g. at 40° C. 0.914; Iod. No. 5.2; R.M.V. 0.42; M. Pt. 39°.

Chinese Vegetable Tallow. This fat or tallow is obtained from the fruit of the tree *Stillingia sebifera* (formerly classified as *Sapium sebiferum, Croton sebiferum,* etc.) of the *Euphorbiaceae.* This tree, which reaches a height of 40 or 50 feet in favorable localities, is native to China, but is now found in northern India, Southern Japan, and the East Indies. It was introduced a good many years ago into the United States, notably California, South Carolina, Florida, Georgia and Texas. The tree thrives best on loamy soils in low situations near water. It comes into bearing when four or five years old, and at the eighth year the crop of seeds ranges from 17 to 25 pounds, whereas fully matured trees bear up to 75 pounds of seed. The fruits are borne in small clusters. At maturity, the outer brown husks split open and expose the three oval "berries," each of which contains a seed. The thick white mesocarp contains the tallow. The "berries" weigh from 0.2 to 0.3 gram. Those from American trees examined by the writer and his assistants contained the following percentages of constituents: Moisture 3.9, tallow 32.4, seed shells 37, kernels 26.7, and oil from kernels 14.25. The kernels contained 53.4 per cent of a liquid oil (see stillingia oil); after extraction of the tallow by solvent, the dried mesocarp residue was found to contain 11.58 of proteins, 29.75 of crude fiber, 48.77 of nitrogen-free extract and 9.9 per cent of ash. The extracted fat had the following characteristics: Sp. g. at 50°/25° 0.8918, $N_D^{60°}$ 1.442; M. Pt. 52°-53° C.; Iod. No. (Hanus) 27.2; Sap. V. 209.5; Acetyl V. 1.4; R.M.V. 0.4; Pol. No. 0.5; Unsap. 0.39%; Sat. acids 66.4%; Unsat. acids 28.6%.

T. P. Hilditch and J. Priestman [*J. Soc. Chem. Ind.,* **49,** 397 T (1930)] examined an authentic sample of the tallow extracted by solvents from seeds collected in Florida and Texas and found that the fatty acids consisted of the following percentages of constituents: oleic 26.9, lauric 1.9, myristic 3.7, palmitic 66.3 and stearic acid 1.2. The fatty acids from a Chinese sample consisted of 2.5 lauric, 3.6 myristic, 57.6 palmitic, 1.8 stearic and 34.5 per cent of oleic acid. They found that fully saturated glycerides were present to the extent of 25 to 28 per cent. In the mixed glycerides fraction, oleodipalmitin pre-

dominated. The American sample contained 27.6 per cent of fully saturated glycerides (largely tripalmitin) and over 60 per cent of mono-oleo-di-saturated glycerides (chiefly oleodipalmitin).

The Chinese tallow (prima) melts from 45° to 50° C., and has the following characteristics: $N_D^{40°}$ 1.4560 to 1.4574; Sap. V. 200 to 207; Iod. No. 20 to 29; Unsap. 1 to 1.3%; R.M.V. 0.2 to 1.2; Pol. No. 0.5 to 0.6; Acid V. 4 to 25; Titer 45° to 53°.

In China, two methods are used for extracting the tallow. One is based on steaming the "berries" in perforated vessels, through which the molten tallow is forced; the other is based on separating the mesocarp by means of fluted rollers without fracturing the seeds, and the tallow is obtained by hot pressing. The product obtained by either method is known to the trade as prima vegetable tallow. In some localities, the whole "berries" are crushed and hot pressed. This yields a soft tallow due to the presence of the liquid kernel oil; it is marketed as "secunda" tallow. The prima grade is hard and brittle.

The tallow is used chiefly for the manufacture of soap and candles. That exported is in the form of blocks or cakes and varies from a very pale to a dark green color. Formerly the exports ranged from 10,000 to 17,000 tons per year, but in recent years they have been very much smaller.

At the present time, there is no production of the tallow in the United States, although in one or two southern localities groves of trees were planted some years ago with a view to the production of the tallow for making soap; but owing to the cost of collecting the fruits, which ripen gradually over a period of some weeks, the ventures were not successful. Also in this country, shortly after maturity, the outer or mesocarp part of the fruit turns dark because of fungus attack, which finally results in its destruction, leaving the blackened seeds still attached to the tree.

Some references dealing with this tallow are as follows:

Klimot, *Monatsh.*, **24**, 408 (1903); **26**, 567 (1905).
Sprinkmeyer and Diedrichs, *Z. Nahr. Genussm.*, **23**, 588 (1912).
Wagner and Lampart, *Z. Nahr. Genussm.*, **27**, 731 (1914).
Diedrichs, *Z. Nahr. Genussm.*, **28**, 222 (1914).
Nakamori, *Z. Ol. Fette. Ind.*, **2**, 394 (1920).
Arch. Pharm., **263**, 186 (1925).
"Chinese Vegetable Tallow," *Chem. Trade J.*, **77**, 722 (1925); **85**, 151 (1929).
"Chinese Vegetable Tallow. Source, Preparation, Sampling and Testing," K. Ho. C. T. Chen, and P. P. Hsu, *Bull. Imp. Inst.*, **36**, 553 (1938); *Oil, Pt. Drug Reptr.*, Nos. 8, 9 and 10 (1938).

Chufa Oil. Chufa oil, which is sometimes called sedge or earth almond (Erdmandeloel) oil, is obtained from the small tuber (when dry it weighs 0.2 to 0.5 gram) of the sedge, *Cyperus esculentus*, native to southern Europe and Africa. It has been cultivated from very early times in Italy and northern Africa. Now it is grown in many countries. In Spain, the freshly gathered tubers are cleaned and pressed. The separated emulsion of juice and oil is cooled or frozen (Horchata de chufas) and consumed in large quantities as a drink.

In the southeastern portion of the United States, chufas have been cultivated for some years and used to fatten hogs.

The European chufas contain from 20 to 28 per cent of oil, 15 to 20 per cent of sucrose, besides starch, gums, etc. The expressed oil is yellow and has a mild fine flavor. Power and Chestnut [*J. Agric. Research,* **26,** 69 (1923)] investigated chufas from Virginia and found that they contained 28 per cent of oil, 14 of sucrose, and about 12 of starch in addition to reducing sugars, gum, etc. Baughman and Jamieson (*ibid,* **26,** 77) examined the four kilos of oil extracted with petroleum ether by Power and Chestnut with the following results: Sp. g. 25°/25° 0.9120, $N_D^{20°}$ 1.4680, Iod. No. (Hanus) 76.5, Sap. V. 191.5, Acetyl V. 10.5, Sat. Acids 17.1%, Unsat. acids 75.8, R.M.V. 0.2, Pol. No. 0.3, and Unsap. 0.6%. Composition: Glycerides of myristic acid 0.01, palmitic acid 11.8, stearic acid 5.2, arachidic acid 0.5, lignoceric acid 0.3, oleic acid 73.3, and linoleic acid 5.9 per cent.

Hill and Twedomedow [*Ber.,* **22,** 1742 (1889)] reported that the chufa oil which they investigated contained myristic acid. Pieraerts [*Mat. grasses,* **16,** 6674 (1924)] confirmed the presence of myristic acid in chufa oil. He stated that the saturated acids (20% of the oil) contained about 40 per cent of myristic acid and 60 per cent of palmitic acid. These figures were based on the fractional precipitation of the barium salts and the analysis of the fractions. With this procedure it is not surprising that he did not detect the presence of stearic, arachidic and lignoceric acids, as reported by Baughman and Jamieson. The oil investigated by Pieraerts had the following characteristics: Sp. g. 15°/15° 0.9176, $N_D^{25°}$ 1.4650, Sol. Pt. +3°, Sap. V. 191.3, Iod. No. 76.9, and Unsap. 0.62 per cent. These figures are about the same as those reported for the American oil (given above), which contained only a trace of myristic acid (0.01%). Since the chufa was introduced from Europe into America the differences in respect to the quantity of myristic acid present with oils are not understood.

F. Josephs [*Fette u. Seifen,* **45,** 292 (1938)] examined the oil from chufas grown in Germany with the following results: Sap. V. 190.4; Iod. No. 88.4; SCN. V. 74.6; Acid V. 0.7. The mixed fatty acids contained the following percentages of constituents: oleic 67.5, linoleic 15.2, and saturated acids 17.3.

Coffee Bean Oil. This oil is found in the seeds of the fruit from the small tree *Coffea arabica* and the much larger (lowland) tree *Coffea liberica,* belonging to the *Rubiaceae.* Commercial coffees come almost entirely from varieties of *Coffea arabica.*

Raw (green or unroasted) coffee usually contains about 10 per cent of oil and wax extractable with petroleum ether. The wax amounts to about 10 per cent of this mixture.

The characteristics are as follows: Sp. g. at 15° C. 0.9438 to 0.9453; $N_D^{25°}$ 1.4678 to 1.4691; Sap. V. 160 to 180; Iod. No. 79 to 98; R.M.V. 0.5 to 0.7; Pol. No. 0.2 to 0.3; Unsap. 6.1 to 10%; Sat. acids 37 to 40%; Unsat. acids 51 to 54%.

R. O. Bengis and R. J. Anderson [*J. Biol. Chem.*, **105**, 139 (1934)] examined the oil extracted from a mixture of Brazilian, Colombian and Venezuelan coffees, before and after roasting, as well as that from an aged roasted coffee. The oil extracted from the unroasted coffee by petroleum ether had the following characteristics: $N_D^{25°}$ in chloroform—17.01°; Sap. V. 179.3; Iod. No. (Hanus) 97.8; Unsap. 9.0%; Sat. acids 39.4% and Unsat. acids 52.3%. The oil contained the following percentages of acids: oleic 22.6, linoleic 25.2, Unsat. hydroxy acid 4.5, palmitic 33.4, stearic 4.4 and teracosanoic 1.6. For data on the oils from roasted and aged roasted coffee, the original articles should be consulted, as well as a later one by Bengis [*Ind. Eng. Chem.*, **28**, 290 (1936)].

Attention is called also to the following references:

"The Chemistry of the Coffee Bean. I. Concerning the Unsaponifiable Matter of the Coffee Bean Oil," R. O. Bengis and R. J. Anderson, *J. Biol. Chem.*, **97**, 99 (1932).

"Coffee Bean Fat and Wax," F. Munk, *Allegem. Oel Fett Ztg.*, **29**, 13 (1932).

"The Characteristics and Composition of Coffee Bean Oil," H. A. Schuette, M. A. Cowley and C. Chang, *J. Am. Chem. Soc.*, **56**, 2085 (1934).

"Composition of the Wax-like Substance from Coffee Berry," H. Wagner, *Z. Unters. Lebensm.*, **76**, 1 (1938).

"Coffee Oil," K. H. Bauer and R. Neu, *Fette u. Seifen*, **45**, 229 (1938), *Chem. Absts.*, **32**, 9534 (1938).

Crotalaria Oil. This oil is found on the pods of the *Crotalaria Valentonii*, belonging to the *Leguminosae*, which is grown as a cover crop in Florida. A sample of the nearly full grown pods gave 9.2 per cent of a brownish yellow oil by extraction with petroleum ether and 6.2 per cent of oil was obtained from another sample of fully matured pods. The seeds contained less than 3 per cent of oil. The pods have the appearance of being supersaturated with oil, and grease everything coming in contact with them.

The oil which was extracted from the green pods was examined in the author's laboratory with the following results: Sap. V. 183.4; Iod. No. (Hanus) 88.2; Acetyl V. 18.1; Acid V. 169; $N_D^{25°}$ 1.4670.

Although the oil was examined directly after extraction, the high acid value indicates that a considerable portion of it normally consists of free fatty acids.

Da (Ambari Hemp) Seed Oil. This oil is found in the seeds of the plant *Hibiscus cannabinus* of the *Malvaceae*, which grows wild in the Transvaal and Natal, but which is cultivated in many parts of tropical Africa. The plant grows from 5 to 11 feet high and has a stem one-half to three-fourths inch thick. It is cultivated chiefly for its fiber [*Bull. Imp. Inst.*, **18**, 430 (1920)]. The seed contains about 20 per cent of oil for which the following characteristics have been recorded; [cf. *Bull. Imp. Inst.*, **24**, 479 (1926)]: Sap. V. 193.2; Iod. No. 94; Acid V. 28.7; Unsap. 3.43%. Other observers report characteristics: Sp. g. at 15° C. 0.9091 to 0.9255; $N_D^{40°}$ 1.4659; Sap. V. 187-189; Iod. No. 90 to 99; R.M.V. 0.5; Sat. acids 25%. [*See* Decker, *Pharm. Weekblad*, **59**, 1296 (1922); Pieraerts, *Mat. grasses*, **19**, 7725 (1927).]

M. R. Bauman [*Chem. Absts.*, **23**, 3117 (1929)] examined the oil from Persian seed, under the name of Kenaph seed oil, with the following results: Sp. g. at 15° C. 0.9261; Sap. V. 194.2; Iod. No. (Hübl) 100; Unsap. 0.4%. Composition: oleic 45.3, linoleic 23.4, palmitic 14, and stearic acid 6 per cent.

Dika Butter or Fat (Irvingia). This fat is obtained from the seeds of the fruit from the tree *Irvingia gabonensis* (*Simarubaceae*), which is found in many localities of West Africa. The fruit is a green drupe (2 × 2.5 inches). The fleshy mesocarp, which has a strong turpentine-like odor, encloses an irregularly oval, elongated, horny-shelled nut in which there is a kernel the size of a pigeon's egg [*Bull. Imp. Inst.*, **20**, 513 (1922)]. The nuts contain from 18 to 20 per cent of kernels with 54 to about 70 per cent of fat. The kernels are used by the natives in the preparation of Dika Bread (Dika or Gaboon Chocolate), a staple article of food [Bolton and Hewer, *Analyst*, **42**, 35 (1917)]. Lewkowitsch [*Analyst*, **30**, 394 (1905)] examined the nuts, kernels, and fat, and observed that the sun-dried kernels kept much better than those left in the nuts. This fat can be used for edible purposes and for making soap, and the press cake could be fed to stock, but little or none of the fat or the kernels is exported.

The characteristics are as follows: Sp. g. at 40/40° C. 0.914; $N_D^{40°}$ 1.4500 to 1.4542; Sap. V. 241 to 250; Iod. No. 1.8 to 9.8; R.M.V. 0.2 to 0.4; Pol. 5.5; Unsap. 0.3 to 0.8%; M. Pt. 38 to 41° C.; Titer 35 to 38° C.

W. J. Bushell and T. P. Hilditch [*J. Soc. Chem. Ind.*, **58**, 24 (1939)] obtained kernels from Sierra Leone, Africa, having 61 per cent of fat. The solvent-extracted fat gave an iodine number of 1.8, a saponification equivalent of 222.6 and contained 0.4 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: capric 3.1, lauric 58.6, myristic 33.4, palmitic 2.0, stearic 1.1 and oleic 1.8. The percentages of the major glycerides in the fat were as follows: Dilauromyristin 64.5, laurodimyristin 13.5 and caprolauromyristin 15.0.

J. Pieraerts [*Bull. Agric. Congo Belg.*, **13**, 68 (1922)] examined a fat giving an iodine number of 9.8. The mixed fatty acids contained the following percentages of constituents: lauric 19.5, myristic 70.5 and oleic 10.

Attention is called to the great difference in the composition of these two dika fats from widely different localities. This would indicate that there is more than one variety of *I. gabonensis*. Further investigation of authentic samples of this fat from the various localities where the tree grows is desirable.

Collin and Hilditch [*J. Soc. Chem. Ind.*, **49**, 138T (1930)] examined the fat from the kernels of *Irvinga barteri*, which were produced in Nigeria. This fat gave an iodine number of 9.1 and contained 1.05 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: lauric 38.8, myristic 50.6, and

oleic acid 10.6. The fat consisted chiefly of lauro-di-myristin and di-lauro-myristin. No evidence was found of the presence of any simple triglycerides.

The seeds of the Asiatic species *Irvingia oliveri* yield the so-called cay-cay fat.

Djave or Adjab Butter. This soft butter, which is ordinarily a liquid, unless large quantities of free fatty acids are present above 25 to 26° C., is obtained from the seeds of the tree *Mimusops djave* (*Sapotaceae*), native of West Africa. It is found in the Cameroons, Gold Coast, Gaboon, Nigeria, and elsewhere. On the Gold Coast the seeds or nuts are known as Abeku, Baku, or Mahogany nuts. In other localities, the tree (and nuts) are called Njave and Djave. In commerce, the lumber from this tree is known as Cameroon mahogany. The seeds, which are about 2.5 to 3 inches long and 1.25 broad, average about 15 to 17 grams in weight. The kernels resemble those of the Shea nut, and contain from 60 to 70 per cent of a yellow oil, which below 20° C. solidifies to a nearly white mass of soft consistency. Depending upon the source, the kernels amount from about 35 to over 65 per cent of the seeds. The natives, who use the oil for edible and other purposes, extract it usually by boiling the crushed seeds in water. The traces of hydrocyanic acid commonly present, because of enzymic action on the cyanogenetic glucosides in the kernels, can be removed by steaming the oil. When properly refined, the product is edible, but in Europe it is only used now for making soap. Owing to the presence of poisonous glucosides and saponins, the press cake is not used for feeding stock nor has it apparently much value as a fertilizer.

The usual range of the characteristics reported by various investigators is as follows: Sp. g. at 40° C. 0.8979, at 100/15° C. 0.860; $N_D^{40°}$ 1.4605 to 1.4610; Sap. V. 182 to 188; Iod. No. 56 to 65; Unsap. 2 to 3%, sometimes higher; R.M.V. 0.8 to 2; Titer 46° to 48°.

Freundlich [*Analyst,* 33, 330 (1908)] has proposed a test typical for this oil (in the crude condition) which is based on the saponification of the sample with alcoholic potassium hydroxide. After cooling and filtering, the acidification of the filtrate with hydrochloric acid is stated to yield a violet pink color in the aqueous layer of the mixture; the refined product would not be expected to give this test. The reliability of this color reaction requires further study.

According to Ran and Simonsen [*J. Soc. Chem. Ind.,* **41**, 902A (1922)], they examined a sample of oil from the seeds of *Mimusops elengi.* The seeds contained 16 per cent of oil which consisted of glycerides of oleic, palmitic, stearic, and a higher-melting saturated acid which was not identified.

Elm-tree Seed Oil. Elm seeds contain about 25 per cent of oil. The range of characteristics reported for oils from the seeds of various species of elms are as follows: Sp. g. 15° .921 to .928; Sap. V. 264 to 279; Iod. No. 15.9 to 37.9; R.M.V. 2.0 to 3.8; Pol. No. 33 to 41; Sol. Pt. 2.0° to 7.1°; Unsap. 1. to 1.4 per cent.

H. A. Schuette and C. M. Lunde [*Oil and Soap,* **13,** 12 (1936)] have examined the oil and seeds of the American elm, *Ulmus americana (Ulmaceae).* The seeds contained the following percentages of constituents: fat 25.55, proteins 42.00, carbohydrates 22.80, fiber 4.40, and ash 5.25. The more important characteristics were as follows: Sp. g. 20/20° 0.9288; $N_D^{20°}$ 1.4554; Sap. V. 273.1; Iod. No. (Wijs) 24.1; SCN V. 16.2; R.M.V. 2.1; Pol. No. 33.9; Unsap. 1.00 per cent. It was calculated that the fatty acids consisted of 82.82 per cent of saturated acids, 8.83 per cent of oleic acid and 8.36 per cent of linoleic acid. Evidence was also obtained that the oil contained almost 50 per cent of capric acid. M. A. Pawlenko [*Chem. Rev. Fett. Harz. Ind.,* **19,** 43 (1912)] was probably the first investigator of the oil to report the presence of a large quantity of this acid.

Katio-Seed Oil. This oil, which is also known locally as Katjoe, Katjia, Kachian, etc., is obtained from the seeds of the tree *Madhuca mottleyana* (*Sapotaceae*), which is abundant in the northwestern portion of Borneo, particularly in the swamps in the vicinity of Sarawak. It is also found in Malaya and elsewhere. The seeds are similar to those of *M. latifolia,* but smaller, weighing 0.3 to 0.4 gram. The thin shell amounts to from 25 to 32 per cent of the seeds. The kernels contain from 50 to about 58 per cent of oil, which is of pale yellow or greenish color when solid (below 15°). The oil is extensively used by the natives for edible purposes, but to date it has not become a product of any commercial importance either in America or Europe.

The characteristics of this oil, samples of which have been examined by Bolton and Revis, Brooks, and at the Imperial Institute (at various times), are as follows: Sp. g. at 15° C. 0.9173; $N_D^{40°}$ 1.4609 to 1.4616; Sap. V. 189 to 193; Iod. No. 53 to 66; Unsap. 0.4 to 0.5%; R.M.V. 0.6 to 0.8; Sol. Pt. 14° to 15°; Titer 36° to 37°.

J. Zimmerman [*Chem. Weekblad,* **30,** 657 (1933)] examined a sample of the oil. It gave an iodine number of 66-7, a saponification value of 191, and a Reichert-Meissl Value of 1.52. The mixed fatty acids contained the following percentages of constituents: palmitic 10.17, stearic 18.56, oleic 68.77 and linoleic acid 2.49.

Phulwara (or Indian) Butter. This product is obtained from the seed of the fruit of the tree *Madhuca* (formerly Bassia) *butyracea* (Nat. order, *Sapotaceae*), which is found up to an altitude of about 15,000 feet, from the Ganges to Bhutan, India. This tree, which reaches a height of about 70 feet, produces fleshy, green, ovoid fruits that contain from 1 to 3 seeds. The seeds average about 0.8 gram in weight and contain about 50 per cent of oil. The kernels contain from 60 to 65 per cent of oil which, when expressed, is almost white and somewhat stiffer than lard. The better grades have little flavor and good keeping qualities. As it is largely used by the natives for edible and other purposes, little is available for export.

This butter has been examined by Lewkowitsch, Bolton and Revis, The Imperial Institute, and by Diedrichs. The characteristics are as

follows: Sp. g. at 100°/15° 0.856 to 0.862; $N_D^{40°}$ 1.4552 to 1.4659; Sap. V. 191 to 200, Iod. No. 40 to 51; R.M.V. 0.4 to 4.3; Unsap. 1.4 to 5% (usually 2 to 2.8%); M. Pt. 39° to 51° C.; Titer 48° to 52°.

W. J. Bushell and T. P. Hilditch [*J. Soc. Chem. Ind.*, **57**, 48 (1938)] have examined the nuts and their fat. The nuts contained 76 per cent of kernels having 61 per cent of fat. The fat, which was extracted with petroleum ether, gave a saponification equivalent of 285.1, an iodine number of 40.6, an acid value of 13, and contained 2.1 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: palmitic 56.6, stearic 3.6, oleic 36.0, and linoleic acid 3.8. A very small quantity of myristic acid may have been included in the figures given for the palmitic acid. From the extensive investigation made on this fat, it was concluded that it contained about 62 per cent of oleo-dipalmitins, 23 of palmito-dioleins, 7 of oleo-palmito-stearins, and 8 of tripalmitin. There may also be present very small quantities of stearo-dioleins and triolein. The terms oleo and olein include also the linoleic acid, the total quantity of which in the fat is small. It should be mentioned that this fat contains much more fully saturated glycerides and much less stearic acid than the other *Sapotaceae* seed fats which have been investigated. Also, it contains an unusually large percentage of palmitic acid.

Shea Butter. This fat is obtained from the nuts of different varieties of the large tree *Butyrospermum parkii,* (*Sapotaceae*) which is particularly abundant on the West Coast of Africa and in the Sudans. In the dried condition, the fruit, which is the size of an ordinary plum, consists of a thin, brownish-red crinkled shell, loosely enclosing a brown, egg-shaped seed. The kernel is enclosed in a fragile shell. According to its origin, the shell ranges usually from 35 to 38 per cent of the seed, but sometimes it amounts to about 50 per cent. The seeds or nuts average about 3 to 3.5 grams in weight. The kernels contain usually from 45 to 55 per cent of fat which at ordinary temperatures is a solid. In trade, it is known as Shea butter, Bambuk butter or Galam butter; native names are Karité, Cé, Kade, Kedempó, etc.

The fat is extracted in a crude manner by the natives. They remove part of the pulp, then bury the seed until the remainder has rotted. The kernels are removed, dried in the sun, then over small stoves, and ground to a paste between stones. The fat is separated by heating the ground material in water. The color of this product varies from a muddy brown to a greenish gray, and has a strong odor and taste. When prepared by modern methods, the color is much less; the refined product is almost white and has little or no odor or taste. The fat is difficult to refine, and when improperly refined, it does not keep well. G. De Belsunce (*Bull. Mat. Grasses,* inst. col. Marseille, **1926,** 55 and 195; **1927,** 14) describes a method for refining the native product which consists of first steaming the fat to remove the disagreeable odor and taste; then it is treated with a solution of sodium carbonate; after the separation of the soap stock, which floats, a regular caustic soda treat-

ment is made; and finally the fat is bleached with persulfate. It is claimed that refining the fat in this manner gives a much smaller loss than when it is refined directly with caustic soda.

The natives use the fat for edible purposes and as an illuminant. In Europe, where considerable quantities of both the nuts and fat are imported, the refined product is used as a cooking fat, and the "oleine" in the manufacture of margarin; the "stearine" as well as the hydrogenated fat is used at times as a cacao butter substitute. The presence of considerable unsaponifiable matter reduces its value for soap making, but contrary to many statements, the unsaponifiable matter does not interfere with its use for edible purposes.

In Europe, the press cake and extracted meal, which are rich in carbohydrates but low in protein (10 to 12%), are used in making "compound cakes" for feeding cattle.

Characteristics. The usual range of the characteristics is as follows: Sp. g. at 15° C. 0.917 to 0.918; $N_D^{40°}$ 1.4635 to 1.4668; Sap. V. 178 to 189; Iod. No. 56 to 65; R.M.V. 1.4 to 2.5; Unsap. 2.2 to 11%; M. Pt. 33 to 42°; Titer 52 to 53.5°.

Bolton and Revis examined the oleine and stearine fractions of the fat. Oleine: Sap. V. 181.6; Iod. No. 62.3; Unsap. 7.7%; R.M.V. 2.16; Pol. No. 0.72; Sol. Pt. 24°. Sterine: Sap. V. 179.7; Iod. No. 51.9; Unsap. 6.25%; Sol. Pt. 34.2°.

Composition. T. P. Hilditch and S. A. Saletore [*J. Soc. Chem. Ind.*, **50**, 468T (1931)] examined a sample of refined Shea butter which gave a saponification equivalent of 314.2, an iodine number of 57.3, and contained 9.5 per cent of unsaponifiable matter. The percentages of the components of the mixed fatty acids were as follows: myristic 0.4, palmitic 8.5, stearic 35.9, oleic 49.9, and linoleic 5.3. The fat contained 2.3 per cent of fully saturated glycerides, approximately 30 of oleo-disaturated, and 65 of dioleo-monosaturated glycerides, on the assumption that triolein probably is absent or not present in larger quantity than the fully saturated glycerides. The small amount of linoleic acid is included with the oleic glycerides. These authors discuss the entirely different but misleading results obtained by Bougault and Schuster [*Compt. rend.*, **193**, 362 (1931)] with the latter's investigation of this fat.

T. G. Green and T. P. Hilditch [*J. Soc. Chem. Ind.*, **57**, 49 (1938)] have made a further investigation of another sample of shea butter. The neutralized fat gave a saponification equivalent of 305.5, an iodine number of 59.1, and contained 7.3 per cent of unsaponifiable matter. The percentages of the components of the mixed fatty acids were as follows: palmitic 5.7, stearic 41, oleic 49 and linoleic 4.3. A small quantity of myristic acid also appeared to be present. In the "liquid" acid fraction, separated from the mixed fatty acids, cinnamic acid was found, which on the basis of the fat amounted to 1.4 per cent. It came from a non-glyceride constituent of the fat. The approximate percentages of the major types of glycerides are as follows: stearo-di-oleins 45, oleo-distearins 35, palmito-dioleins 10, and probably not more

than 5 per cent of palmito-stearins and triolein. The presence of a similar quantity of oleopalmito-stearin is also possible. The small quantity of linoleic acid is included in the terms oleo and olein used above. The linoleic acid, however, is segregated in this and similar fats in the di- or tri-unsaturated glycerides. For other details and data of this extensive investigation, the original should be consulted.

The unsaponifiable constituents of shea butter have been investigated by I. M. Heilbron, G. L. Moffet and F. S. Spring, [*J. Chem. Soc.* **1934,** 1583].

Attention is also called to the following references:

"The Feeding Value of Shea Nut Cake," *Bull. Imp. Inst.*, **29,** 65 (1931).
"Shea Nuts from Nigeria," *Bull. Imp. Inst.*, **29,** 407 (1929); **31,** 334 (1933).
"Shea Nuts from the Gold Coast," *Bull. Imp. Inst.*, **30,** 282 (1932).
"Shea Nuts," H. W. Avis, *Food Mfr.*, **8,** 95 (1933).
"Unsaponifiables of Shea Butter," Bauer and Umbach, *Fette u. Seifen*, **1937,** 283; *Oil Col. Trds. J.*, **92,** 1051 (1937).
"Shea (Sudan) Kernels and Butter," *Bull. Imp. Inst.*, **33,** 289, (1935).

Dumoria Oil. This oil is obtained from the seeds of *Dumoria africana,* a native of Africa. The seeds weigh from 11 to 24 grams. The kernels contain about 32 per cent of fat which when extracted is pale yellow and almost tasteless. J. Pieraerts, J. Adriaens and J. Meulenberg [*Chem. Absts.*, 24, 3665 (1930)] examined the fat with the following results: Iod. No. 42.8 and 47.5; Sap. V. 186-7; Acetyl V. 6 and 6.6; R.M.V. 0.84 and 1.16; Unsap. 0.9%; Pol. No. 2.67; Acid V. 12 and 17; Solid Acids 46%, consisting chiefly of stearic acid along with a small quantity of palmitic acid. The characteristics were determined both on the cold- and hot-expressed oils. The large quantity of stearic acid present is noteworthy.

Ebor Seed Butter. This fat or butter is found in the seeds from the tree *Dipteryx oleifera,* belonging to the *Leguminosae,* which is found in various parts of Central America. The seeds, which resemble tonka beans but have no odor, are about 2 inches long and contain about 20 per cent of a soft fat with a flavor which prevents its use for edible purposes, but which may be removed by the deodorization process.

The characteristics which have been reported, are as follows: $N_D^{40°}$ 1.4600; Sap. V. 181; Iod. No. 72.5; Unsap. 1.6%.

Tonka Bean Oil. This oil is found in the seed of the tree *Dipteryx odorata,* of the *Leguminosae* which grows in Central and South America. It is being cultivated in Malaya, Trinidad, Venezuela, and perhaps elsewhere. The fruit is a pod about two inches long, which contains a single shiny-black, fragrant seed, which after a suitable curing process is used chiefly for scenting snuff and tobacco; but some of the oil is extracted and used as a flavoring which is due to coumarin.

C. D. V. Georgi and G. L. Teik [*J. Soc. Chem. Ind.*, **50,** 318T (1931)] stated that the average weight of Malayan beans was 3.4 g. and that they contained 26.5 per cent of oil. The characteristics of the oil were as follows: $N_D^{27°}$ 1.4689; Sap. V. 198.5; Iod. No. (Wijs) 72.6; Acid V. 1.0; Unsap. 0.5 per cent; M. Pt. about 12° C.

T. P. Hilditch and W. J. Stainsby [*J. Soc. Chem. Ind.*, **56**, 197T (1934)] examined a sample of the oil expressed in Malaya and oil which they extracted with petroleum ether from Malayan beans. These beans contained 34 per cent of oil. The expressed oil gave a saponification value of 192.7, an iodine number of 76.7, and contained 0.6 per cent of unsaponifiable matter. The extracted oil gave a saponification value of 190.7, an iodine number of 78.9, and contained 0.4 per cent of unsaponifiable matter.

The mixed fatty acids of the expressed and extracted oils contained respectively the following percentages of constituents: oleic 61.0, 59.6, linoleic 13.2, 15.4, palmitic 5.1, 6.1, stearic 5.9, 5.7, and C_{20}, C_{24} 14.8, 13.2. The investigators state that it is very probable that tonka bean oil contains normal arachidic, behenic, and lignoceric acids, as is the case with peanut oil [(Jantzen and Tiedcke, *J. prakt. Chem.*, **127**, 277 (1930)]. Another seed oil is that from the *Pongamia glabra*, belonging also to this family, which contains notable quantities of these acids.

Ergot (Secale) Oil. This oil is obtained by extraction with petroleum ether of ergot (*Secale cornutum*), which is the dried sclerotium of the fungus *Claviceps purpurea* developed on rye plants, prior to the preparation of the medicinal extract. Ergot contains from 30 to 35 per cent of oil. The extracted oil varies in color from yellow to brown and was the original source of ergosterol [Tauret, *Ann. chim. phys.*, (6) **20**, 289 (1890); *ibid.*, (8) **15**, 313 (1908)], which later was found in yeast, etc. Rosonheim and Webster [*Biochem. J.*, **21**, 389 (1927)] have shown that this sterol is the parent substance of the antirachitic vitamin D and it is converted into the latter by irradiation with ultraviolet light. Some other references are as follows: "The Sterols of Ergot," Hart and Heyl, *J. Am. Chem. Soc.*, **52**, 2013 (1930); "Color Reaction of Ergosterol," R. Meisemaecken, *J. Pharm. Chem.*, **122**, 380 (1930); [*cf. Compt. rend.*, **190**, 216 (1930); *Chem. Absts.*, **24**, 1657 (1930)]. Also see other references under Ergosterol. Ergot oil is used to some extent as a source of ergosterol, but the latter is more commonly extracted from yeast fats, from which it is obtained more readily and in larger quantity. Ergot oil is also used by soap makers.

Baughman and Jamieson [*Oil and Fat. Ind.*, **5**, 85 (1928)] examined the oil extracted from a large composite sample of Austrian, Russian and Spanish Ergot with the following results: Sp. g. at 25° C. 0.9222; $N_D^{25°}$ 1.4691; Sap. V. 197; Iod. No. (Hanus) 73.8; Acetyl V. 7.3; R.M.V. 0.3; Pol. No. 0.4; Unsap. 1.18%; Acid V. 3; Sat. acids 26.5%; Unsat. acids 68.1%.

The oil contained the following percentages of acids: oleic 59.8, linoleic 8.3, myristic 0.29, palmitic 20.5, stearic 5.1, and arachidic acid 0.65.

This oil has been the subject of investigation at various times since 1832 by various workers. Most of these found that the oil gave a high acetyl value—from 27 to 63 [*Cf.* Mjoen, *Arch. Pharm.*, **234**, 278

(1896); Rathje, *ibid.*, **246,** 696 (1908)]. Dieterle, Diester, and Thimann, *ibid.*, **265,** 171 (1927) found their sample of oil gave an acetyl value of 60.4, but were unable to isolate any hydroxy acid, as did Matthes and Schütz [*ibid.*, **265,** 541 (1927)].

H. Vandermeulen [*J. Pharm. Belg.*, **21,** 195, 213 (1939), *Analyst,* **64,** 357 (1939)] examined two samples of extracted ergot oil giving the following characteristics: Sp. g. at 15° C. 0.9144 and 0.9237; $N_D^{20°}$ 1.4685 and 1.4696; Sap. V. 172 and 182; Iod. No. (Hanus, 3 hrs.) 62 and 65; Pol. No. 3.14; Unsap. 3.3 and 1.3 per cent.

The mixed fatty acids contained the following percentages of constituents: 0.1 acetic, 0.01 caproic, 30 palmitic, 12 stearic, 23 oleic, 34 ricinoleic, and a trace of linoleic acid. It will be noted that this oil is very different in composition from that examined by Baughman and Jamieson.

The Flacourtiaceae and Their Oils. Only those species, the seeds of which contain oils that show a high specific rotation, are of special interest. Such oils contain glycerides of the chaulmoogric group of acids. All contain chaulmoogric and probably gorlic acid, but there are a few that contain very little or no hydnocarpic acid. Some of these species are bushes and the others are trees. Those that flourish in tropical or semi-tropical regions are with few exceptions those that yield the optically active oils, whereas those growing in more temperate localities are characterized by having seeds which contain but small quantities of optically inactive oils. Whether or not any exceptions to this rule exist, remains to be determined.

In view of the large number of oil seeds in the tropics it is interesting to note that many thousands of years ago the natives of Africa, Asia and South America found and used the seeds and later the oil separated from them for the treatment of leprosy, skin diseases and wounds. In Burma and neighboring regions, the natives had the true *Chaulmoogra* (*Taraktogenos kurzii*) seeds; in Siam, East India and other regions, seeds of various *Hydnocarpus* species; in Africa, the seeds of *Oncoba* species; and in South America, seeds of some of the *Carpotroche* species as well as those of *Lindackeria* and *Mayna* species.

In very early times, the Chinese imported chaulmoogra seeds from Burma, Assam, etc., and expressed the oil for their own use; but apparently many centuries ago they learned of the superior quality of the oil from the seeds of certain species of *Hydnocarpus* growing in Siam and India and at that time gave up largely the importation of chaulmoogra seeds. On the other hand, the superior quality of some of these oils, as compared with chaulmoogra oil, has but recently been realized by those in America and Europe. The writer believes that eventually the oil from *Carpotroche brasiliensis* (or closely related species) may be shown to be superior to that from any other species for use in the treatment of leprosy. As only limited quantities of this oil are prepared from seeds collected by the natives in Brazil, it is apparent that larger quantities can be regularly obtained only by the

systematic cultivation of these trees. Before this can be undertaken much remains to be learned in regard to the conditions of cultivation necessary for the successful production of this crop.

At various tropical experiment stations, study has been in progress over a period of some years on the cultivation of chaulmoogra, gorli (*Oncoba echinata*) and certain species of Hydnocarpus. Before any commercial plantings of any of the species are undertaken in localities outside of their natural habitat, it should be ascertained whether or not the plants will produce a satisfactory crop of fruits. For example, difficulties not yet overcome have been experienced in getting hydnocarpus trees in Central America to bear fruit. The oils from the seeds of many species remain to be studied.

For those interested in these plants and their seed oils, the following partial list is given:

A Partial List of *Flacourtiaceae*

Asiatic Species

Taraktogenos kurzii
Hydnocarpus alcalae
Hydnocarpus alpina

Hydnocarpus anthelminthica
Hydnocarpus castanea

Hydnocarpus cauliflora
Hydnocarpus curtisii
Hydnocarpus heterophylla
Hydnocarpus hutchinsonii
Hydnocarpus ilicifolia
Hydnocarpus ovoidea
Hydnocarpus subfalcata
Hydnocarpus venenata
Hydnocarpus wightiana
Hydnocarpus woodii

African Species

Oncoba echinata
Oncoba klainii (glauca)
Oncoba spinosa
Oncoba welwitschii

Tropical American Species
(Chiefly Eastern South America)

Carpotroche amazonica
Carpotroche brasiliensis
Carpotroche crassiramia (Costa Rica, C. A.)
Carpotroche denticula
Carpotroche glaucescens (Costa Rica, C. A.)
Carpotroche grandiflora
Carpotroche intergrifolia
Carpotroche laxiflora
Carpotroche longifolia
Carpotroche platyptera
Carpotroche paludosa
Carpotroche surinamensis
Carpotroche sulsava
Lindackeria latifolia
Lindackeria maynensis
Lindackeria paraensis
Lindackeria paucifolia
Mayna echinata

Attention is called to Geraldo Kuhlmann's excellent monograph on the Brazilian species of *Carpotroche, Mayna* and *Lindackeria* published in *Memorias do Instituto Osnaldo Crux,* 21, Part 2, pp. 381 and 403, 1928. The following specific rotations are given for the oils from the seeds of eight species:

	$[\alpha]_D^{30°}$		$[\alpha]_D^{30°}$
Carpotroche brasiliensis	+52.8	*Lindackeria maynensis*	+48.5
Carpotroche longifolia	+41.0	*Lindackeria paraensis*	+43.4
Carpotroche intergrifolia	+25.5	*Lindackeria pauciflora*	+39.1
Lindackeria latifolia	+41.5	*Mayna echinata*	+50.4

Carpotroche (Oleo de Sapucainha) Oil. This oil is obtained from the seeds of the fruit from the tree *Carpotroche brasiliensis,* native

to Brazil, which is found in the mountainous forests in the states of Bahia, Espirito Santo, Minas Geraes, Piauhy, and Rio de Janeiro. The average weight of the seeds is 0.65 and the kernels 0.42 gram. Thoroughly matured kernels contain from about 60 to 63 per cent of oil. The oil expressed from sound kernels is pale yellow, limpid, and is also characterized by freedom from free fatty acids, sometimes containing only 0.2 per cent. The seeds have excellent keeping properties. Oil expressed from the whole seed is more or less brownish, because of coloring matter extracted from the brown shells. The samples of oil so far examined do not deposit "stearine" unless cooled below 15° C.

The oil which is prepared on a small commercial scale in Brazil is used as a parasiticide, a specific for dermatosis, and for the treatment of leprosy, as well as for a veterinary medicine.

The usual range of the characteristics of the oil is as follows: Sp. g. at 25° C. .9486 to .9563; $N_D^{25°}$ 1.4750 to 1.4793; $[\alpha]_D^{25°}$ +52 to +55°; Sap. V. 199 to 204; Iod. No. 101 to 108.

In 1930 the writer expressed the oil from the kernels of over 20 lbs. of seed sent by Dr. B. H. Rolfs from a cultivated tree at Vicosa, Brazil. These kernels contained 2.5 moisture and 63.4 per cent of oil (on the basis of the whole seed, 40.9 per cent). The oil had the following characteristics: Iod. No. (Hanus) 108.6; Sap. V. 201.1; Acid V. 0.4; $N_D^{25°}$ 1.4792; $[\alpha]_D^{20°}$ +58.9 in chloroform; Sat. Acids (Bertram's method) 1.44%.

The press cake contained 550 ppm of hydrogen cyanide, which showed the presence of a cyanogen glucoside. It would be suitable only for use as a fertilizer.

A number of years ago, 2 samples of the commercial oil were secured from the Brazilian Director of Agriculture through the Office of Foreign Plant Introduction, United States Department of Agriculture, which were examined in the writer's laboratory with the following results: Sp. g. at 25° C. 0.9545; $N_D^{20°}$ 1.4812; Iod. No. (Hanus) 102 to 103.5; Sap. V. 202.5, Acetyl V. 5.8; R.M.V. 0.7; Pol. No. 0.7; Unsap. 0.6%; Acid V. 1.8; $[\alpha]_D^{20°}$ +53.9° to 54.9°.

H. I. Cole and H. T. Cardoso [*J. Am. Chem. Soc.*, **60**, 614 (1938)] examined a sample of the cold-pressed oil and obtained the following results: Sp. g. at 25° C. 0.955; $N_D^{25°}$ 1.4793; $[\alpha]_D^{25°}$ +52.4°; Sap. V. 201.8; Iod. No. 103. The mixed fatty acids were found to contain the following percentages of constituents: chaulmoogric 24.4, hydnocarpic 45.0, gorlic 15.4, oleic 6.3 and palmitic 6.6. Decomposition products from the distillation of the esters amounted to 2.3 per cent.

The authors called attention to the dehydrochaulmoogric found in the oil by H. Paget (*J. Chem. Soc.*, **1937**, 955), which was identical with that previously known as gorlic acid. It was named by Andre and Jonatto [*Bull. soc. chim.*, **43**, 347 (1928)], who found it in gorli seed oil.

Attention is called to the following references: "Physiologic Action of Ethyl Esters of Fatty Acids in Oil of Carpotroche," T. Martins, *Compt. rend. soc. biol.*, **96**, 474 (1927). "Carpotroche Oil," Pio Correa,

Mat. grasses, **20,** 8054 (1928). "Domesticating Anti-Lepric species in Brazil," P. H. and C. Rolfs, *Leprosy Review,* **9,** Nos. 3 and 4 (1938).

Chaulmoogra Oil. This oil is obtained from the seeds of the fruit from the tree *Taraktogenos kurzii,* which is found growing in various parts of Burma, Assam, and lower Bengal. Experimental plantings have been made in various tropical regions, including the Philippines and Hawaii. As the wild trees in India bear irregularly, it is customary for the natives to enter the forests once in three years to collect the seeds, when a full crop is expected. The seeds, which vary much both in shape and size, have the appearance of brown pebbles. They weigh from about a gram to slightly over 2 grams. The percentage of kernels in the seeds varies from about 73 to 85. Mature sound kernels contain from 48 to 55 per cent of oil. The oil, depending upon its quality, is liquid or semi-liquid at ordinary temperatures and varies in color from pale yellow to dark brown. It possesses a characteristic odor and a somewhat acrid taste. As the seeds contain a reactive hydrolytic enzyme and have poor keeping qualities, the commercial oil for the most part contains a very considerable quantity of free fatty acids. It should be also noted that the commercial oil not infrequently contains more or less of oil from seeds of other but closely related species of *Hydnocarpus.*

Attention is called to the illustrated United States Department of Agriculture Bulletin 1057 by J. A. Rock, which is entitled "The Chaulmoogra Tree and Some Related Species," and to "A Comparative Analytical Study of Various Oils in the Chaulmoogra Group" by G. Perkins and A. Cruz, *Phil. J. Sci.,* **23,** 543 (1923).

Chaulmoogra, as well as the oils from certain species of *Hydnocarpus, Oncoba* (Africa) and *Carpotroche* (Brazil) have been used for centuries by the natives for the treatment of leprosy and other skin diseases. In recent years, the use of this oil for the treatment of leprosy has been largely superseded by *Hydnocarpus anthelminthica* and *H. wightiana,* both of which are cheaper and of very much better quality.

F. B. Power and F. H. Gornall [*J. Chem. Soc.,* pt. II, **85,** 838, 851 (1904)] discovered that the oil contained chaulmoogric acid ($C_{18}H_{32}O_2$) and hydnocarpic acid $C_{18}H_{28}O_2$. They also found that these acids had a five-membered cyclic structure.

H. I. Cole and H. T. Cardoso [*J. Am. Chem. Soc.,* **61,** 3442 (1939)] made an extensive investigation of the cold-expressed oil from seeds grown at the Escola Superior de Agricultura at Vicosa, Minas Geraes, Brazil. The characteristics of the oil were as follows: Sp. g. at 25°/25° C. 0.952; $N_D^{25°}$ 1.4790; $[\alpha]_D^{25°}$ +49.8°; Sap. V. 200.6; Iod. No. (Hanus) 101.5; Acid V. 2.6; Unsap. 0.29%. The percentage composition of its mixed acids was found to be as follows: chaulmoogric 22.5, hydnocarpic 34.9, gorlic 22.6, lower homologs of hydnocarpic 0.4, palmitic 4.0, and oleic acid 14.6. At the time this investigation was made, the oil had been stored for 3 years, but during that time it had changed but very little and upon injection it showed no irritating

effects. It showed also that when the oil is expressed from sound matured seed, it has excellent keeping properties.

The usual range of the characteristics reported for commercial chaulmoogra oil from India and Burma is as follows: Sp. g. at 30° C. 0.945 to 0.952; $N_D^{40°}$ 1.4720, at 25° C., 1,4777 to 1.4779, at 30° C. 1.4753 to 1.4771; $[\alpha]_D^{30°}$ +45 to +53; Sap. V. 198 to 208; Iod. No. (Hanus) 98 to 105. Solid Pt. 5° to 20° C.

There is no specific test for chaulmoogra oil. The Lefschutz test [*Chem. Zeit.*, **45**, 1264 (1921)], which is also given by some of the other closely related oils, is made as follows: Dissolve 1 drop of the sample in 0.5 cc. of chloroform and add 1.5 cc. of glacial acetic acid. Then add 4 or 5 drops of sulfuric acid and mix. A grass-green color gradually develops which is reddish violet by transmitted light. The freshly prepared oil does not give the test unless a crystal or two of benzoyl peroxide is previously added and the oil thoroughly shaken. Information on cultivating experiments in Ceylon of chaulmoogra and hydnocarpus trees will be found in *Bull. Imp. Inst.*, **27**, 365 (1929).

Gorli Seed Oil. This oil is found in the seed of the fruit of the tree *Oncoba echinata*, belonging to the *Flacourtiaceae* family. It grows to a height of about 20 feet and is indigenous to certain parts of tropical Africa, including Guinea, Ivory Coast, Nigeria and Sierra Leone; it is being grown on an experimental scale in Costa Rica, Puerto Rico and elsewhere. The thorny fruits, which resemble somewhat chestnut burrs, burst open after reaching maturity and expose the seeds. The small brown seeds weigh about 0.05 gram and contain from about 47 to 52 per cent of oil which at ordinary temperatures is a hard, white solid with a slight, but characteristic odor. For centuries, the African natives used this product for local applications in the treatment of skin diseases, including leprosy.

E. André and D. Jonatto [*Bull. soc. chim.*, (4), **43**, 347 (1928)] found that the fatty acids from this oil consisted of about 80 per cent of chaulmoogric acid, about 10 of palmitic acid, and about 10 of a liquid unsaturated acid which was discovered and named gorlic acid ($C_{18}H_{30}O_2$) by these investigators. It belongs to the chaulmoogric (cyclopentane group) acid series and contains two ethylene linkings. The calculated or theoretical iodine number of this acid is 181.4.

H. I. Cole and H. T. Cardoso [*J. Am. Chem. Soc.*, **60**, 617 (1938)] examined a sample of the oil and obtained the following results: $[\alpha]_D^{25°}$ +51.70°; Sap. V. 193.7; Iod. No. (Haus) 96.4; Acid V. 8.6. The percentage composition of the fatty acids is as follows: chaulmoogric 74.9, gorlic 14.7, oleic 2.2, and palmitic 7.8. The isolation and properties of gorlic acid, as well as for the ethyl and methyl esters, is described by these authors in *J. Am. Chem. Soc.*, **60**, 612 (1938).

The usual range of the characteristics is as follows: Sp. g. at 40° C. 0.9356, at 100/15° C. 0.898; $N_D^{31°}$ 1.4740, at 40° C. 1.4720; Iod. No. 94 to 100; Sap. V. 190 to 194; Unsap. 1 to 1.6%; $[\alpha]_D^{20°}$ +48 to +50

(in chloroform); M. Pt. 42° to 44° C.; Acetyl V. 3.7; R.M.V. 0.0.; Pol. No. 0.3.

Most observers have reported iodine numbers above 97, but the author, who expressed a large quantity of the fat from seed grown in Costa Rica, found that this sample gave an iodine number of 94.2 by the Hanus method. The acetyl, Reichert-Meissl and Polenske values given above were also determined on this sample.

The medicinal value of oncoba oils is discussed in *Bull. Imp. Inst.*, **21**, 585 (1923). It was also shown that the oil from the seed of *Oncoba spinosa* from Sierra Leone did not contain any of the chaulmoogric series of acids.

Oncoba Klainii (Caloncoba glauca) Seed Oil. Peirier [*Chem. Absts.*, **24**, 3084 (1930)] examined the seeds and fat of this small African tree, and described their occurrence and botanical characters. The seeds, which are contained in a fleshy fruit, average in weight about 0.11 gram and consist of 45.5 of shell and 54.5 per cent of kernel. The fat content of the seed is 40.2 and the kernel 47.5 per cent. The characteristics reported for the fat are as follows: M. Pt. 38.4° C.; Sp. g. at 45° C. 0.928; $N_D^{45°}$ 1.4685; $[\alpha]_D^{26°}$ +40. E. Perrot [*Chem. Absts.*, **23**, 4531 (1929)] reported that the seeds from the French Cameroons examined by him consisted of 36.4 of shell and 63.6 per cent of kernel. The seed contained 30 per cent of a semi-solid yellow fat which gave an iodine number of 86.3. The extracted meal contains a cyanogenetic glucoside, as shown by Peirier *(loc. cit.)*.

Oncoba welwitschii (Caloncoba wel.) Seed Oil. This small West African tree has a fleshy fruit which contains seeds that average 0.033 gram in weight. Peirier [*Chem. Absts.*, **24**, 3084 (1930)] has examined the seeds and fat with the following results: The seeds consisted of 58 per cent of shell and 42 per cent of kernels. The seeds contain 35.6 per cent of a solid fat (kernels 54), which gave the following characteristics: M. Pt. 40° C.; Sp. g. at 45° C. 0.9386; $N_D^{45°}$ 1.4719; $[\alpha]_D^{26°}$ +47.7. No hydrocyanic acid could be detected in the extracted meal, indicating the absence of cyanogenetic glucosides. For information in regard to the botanical characters of this species the original reference must be consulted.

Perrot and Francois [*Chem. Absts.*, **24**, 466 (1930)] also examined this fat and reported the following characteristics: M. Pt. 38° C.; Iod. No. 84; Sap. V. 194; $N_D^{30°}$ 1.4750; $[\alpha]_D$ +54° 8′. They do not recommend the therapeutic use of this fat.

Spinosa Oil. This oil is obtained from the seeds of the *Oncoba spinosa*, which is found in Sierra Leone and other tropical localities of Africa. The seeds contain about 35 per cent of oil. The oil, which was examined at the Imperial Institute [*Bull. Imp. Inst.*, **21**, 585 (1923)], gave the following characteristics: Sp. g. at 15° C. 0.9303; $N_D^{40°}$ 1.474; Sap. V. 192.2; Iod. No. 177; Unsap. 1.3 per cent; R.M.V. 0.5; Pol. No. 0; Acid V. 12.1; Titer 23.4°; $[\alpha]_D$ 0. A film of oil on glass dried in 3 to 4 days, showing, as would be expected from the high iodine

number, that it was a strong drying oil, but owning to the difficulty of separating the seeds from the pulp of the fruit, it will not become of commercial importance.

Hydnocarpus Oils. These oils are obtained from the seeds of various species of trees belonging to the natural order of *Flacourtiaceae* (formerly known as *Bixineae*). The seeds are borne in fruits, the size of which in some cases is given below. As the seeds of most of the species, like those of *T. kurzii,* contain more or less cyanogenetic glucosides, the press cakes from the expression of the oils are suitable only for use as fertilizer. For the most part, the seeds from these species have good keeping properties in contrast to those of the chaulmoogra; consequently, the expressed hydnocarpus oils are, with few exceptions, characterized by having but small quantities of free fatty acids. In various tropical regions, cultivating experiments have been in progress for some years with one or more of these species, *H. wightiana* and *H. anthelminthica* being those most commonly studied [*Bull. Imp. Inst.,* **27**, 107 (1929)]. It is most desirable that further exploration should be made, as without doubt there are still other species as yet unknown which may be of value for cultivation.

The tree *Hydnocarpus alcalae* is found in parts of the Philippines. According to Perkins and Cruz [*Phil. J. Sci.,* **23**, 543 (1923)], the fruits are 8 inches long and 4 inches in diameter. The seeds weigh from 2 to 4 grams. The kernels contain from 35 to 40 per cent of oil which has the following characteristics: Sp. g. at 30° C. 0.948; $N_D^{30°}$ 1.4763; Sap. V. 202; Iod. No. 94; M. Pt. 32° C.; $[\alpha]_D^{30°}$ +49.6° [*Cf.* Santos and West, *Phil. J. Sci.,* **40**, 485 (1929)]. Perkins and Cruz (*loc. cit.*) found that the oil contained a large quantity of chaulmoogric acid, but little or no hydnocarpic acid is present. Palmitic and oleic acids were detected. Insofar as is known, the oil is not produced on a commercial scale.

These investigators also examined the oil from the seeds of the tree *Hydnocarpus hutchinsonii,* which is found in North Borneo, Eastern Mindanao, Basilan Island and the Sulu Archipelago. The fruit is nearly spherical in shape and has a diameter of 3 to 4 inches. The seeds weigh from 1.5 to 2 grams. The characteristics of the oil are as follows: Sp. g. at 30° C. 0.943; $N_D^{30°}$ 1.4743; Sap. V. 199; Iod. No. 84; Sol. Pt. 23° C.; $[\alpha]_D^{30°}$ +42°.

The tree *Hydnocarpus alpina,* which grows from 60 to 90 feet high, is found in Ceylon and the East Indies. The wood of this tree has long been used for making furniture, etc. The seeds are unusually large, being similar in this respect to those of *H. anthelminthica.* The oil content of the seeds or kernels apparently is not mentioned in the literature. The oil is prepared and used by the natives in some regions for medicinal purposes as well as an illuminant.

The first examination of the oil was made by Sendrich, Koch and Schwarz [*Z. Nahr. Genussm.,* **22**, 441 (1911)], with the following results: Sap. V. 209; Iod. No. 84; $[\alpha]_D^{20°}$ +49°. Wolf and Koldewijn

[*Pharm. Weekblad.*, **49**, 1049 (1912)] found: Sp. g. at 100° C. 0.898; Sap. V. 207; Iod. No. 84; $N_D^{40°}$ 1.4709; M. Pt. 22° to 26° C.; Acid V. 0.35; $[\alpha]_D$ +49.5°. More recently Andre [*Compt. rend.*, **181**, 1089 (1925)] obtained the following characteristics: Sp. g. at 32° C. 0.9346; $N_D^{20°}$ 1.4764; Sap. V. 201; Iod. No. (Hanus) 95; $[\alpha]_D$ +57°.

The tree *Hydnocarpus anthelminthica* is indigenous to Thailand and Cochin China, but is being cultivated in other tropical regions. It has been introduced into Hawaii, where over 3000 trees are now growing. The seeds from the fruit of this tree weigh from 1 to about 2.0 grams each and contain about 30 per cent of their weight of kernels. The whole seed has from 12 to about 18 per cent of oil (kernels 60%). As the seeds have good keeping qualities, the oil from them is usually low in free fatty acids. The oil, which is solid at ordinary temperatures (M. Pt. 20° to 25° C.), is now being more extensively used in the treatment of leprosy.

Power and Barrowcliff [*Trans. Chem. Soc.*, **87**, 884 (1905)] first examined the oil and found that it contained chaulmoogra and hydnocarpic acids. Later it was studied by Perkins and Cruz [*Phil. J. Sci.*, **23**, 543 (1923)] and by A. Marcan [*J. Soc. Chem. Ind.*, **45**, 305T (1926)], who examined 23 samples. The range of the characteristics reported by these observers is as follows: Sp. g. at 30° C. 0.943 to 0.952; $N_D^{30°}$ 1.473 to 1.4753; $[\alpha]_D^{30°}$ +47.1° to +52.5°; Sap. V. 191.4 to 226.5; Iod. No. 84.5 to 86.4, (Wijs) 88.6 to 90.6; Acid V. 0.2 to 9.8.

H. I. Cole and H. T. Cardoso [*J. Am. Chem. Soc.*, **61**, 3444 (1939)] have made an exhaustive investigation on oil imported from Thailand and held in storage for over 5 years. They determined the following characteristics: Sp. g. 25°/25° C. 0.952; $N_D^{25°}$ 1.4772; $[\alpha]_D^{25°}$ +49.70°; Sap. V. 203.3; Iod. No. (Hanus) 89.2; Acid. V. 5.8; Unsap. 0.50 per cent. The mixed fatty acids contained the following percentages of constituents: chaulmoogric 8.7, hydnocarpic 67.8, gorlic 1.4, lower homologs of hydnocarpic acid 0.1, oleic 12.3, and palmitic acid 7.5.

This oil is now extensively used in the treatment of leprosy, and ranks next to that from *H. wightiana* in therapeutic importance.

The tree *Hydnocarpus ilicifolia* is indigenous to Thailand. In certain localities these trees are reported to be very numerous. According to A. Marcan [*J. Soc. Chem. Ind.*, **45**, 305T (1926)] the seeds contain about 77 per cent of kernels. Those examined contained 6.9 per cent of moisture and 33.6 per cent of oil, besides some cyanogenetic glucosides. The oil has the following characteristics: Sp. g. at 30° C. 0.947; $N_D^{30°}$ 1.4763, at 40° C. 1.4723; Sap. V. 213.1; Iod. No. (Wijs) 89.7; M. Pt. 23° to 28.2° C.; $[\alpha]_D^{30°}$ 51.2°; Acid V. 0.6; Titer 42.5°.

The oil contains both chaulmoogric and hydnocarpic acids. From the characteristics, it appears similar to the oil from the seeds of *H. anthelminthica*, which are used for the commercial production of oil in Thailand.

The tree *Hydnocarpus subfalcata* [*Phil. Bur. Sci. Bull.* **105** (1922)] is found in various parts of the Philippines, including Cagayan, Luzon,

Mindanao, Pangasinan, Samar, Siberyan, and Zambales. It bears small green fruits which contain from 2 to 8 small seeds. The seeds weigh about 0.7 gram. The kernels contain about 36 per cent of oil. Perkins and Cruz [*Phil. J. Sci.*, **23**, 543 (1923)] found the following characteristics: Sp. g. at 30° C. 0.951; $N_D^{30°}$ 1.4761; Sap. V. 206; Iod. No. (Hanus) 89; Sol. Pt. 21°; $[\alpha]_D^{30°}$ +46.7°. Apparently no use is made of this oil at the present time.

The tree *Hydnocarpus heterophylla* is found in the Dutch East Indies. The seeds contain about 33 per cent of oil. D. R. Koolhaas [*Rec. trav. chim.*, **49**, 108 (1930); *Chem. Absts.*, **24**, 2433 (1920)] has examined the oil with the following results: Sp. g. at 27° C. 0.952; $N_D^{27°}$ 1.4679; $[\alpha]_D^{27°}$ +43.1; Iod. No. 73.3; Sap. V. 194; Acid V. 0.86. The oil contains both chaulmoogric and hydnocarpic acids as glycerides.

The trees and fruits of *Hydnocarpus curtisii* and *H. castanea* have been described by J. F. Rock [*U. S. D. A. Bull.*, **1057** (1922)]. They were found in Burma. It would be desirable to have a thorough examination made of the oils from the seeds of these trees.

The tree *Hydnocarpus venenata*, which is found in Ceylon, Deccan, and Burma, produces seeds which are similar to but smaller than those of *H. wightiana*. The seeds weigh about 0.3 gram. Sound, mature kernels probably contain 40 per cent or more of oil. Several investigators have examined the oil. Wolff and Koldewijn [*Pharm. Weekblad.*, **49**, 1049 (1912)]: $N_D^{40°}$ 1.471; Sap. V. 207; Iod. No. 84; M. Pt. 22° to 26° C.; Sol. Pt. 22° C.; Acid V. 0.35; $[\alpha]_D$ +49.5°. Brill [*Phil. J. Sci*, **16**, 75 (1916)]: Sp. g. at 30° C. 0.9475; $N_D^{20°}$ 1.4770; Sap. V. 200; Iod. No. 99; $[\alpha]_D$ +52°. Perkins and Cruz [*Phil. J. Sci.*, **23**, 543 (1923)]: Sp. at 30° C. 0.947; $N_D^{30°}$ 1.4769; Sap. V. 191; Iod. No. (Hanus) 90.7; Sol. Pt. 20° C.; $[\alpha]_D^{30°}$ +43.9°. The oil contains both chaulmoogric and hydnocarpic acids (Brill).

The tree *Hydnocarpus wightiana* is native to the western peninsula of India and is found from South Concan to Travancore. The seeds weigh slightly more than a gram each and contain about 60 per cent of oil. Both the seed and the expressed oil are exported from Enakulam. The oil has long been used in western India as well as in parts of China for the same medicinal purposes as chaulmoogra oil. Because of the better condition of the seed when collected, the hydnocarpus oil on the market is of much better quality than the bulk of the commercial chaulmoogra oil. In recent years, the cold-pressed oil from sound seed has been extensively used in the treatment of leprosy in India and elsewhere. When necessary, this, as well as other oils of this group, can be refined by caustic soda and deodorized as shown by Perkins, Cruz, and Reyes, [*Ind. Eng. Chem.*, **19**, 939 (1927)]. The properly refined product can be injected intramuscularly or subcutaneously without irritation, and the same appears to be true of the best grade of unrefined hydnocarpus oil. F. B. Power and M. Barrowcliff [*Trans. Chem. Soc.*, **87**, 884 (1905)] made an extensive examination of this oil. They found that it contained chaulmoogric and hydnocarpic acids, the latter in

much larger quantity than was found in chaulmoogra oil. No palmitic acid could be detected. Those interested in the preparation of hydnocarpic acid in quantity should consult Perkins, Cruz, and Reyes (*loc. cit.*).

Characteristics.—Sp. g. at 25° C. 0.958; $N_D^{30°}$ 1.4763 to 1.4772; Sap. V. 200 to 208; Iod. No. 93 to 101; $[\alpha]_D^{15°}$ in $CHCl_3$ +51.0° to +57.7°; M. Pt. 22° to 24° C. The sample of oil examined by André [*Compt. rend.*, **181**, 1089 (1925)] gave the following results: Sp. g. at 32° C. 0.9330; $N_D^{29°}$ 1.4780; Sap. V. 197.2; Iod. No. (Hanus) 103; $[\alpha]_D$ +57°; M. Pt. 20.5° C. Reference: "Reduction of Irritation by Iodized Ethyl Esters of *H. wightiana* Oil," H. I. Cole, *Phil. J. Sci.*, **40**, 503 (1929).

H. I. Cole and H. T. Cardoso [*J. Am. Chem. Soc.*, **61**, 2351 (1939)] made an extensive investigation of this oil. The cold-pressed oil gave the following characteristics: Sp. g. 25°/25° C. 0.9549; $N_D^{25°}$ 1.4799; $[\alpha]_D^{25°}$ +55.0°; Sap. V. 201; Iod. No. (Hanus) 98.4; Acid V. 5.4; Unsap. 0.25 per cent. The percentage composition of its mixed acids was found to be as follows: chaulmoogric 27.0, hydnocarpic 48.7, gorlic 12.2, oleic 6.5, palmitic 1.8, and lower homologs of chaulmoogric acid (alepric, $C_{12}H_{20}O_2$, aleprylic, $C_{10}H_{16}O_2$, aleprestic, $C_{10}H_{16}O_2$, and aleprolic, $C_6H_8O_2$) 3.4. This oil is quite similar to that from *Carpotroche brasiliensis*. Procedures for the purification and esterification of oils from the seeds of *H. anthelminthica* and *H. wightiana*, for therapeutic purposes have been described by Cole and Cardoso. [*International Journal of Leprosy*, **4**, 455 (1936)].

The tree *Hydnocarpus woodii* is found in British North Borneo. It produces roughly spherical fruits about 2.5 inches in diameter which contain seven or more seeds that vary greatly in shape. Some are wedge-shaped and others are more or less spherical. Depending upon the shape, the length or diameter is from 1 to 1.3 inches. The seeds usually weigh from 3.2 to 4.2 grams and the kernels from about 1.8 to 2.1 grams. The proportion of kernels to shells, as in the case of the seeds of other species of hydnocarpus, is subject to wide variation. One lot of seeds examined at the Imperial Institute, [*Bull. Imp. Inst.*, **27**, 12 (1929)] contained 61 per cent, whereas those of a second lot contained 46 per cent of kernels. The kernels with 7.8 to 8.1 per cent of moisture contained from 55 to 57 per cent of oil. The oil was a cream-colored solid which gave the following characteristics: Sp. g. at 100/15° C. 0.8989; $N_D^{40°}$ 1.471; Sap. V. 202.4; Iod. No. (Hübl. 17 hrs.) 85.8; Unsap. 0.5%; Acid. V. 32.8; M. Pt. 28.5° C.; $[\alpha]_D^{20°}$ in $CHCl_3$ +53.1°. Perkins and Cruz [*Phil. J. Sci.*, **23**, 543 (1923)] found the following: $N_D^{30°}$ 1.473; Sap. V. 192; Iod. No. (Hanus) 68.5; Sol. Pt. 18° C.; $[\alpha]_D^{30°}$ +45.9°. *Cf.* Perkins, Cruz, and Reyes, *Ind. Eng. Chem.*, **19**, 942 (1927). The oil contains both chaulmoogric and hydnocarpic acids as glycerides.

Macrocarpa Oil. This oil is obtained from the seeds of the tree *Asteriastigma macrocarpa*, a native of southern India which is found

in the state of Travancore. On account of the large size and shape of the fruit, it is known locally as the cannon ball tree. The fruit is about 5 inches in diameter and the seeds are larger than those of the chaulmoogra tree. The oil content of the seeds is probably about 40 per cent. André [*Compt. rend.*, **181**, 1089 (1925)] examined the oil with the following results: Sp. g. at 32° C. 0.9217; $N_D^{25°}$ 1.4725; Sap. V. 189.4; Iod. No. 82.8; $[\alpha]_D$ +44°; M. Pt. 37° to 39° C.

D. H. Peacock and G. K. Aiyar (*Burma Forest Bull.*, **1930**, No. 21, 11) state that the seeds contain from 36 to 57 per cent of oil. The range of the characteristics of the oil is as follows: $[\alpha]_D^{30°}$ +38.8° +55.6°; Iod. No. 103 to 127; Sap. V. 192 to 204. Peacock and C. Thoung [*J. Soc. Chem. Ind.*, **50**, 7T (1931)] reported characteristics as follows: $[\alpha]_D^{29°}$ +52.8°; Sp. g. at 25° C. 0.9501; $N_D^{29°}$ 1.4790; Iod. No. 112.3; Sap. V. 195.6; Unsap. 3.0 per cent. Chaulmoogric acid was identified. Although hydnocarpic acid was not detected, it may be also present in the oil.

The oil is similar to that from chaulmoogra seeds. Further information on the characteristics and composition is desirable as well as on the keeping quality of the seeds.

Pitjoeng or Samaun Oil. This oil is obtained from the seeds from the fruit of the tree *Pangium edule*, indigenous to the Malayan Archipelago and widely distributed in the Philippines and neighboring islands. The seeds weigh from 11 to 15 grams. The seeds contain 15 to 20 per cent of oil. According to Wijs [*Chem. Rev. Fett Harz Ind.*, **18**, 158 (1911)], the Java natives express the oil and use it for edible purposes. The following characteristics were determined by Perkins and Cruz [*Phil. J. Sci.*, **23**, 543 (1923)]: Sp. g. at 30° C. 0.925; $N_D^{30°}$ 1.472; Sap. V. 200; Iod. No. (Hanus) 78.5; Sol. Pt. 7° C.; $[\alpha]_D^{30°}$ +15.7°.

H. C. Brill [*Phil. J. Sci.*, **A**, **12**, 37 (1917)] studied this oil and concluded that it contained some of the chaulmoogric group of acids, but Perkins and Cruz (*loc. cit.*) could not detect the presence of these acids. C. D. V. Georgi and G. L. Teik (*Brit. Chem. Absts.*, B, **1930**, 154) report that the oil which they examined gave no optical rotation. It had the following characteristics: Sp. g. at 30/15° 0.9132; $N_D^{30°}$ 1.4660; Iod. No. (Wijs) 108.3; Sap. V. 196.5; Acid V. 0.2; Unsap. 0.6%; Titer 20.4°. The seeds contain a cyanogenetic glucoside.

Gemsbok Bean Oil. This oil is obtained from the seeds of the plant *Bauhinia esculenta*, which grows in the Southwest Protectorate, Africa. The seeds weigh about 2 grams and the kernels about 1 gram. The seeds, which are a dark reddish brown, have woody shells and the kernels are cream-colored. The kernels contain nearly 42 per cent of oil. According to the Imperial Institute [*Bull. Imp. Inst.*, **19**, 143 (1921)], the oil has the following characteristics: Sp. g. at 15/15° C. 0.9211; $N_D^{40°}$ 1.464; Iod. No. 95.6; Sap. V. 190.0; Unsap. 0.8%; R.M.V. 0.3; Pol. No. 0.1; Acid V. 0.6; Titer 30.6°. The oil has a pleasant odor and taste, and is of a golden yellow color.

Characteristics of Chaulmoogra and Related Oils.

Source of Oils Species	Specific Gravity at 30° C.	Refractive Index at 30° C.	Sapon. Value	Iodine No.	Specific Rotation +
Taraktogenos kurzii	0.945 to 0.952 40° C.	1.4753 to 1.4771 40° C.	198 to 208	98 to 105	45° to 53°
Oncoba echinata	0.9356 25° C.	1.4740 20° C.	190 to 194	94 to 100	48° to 50°
Carpotroche brasiliensis	0.9545	1.4812	202.5	102 to 104	53.9° to 54.9°
Hydnocarpus alcalae	0.948	1.4763	202	94	49.6°
Hydnocarpus alpina	32° C. 0.9346	40° C. 1.4709	201 to 209	84 to 95	49° to 57°
Hydnocarpus anthelminthica	0.943 to 0.950	1,4733 to 1.4753	191 to 226	84 to 99	47° to 52°
Hydnocarpus cauliflora	0.946	1.4732	201	84	42°
Hydnocarpus ilicifolia	0.947	1.4763	213 1	89.7	51.2°
Hydnocarpus hutchinsonii	0.943	1.4743	199	84	42°
Hydnocarpus ovoidea	0.915	1.4637	215	47	1°
Hydnocarpus subfalcata	0.951	1.4761	206	89	46.7°
Hydnocarpus venenata	0.947	1.4769	191 to 200	90.7 to 99	44° to 52°
Hydnocarpus Wightiana	0.947 to 0.958 100/15° C.	1.4763 to 1.4772	200 to 208	93 to 101	51° to 57°
Hydnocarpus Woodii	0 8989 32° C.	1.4730	192 to 202	69 to 86	45.9° to 53°
Asteriastigma macrocarpa	0.9217	1.4725	189.4	82.8	44° to 55.6°

The meal is free from alkaloids and cyanogenetic glucosides. It contains on a basis of 7 per cent oil and 6.4 of moisture, 52.2 per cent of crude proteins, 27.4 of carbohydrates and 2.1 per cent of crude fiber. It is stated that these seeds are used for native consumption and for feeding animals.

Hazel (Filbert) Nut Oil. This oil is obtained from the nuts of the tree *Corylus avellana* of the *Betulaceae,* which is cultivated in Europe, the United States and elsewhere. The kernels contain from 50 to 60 per cent of oil. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.917, at 20° C. 0.9144; $N_D^{25°}$ 1.4691, at 40° 1.4612; Sap. V. 190 to 197; Iod. No. 84 to 90; Unsap. 0.3 to 0.5 per cent; Sat. acids 4.8 to 8.0 per cent; Unsat. acids 87 to 91 per cent; Sol. Pt. −18° C.; Titer 19° to 20°.

H. A. Schuette and C. Y. Chang [*J. Am. Chem. Soc.,* **55,** 3333 (1933)] expressed some of this oil from the shelled nuts; it gave an iodine number (Hanus) of 85.5, a saponification value of 191.1, and contained 0.5 per cent of unsaponifiable matter. The percentages of acids in the oil were as follows: myristic 0.22, palmitic 3.06, stearic 1.59, oleic 88.1, and linoleic 2.87 per cent.

The oil which S. H. Bertram [*Chem. Absts.,* **31,** 897 (1937)] examined gave an iodine number (Hanus) of 86.8, a saponification value of 192.0 and contained 0.35 per cent of unsaponifiable matter. The percentages of acids reported were as follows: saturated 8.0, oleic 78.2, and linoleic 9.1 per cent.

The oil is used chiefly for edible purposes and making soap, but sometimes to adulterate almond oil. No distinctive color test is known for this oil.

Horse Chestnut Oil. This oil is found in the seed of the tree *Aesculus hippocastanum* of the *Hippocastanaceae.* The kernels contain from 3 to 6 per cent of oil, whereas edible chestnuts contain only about one per cent. The characteristics of one sample of the extracted oil were as follows: $N_D^{20°}$ 1.4747; Sap. V. 194.5; Iod. No. 95.4; Acetyl V. 13.5; R.M.V. 1.54; Pol. No. 0.42; Unsap. 2.5 per cent. H. P. Kaufman and J. Baltes [*Fette u. Seifen,* **45,** 175 (1938)] found that the mixed fatty acids from a sample of the oil contained the following percentages of constituents: oleic 67.2, linoleic 22.7, linolenic 2.2, palmitic 4.4, and stearic acid 3.6.

Illipé (Mowrah) Butter or Tallow. This fat is obtained from the seeds of the fruits of the trees *Madhuca* (*Bassia*) *longifolia* and *latifolia* (*Sapotaceae*), both of which are indigenous to India. It should be observed that the seeds and their fats are known locally by a number of names other than those given; the more important of these are in the index.

The tree *M. longifolia* grows in Southern India and reaches a height of about 50 feet. It produces green, ovoid fruits which usually contain 1 to 2 seeds, but sometimes 3 or 4.

The tree *M. latifolia* grows in Central India, including the northern parts of Bombay Presidency, the Nizams Dominions and Bengal. It

reaches a height from 50 to 60 feet and bears fleshy green, ovoid fruits containing from 1 to 4 seeds. The tree is found up to 4000 feet above sea level.

A variety of the *M. longifolia,* formerly classified as *M. malabarica,* is found in Western Ghats from Kanaria to Travancore and in the Himalayan regions.

Considerable quantities of illipé seeds at various times are exported to Europe. Those from Central India are from *M. latifolia,* while those from farther south are usually a mixture of the two species. The seeds of these species as well as those from the *M. butyracea,* the source of Phulwara butter, all have a resemblance in structure, but vary in size. The seeds from *M. longifolia* are somewhat longer and less rounded than those of *M. latifolia.* The latter seeds average 2 grams, while those of the *M. longifolia* average about 1.5 grams in weight. The percentage of shell or husks varies from 22 to 25 and the oil content of the seeds of both species is from about 50 to 60 per cent. The seeds which are not exported are pressed locally in ghammes, but in a few places hydraulic presses or Anderson Expellers are used.

The press cake, which contains a saponin-like substance, is used chiefly as a fertilizer, but some is used as an insecticide. It has been fed to cattle without apparent ill effects [*Biochem. J.,* **4,** 93 (1910)], although it has been generally considered poisonous. However, much further experimentation is necessary in order to settle this question.

The crude oil or butter, depending somewhat upon the method employed, varies from yellow to green and is used extensively in India for the manufacture of soap and candles, as an illuminant and in the treatment of skin diseases; but after refining it is used for edible purposes. In Europe, it is chiefly used by the candle and soap industry. In contrast to most of the crude product, the refined oil has a slight, rather pleasant taste and odor, and has little or no color.

It should be noted that the name "Illipé" is often applied to the seeds and fat from various species of *Shorea* (Nat. order, *Dipterocarpaceae*), which are native to the Straits Settlements, Borneo, etc., and are the sources of Borneo Tallow, also known in trade as "Green Butter."

T. P. Hilditch and M. B. Ichaporia [*J. Soc. Chem. Ind.,* **57,** 44 (1938)] have made an extensive investigation of the fatty acids and glycerides of this fat. The crude expressed commercial fat from Baroda gave a saponification equivalent of 290.2, an iodine number of 63.9, an acid value of 20.1, and contained 2.1 per cent of unsaponifiable matter. Prior to further examination it was refined with alkali carbonate. The mixed fatty acids from the neutralized fat contained the following percentages of constituents: palmitic 23.7, stearic 19.3, oleic 43.3, and linoleic 13.7. No other acids were detected. Dhingra, Seth and Speers [*J. Soc. Chem. Ind.,* **52,** 116T (1933)] reported that their mixed fatty acids contained 1 per cent of myristic, 16 of palmitic, 25.1 of stearic, 3.3 of arachidic, 45.2 of oleic, and 9.4 of linoleic acid. The original sample of solvent-extracted fat gave a saponification

equivalent of 293.6, an iodine number of 55.8, and contained one per cent of unsaponifiable matter.

Hilditch and Ichaporia stated that the probable percentage composition of their sample of fat was as follows: fully saturated glycerides 1.2, mono-oleo-glycerides 27.8, and di-oleo-glycerides 71.0. The molar percentages of the various glycerides was 0.9 of oleo-dipalmitins, 26.9 of oleo-palmito stearins, 41.3 of palmito-dioleins, and 29.7 of stearo-dioleins. Possibly very small quantities of oleodistearin and a small quantity (less than 5%) of tri C_{18} unsaturated glycerides may be present. The term "oleo" includes both oleic and linoleic acids.

Mowrah fat follows the usual rule for seed fats, namely, the even distribution of the fatty acids among the glycerol molecules. For other details and discussion of the results, the original should be consulted.

N. N. Godbole and P. D. Serwastava [*Fette u. Seifen,* **44,** 142 (1937)] have given data on the unsaponifiable matter in this and other Madhuca seed fats.

Under "Lead Arsenate in Turf Treatment" [*Chem. Trd. J.* and *Chem. Eng.,* **97,** 328 (1935)], mention is made of the use of mowrah meal on golf greens in England for killing earth worms and slugs.

The range of the characteristics of these two fats is as follows:

Madhuca (*Bassia*) *latifolia.*—Sp. g. at 100/15° C. 0.857 to 0.870; $N_D^{40°}$ 1.4577 to 1.4610; Sap. V. 188 to 197; Iod. No. 53 to 70; Unsap. 0.8 to 3.5%; R.M.V. 0.7 to 1.7; Pol. No. 0.9.

Madhuca (*Bassia*) *longifolia.*—Sp. g. 100/15° C. 0.856 to 0.864; $N_D^{40°}$ 1.4589 to 1.4621; Sap. V. 188 to 202; Iod. No. 58 to 63; Unsap. 1.4 to 2.6%; R.M.V. 1.4 to 3.6; Titer 36° to 45°.

Siak (Njatuo or Taban Merak) Fat or Tallow. This fat is obtained from the seeds which are known in commerce as "Large Siak Illipé Nuts" from the tree *Palaquium oleosum* and "Small Siak Illipé Nuts" from the *P. Oblongifolium,* both of the natural order of *Sapotaceae.* These trees are found in Malaya and elsewhere. The large Siak nuts are about 1.25 inches long and 0.75 in diameter, and weigh about 3 grams. The small Siak nuts weigh about 1.4 grams and contain from 50 to 55 per cent of fat: the others, from 43 to about 47 per cent.

The fat from the nuts of both species is similar in appearance and is yellow or greenish yellow in color. The natives use both fats for edible and other purposes; but when refined the fats are commonly sold as cacao butter substitutes.

The characteristics are as follows: *Large Siak.*—Sap. V. 187; Iod. No. 38; Unsap. 1.2%; M. Pt. 36° to 39° C.; $N_D^{40°}$ 1.4573. *Small Siak.*—Sp. g. at 100/15° C. 0.8553; $N_D^{40°}$ 1.4630; Sap. V. 182; Iod. No. 51; M. Pt. 31° to 36° C.; Unsap. 7 to 8%.

It will be observed that the iodine number and the unsaponifiable matter are much higher than those given for the fat from the large nuts.

T. P. Hilditch and W. J. Stainsby [*J. Soc. Chem. Ind.,* **53,** 197T (1934)] found that the Malayan kernels contained 52 per cent of fat.

The fat extracted with petroleum ether gave a saponification value of 189.1, an iodine number of 33.9, and contained 0.6 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: myristic 0.2, palmitic 5.9, stearic 54 and oleic 39.9. The fat contains about 77 per cent of mono-oleo-disaturated, 21 of dioleostearin, and 1.8 of fully saturated glycerides.

It is interesting to note that DeJough and de Haas [*Chem. Ztg.*, **66**, 780 (1904)] deduced that the mixed fatty acids from a sample of the fat contained 6.5 per cent of palmitic, 57.5 of stearic and 36 of oleic acid.

Although the fat from *P. oleosum* is at times called Borneo Tallow, this name is unjustifiable, as the latter comes from Shorea Species.

Imburana or Amburana Oil. It is found in the winged seeds of the tree *Torresea cearensis*, a member of the *Leguminoseae*, which grows in the dryer regions extending from the Brazilian state of Ceara into northern Argentina. The seeds contain about 28 per cent of oil, for which F. Berger [*Scienta Pharm.*, **11**, 122 (1938)]; *Chem. Absts.*, **33**, 1528 (1939)] reported the following characteristics. Sap. V. 198.6; Iod. No. 116.6; Acid V. 6.49.

Inoy Kernel Oil. This oil is obtained from the seeds of the plant *Poga oleosa*, a native of West Africa. The kernels contain from 57 to about 60 per cent of oil. The oil has a peculiar odor and a disagreeable taste. The range of the characteristics which have been reported by various investigators [*Analyst*, **34**, 167 (1909); **36**, 21 (1911); *Bull. Imp. Inst.*, **4**, 201 (1906)] are as follows: Sp. g. at 15° C. 0.896 to 0.918; $N_D^{40°}$ 1.4610; Sap. V. 184 to 193; Iod. No. 89 to 94; R.M.V. 1.45; Unsap. 0.35%; Titer 22° to 24.5°.

Jaboty Butter or Tallow. This fat is reported to be obtained from the kernels of the "nuts" from the South Amercian tree *Erisma calcaratum* (and *E. uncinatum*) belonging to the *Vochysiaceae*. The nuts weigh from 5 to 8 grams and contain from 53 to 70 per cent of kernels. The kernels vary in oil content from 42 to 53 per cent. The brittle, hard, light yellow fat has good keeping qualities and probably could be used as an edible fat as well as for the manufacture of candles and soaps. The range of the characteristics is as follows: $N_D^{40°}$ 1.4499 to 1.4506; Sap. V. 229-236; Iod. No. 15 to 23; Unsap. 0.5 to 1.0%; M. Pt. 40° to 46° C.; Acid V. 0.4 to 7.0.

A. Steger and J. van Loon [*J. Soc. Chem. Ind.*, **54**, 1095 (1935)] state that Jaboty butter is obtained from the seeds of the trees *Erisma calcaratum* and *E. uncinatum*. The fat from the kernels of *E. calcaratum* gave an iodine number of 23, a saponification value of 233.5, and melted at 45° C. The fat extracted from the kernels of the Brazilian red-flowered guaruba (*E. uncinatum*) had the following characteristics: Sp. g. at 78°/4 C. 0.8760; $N_D^{77°}$ 1.4360; Sap. V. 233; Iod. No. (Wijs) 5.4; Acid V. 20.0; Acetyl V. 10.0; R.M.V. 0.93; Pol. No. 3.1; M. Pt. 41.5° C. A commercial sample gave Sp. g. at 78°/4 C.

0.8764; $N_D^{77°}$ 1.4366; Sap. V. 236.1; Iod. No. (Wijs) 4.8; R.M.V. 1.3; Pol. No. 4.2; Acid V. 3.1; M. Pt. 43° C.

The mixed fatty acids contained the following percentages of constituents: lauric 23.9, myristic 52.8, palmitic 18.9, oleic 2.8, and 1.6 of a "viscous residue" which gave an iodine number of 67.0.

Japan Tallow. This product, which is also known as Japan wax, is obtained from the berries of a number of species of sumach trees which grow in China, Indo-China, Japan, Madagascar, and India. The more important species are *Rhus succedanea, R. vernicifera, R. sylvestris,* and *R. acuminata.* The trees are cultivated primarily for the production of lacquer, the tallow being merely a by-product. The tallow is prepared only in China, Japan and India. The annual production in China is probably about 3000 tons. A considerable part of this is refined in Japan and exported from Kobe. The Japanese producing centers are the prefectures of Kumanoto, Juknoka, Ehime, Shimane and Wakagama. The native product is brought to the ports of Kobe and Osaka, where it is refined for the trade. The annual production is fairly constant and amounts to about 13.5 million pounds.

The mature berries contain from 20 to about 30 per cent of the tallow. They are crushed and, after removal of the kernels, the tallow is expressed from the crushed material. On account of the growing demand for the tallow, it has become customary to add a small quantity of the oil pressed from the sumach kernels (which contain 30 to 34 per cent of oil) or other oil, such as perilla, to the press cake and to make a second pressing, the object being to get a larger yield of the tallow. This practice accounts for the wide variation in the composition of the commercial product in recent years. The crude product is a coarse, greenish solid which contains more or less vegetable matter and water. This is melted, filtered, and allowed to fall into cold water, which is stirred so that the fat solidifies into the form of thin flakes. These are placed in shallow trays and exposed to the sun, being frequently turned and watered to facilitate the bleaching. The bleached fat is then melted and cast into cakes, 6 inches square and 1 inch thick. The bleached product is cream-colored, but upon standing it gradually becomes dark yellow. It is chiefly used in the preparation of various polishes.

The characteristics of Japan tallow are as follows: Sp. g. at 15/15° C. 0.975 to 1.000, at 99/15° C. 0.875 to 0.877; Sap. V. 209 to 220; Iod. No. 5 to 17; Unsap. 0.5 to 1.7%; M. Pt. 50° to 54° C.; $N_D^{40°}$ 1.4552 to 1.4576; Titer 55° to 58°.

M. Tsujimoto [*J. Soc. Chem. Ind., Japan,* **10,** 212 (1935); *Chem. Absts.,* **29,** 6448 (1935); *Analyst,* **60,** 632 (1935)] examined the fat from the fruits of *Rhus succedanea,* with the following results: Sap. V. 208.1; Iod. No. 13.4; R.M.V. 0.3; Acid V. 15.9; M. Pt. 53-53.5°; Unsap. 0.77 per cent. The mixed fatty acids which melted at 63° C. were found to contain the following percentages of constituents: palmitic 77, stearic (and arachidic) 5, dibasic acids 6, oleic 12, and a trace of linoleic acid.

Adulterants are readily detected, as they lower the gravity, melting point and saponification value and increase the iodine number. Also, the examination should include the determination of moisture, which is present sometimes in excessive amounts. Those interested should consult *Bull. Econ. Madagascar,* **18,** 215 (1921).

Kapok Oil. This oil is obtained from the seed of the tree *ceiba pentandra (Eriodendron anfractuosum)* which is now found growing in many tropical countries. The tree, which belongs to the natural order of *Bombacaceae,* grows to a great size in the wild state, but under cultivation it is usually a slender tree seldom exceeding 50 feet in height. The fruit is a more or less oblong pod, about 6 inches long and 2 in diameter. The hairs or lint are attached to the inner walls of the pod and not to the seed, as is the case with the cotton seed. It is on account of the cotton-like appearance of the fiber that the kapok is known as the cotton or silk cotton tree. The seeds, which are black and about the size of small peas, consist of about 60 per cent of kernel and 40 of shell. The kernels contain about 40 per cent of oil; on the basis of the whole seed, 20 to 25 per cent.

As the kapok tree is cultivated for the fiber or floss, the seeds are a by-product of this industry. Java produces about 90 per cent of the kapok, but increasing quantities are being grown in Ceylon, India, Indo-China, the Philippines, Malaya, and South America. (South American species are *Bombax ceiba, B. chorisia, C. saenauna,* and *Ochroma lagopis*). Although the kapok tree is found in many localities of East and West Africa, it is cultivated in Tanganyika and Togoland. This tree grows in the Gold Coast, Kenya, the Sudan, the West Indies, Mexico, parts of South America, and the tropical portion of Australasia.

The tree grows best on a deep well-drained sandy loam, in the tropics at an elevation under 1500 feet above sea level, where there is abundant rain during the growing season and a dry period from the time the flowers are setting until after the pods are collected. Owing to the habit of dropping the leaves, the tree can resist long periods of drought. For further details see *Bull. Imp. Inst.,* **24,** 18 (1926).

J. E. Opsomer [1932 Bull. Agric. Belgian Congo; *Bull. Agric. Sci. Pract.,* **24,** 433 (1933)] gives much information on the propagation, planting and cultivation of kapok, as well as on harvesting the crop. The trees in favorable environment begin to bear four years after planting and a full-sized crop is obtained when the trees are fourteen years old.

The seeds produced in Java which are not crushed by local oil mills are exported, chiefly to Europe. Holland is the largest producer of the oil. At times some thousands of tons of the seed have been imported and processed in the United States. The crude oil, depending upon the quality, varies from light yellow to brown. After refining, it is used for the same purposes as refined cottonseed oil. Experience has shown that a somewhat longer period of agitation, both before and after heating the crude oil during caustic soda refining, is necessary

for a satisfactory separation or "break" than is ordinarily required by hot-pressed cottonseed oil.

The press cake and meal are used as feed for cattle.

The usual range of the characteristics is as follows: Sp. g. at 15° C. 0.920 to 0.933; $N_D^{40°}$ 1.4605 to 1.4657, at 25° 1.4691 to 1.4696; Sap. V. 189 to 195; Iod. No. 86 to 100; SCN V. 70.9; Unsap. 0.8 to 1.6%; R.M.V. 0.1 to 0.2; Pol. No. 0.1 to 0.3; Titer 27 to 32°.

E. P. Griffing and C. L. Alsberg [*Ind. Eng. Chem.*, **23**, 908 (1931)] examined the oil from sample of seed from Java. This oil, which gave an iodine number (Hanus) of 94.1 and a saponification value of 191.6, contained 17.15 per cent of saturated and 76.32 per cent of unsaturated acids. The oil was found to contain 49.6 per cent of oleic acid and 26.7 per cent of linoleic acid.

A. O. Cruz and A. P. West [*Phil. J. Sci.*, **46**, 131 (1931)] investigated oil expressed from Philippine seed. It gave an iodine number (Hanus) of 95.6 and contained 18.6 per cent of saturated acids. The percentages of fatty acids in the oil were as follows: oleic 49.8, linoleic 29.3, myristic 0.3, palmitic 15.9, stearic 2.3, and arachidic acid 0.8 per cent.

V. C. Mehlenbacher [*Oil and Soap*, **14**, 118 (1937)] found that a sample of refined kapok oil, which gave an iodine number (Wijs) of 100.5 and a thiocyanogen value of 70.95, contained 16.3 per cent of saturated acids, 48.2 of oleic acid, and 34.1 of linoleic acid, all of which are in terms of triglycerides. Also, he discusses refining and gives a table of data for the laboratory refining of 26 samples of imported kapok oil.

Jamieson and McKinney [*Oil and Soap*, **13**, 233 (1936)] examined the oil expressed from Java seed by the Pacific Vegetable Oil Company, San Francisco, California. The oil gave the following characteristics: $N_D^{25°}$ 1.4696; Sap. V. 190.7; Iod. No. (Hanus) 96.0; Acid V. 3.7; Acetyl V. (André-Cook) 12.9; Unsap. 0.8%; Saturated acids 19.0% and unsaturated acids 74.3%. The oil contained the following percentages of acids: oleic 43.0, linoleic 31.3, palmitic 9.77, stearic 8.00, arachidic 1.2, and lignoceric acid 0.23.

Tests.—Kapok oil gives the Halphen color reaction much more strongly than does cottonseed oil. The presence of 0.05 per cent of this oil in other oils can readily be detected by the Halphen test. Besson [*J. Soc. Chem. Ind.*, **34**, 184 (1915)] states that these oils may be distinguished by shaking a chloroform solution of the sample with a 2 per cent absolute alcoholic solution of silver nitrate. Kapok oil almost at once gives a coffee-brown coloration. Cottonseed oil, after standing some hours, gives only a yellow coloration. The dried insoluble fatty acids of kapok oil give a brown color with this silver nitrate test [Sprinkmeyer and Diedricks, *Analyst*, **38**, 467 (1913)].

V. C. Mehlenbacher [*Oil and Soap*, **13**, 136 (1936)] has made an extensive study of all the color tests proposed for kapok oil and concludes that the Besson one is best.

It may be of interest to know that according to L. H. Dewey (*1928 U. S. Dept. Agric. Yearbook*, p. 403), there are 54 species of fiber-producing trees which belong to 4 genera as follows: 11 species of *Ceiba*, 25 of *Bombax*, 7 of *Chlorisia*, and 11 of *Gossampinus*.

Indian Kapok Oil. This kapok oil is obtained from the seed of the large tree *Bombax malabaricum,* which is found throughout India and Ceylon. (Java kapok is *Ceiba pentandra,* which also belongs to the *Bombacaceae.*) The small, dark brown seeds contain from 20 to 23 per cent of oil. In India, where a small quantity of the oil is expressed, it is used as a burning oil, but like the oil from Java kapok seed it could be used for edible purposes and for soap making.

The following characteristics are reported by the Imperial Institute [*Imp. Inst. Bull.*, **18**, 335 (1920)]: Sp. g. at 15/15° C. 0.9208 to 0.9300; $N_D^{40°}$ 1.4610; Iod. No. 74 to 78; Sap. V. 193 to 194; Unsap. 1%; R.M.V. 0; Pol. No. 0.5; Titer 38.0°. The oil gives an intense Halphen test. It will be observed that the iodine number is much lower than that of the European commercial (Java) oil, which ranges from 86 to 98.

The extracted meal gave the following results: moisture 11.4, crude proteins 36.5, fat 0.8, fiber 19.9, carbohydrates, etc. (by difference) 24.7 and ash 6.7 per cent.

It is believed that the meal would be a more valuable feeding stuff than that from the Java seed. Some day this excellent oil may become of commercial importance.

Koeme (Jiconga) Seed Oil. This oil is obtained from the seeds of the *Telfairia pedata,* a tall climbing plant of tropical Africa belonging to the *Cucurbitaceae.* The flat yellow seeds, which are enclosed in a large pulpy fruit, are known as "jiconga nuts" in some localities. The triangular flat seeds, which vary in length from 0.75 to 1.5 inches are recognized easily by the tough interlaced matting which firmly encloses them, but is distinct from the seed coat. The kernels contain from 59 to 63 per cent of oil, equivalent to 35 to 38 per cent of the whole seed. No machine has been developed for the removal of the kernels from the seed; consequently, the oil is not produced on a commercial scale. The seed coat or shell contains a bitter substance which partly passes into the expressed or extracted oil from the whole seeds. The oil from the separated kernels is pale yellow, but when viewed by reflected light usually shows a slight red or green fluorescence. The usual range of the characteristics obtained by various observers is as follows: Sp. g. at 15° C. 0.918 to 0.919; $N_D^{40°}$ 1,4623 to 1.4633; Sap. V. 193 to 197; Iod. No. 89 to 101; Unsap. 0.3 to 0.9%; Acid V. 0.3 to 2.4; Titer 38.8° to 41.8°.

W. C. Smit and J. van Loon [*Fettchem. Umschau,* **43**, 71 (1936)] examined Transvaal seed and the oil. The seeds, each of which weighed about 6 g., contained a single kernel weighing about 3.6 g. The kernels contained 61.6 per cent of oil, or 37.1 per cent on the basis of the whole seed. The characteristics of the oil were as follows: $N_D^{70°}$ 1.4511; Sap. V. 193.7; Iod. No. (Wijs) 88.2; SCN V. 52.7, Acetyl V. 9.6; R.M.V. 0.48; Unsap. 0.9%; volatile 3.3%.

The oil contained the following percentages of acids: palmitic 24.3, stearic 18.2, oleic 11.4, linoleic 32.6 and linolenic acid 5.0.

It should be noted that the telfairic acid described by H. Thoms [*Arch. Pharm.*, **238**, 48 (1900)] as a constituent of this oil has been found to be ordinary linoleic acid by G. D. Goodall and R. D. Haworth (*J. Chem. Soc.*, **1936**, 399) and by Smit and van Loon.

Krobonko Seed Oil. This oil is found in the seeds of the *Telfairia occidentalis* of the *Cucurbitaceae* family, native to West Africa. The seeds consist of 68.8 per cent of kernel and 31.2 of shell. The kernels contain about 48 per cent of oil. The dark brown, viscous oil extracted by Grimme [*Chem. Rev.*, **17**, 267 (1910)] gave the following results: Sp. g. at 50° C. 0.9135, Sap. V. 262.2; Iod. No. (Wijs) 43.4; Unsap. 0.38%. E. H. Farmer and E. S. Paice (*J. Chem. Soc.*, **1935**, 1630) have showed that the oil contains elaeostearic acid, but did not determine the quantity present in the oil nor did they give the characteristics of the oil.

Kokum (Goa) Butter. This product is obtained from the seeds of the fruit of the *Garcinia indica (Guttiferae)* a tree growing in India and the East Indies. The small, black, ovoid seeds, which are enclosed in a fleshy fruit, contain from 23 to 26 per cent of a grayish white fat having but slight odor and taste. It is for the most part obtained by the crude native method of boiling the crushed kernels in water. It is finally marketed in egg-shaped balls. In India, it is used for edible purposes. The characteristics are as follows: $N_D^{40°}$ 1.4565 to 1.4575; Sap. V. 187 to 191.7; Iod. No. 25 to 36; Unsap. 2.3%; R.M.V. 0.1 to 1.0; M. Pt. 40° to 43° C.; Titer 60°.

N. L. Vidyarthi and C. J. D. Rao [*J. Indian Chem. Soc.*, **16**, 437 (1939)] examined a sample of fat which melted at 39.4° C., gave a saponification value of 189.2 and Iod. No. (Wijs) 36.7, and contained 1.2 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: oleic 41.5, myristic 1.2, palmitic 5.3, and stearic acid 52.0. The percentages of component glycerides were calculated to be as follows: tri-stearin 2.0, oleo-di-stearin 59, di-oleo-stearin 21, oleo-palmito-stearin 14, oleo-di-palmitin 2, and palmito-di-olein 2.

T. P. Hilditch and K. S. Murti [*J. Soc. Chem., Ind.*, **60**, 16 (1941)] found that the mixed fatty acids contained the following percentages of constituents. *G. Indica*—palmitic 2.5, stearic 56.4, oleic 39.4, and linoleic 1. *G. morella*—palmitic 0.7, stearic 46.4, arachidic 2.5, oleic 49.5 and linoleic 0.9.

Gamboge Butter. This fat is obtained from the seeds from the fruit of the tree *Garcinia morella,* found in Ceylon, Mysore, and on the western coast of India. It is known in various localities as "Gurgi" or "Murga" and is used in cooking, as an ointment and as an illuminant. The characteristics are as follows: Sp. g. at 50/50° C. 0.900; Sap. V. 195 to 198; Iod. No. 54 to 56; R.M.V. 0.6 to 0.7; M. Pt. 34° to 37° C.

D. R. Dhingra, G. L. Seth, and P. C. Speers [*J. Soc. Chem. Ind.*, **52**, 116T (1933)] examined the kernels and fat. The kernels contained 57.5 per cent of fat. The fat had the following characteristics: $N_D^{40°}$ 1.4612; Sap. Equiv. 294.0; Iod. No. 48.3; Acid V. 5.4; Unsap.

0.1%. The mixed fatty acids contained the following percentage of constituents: oleic 43.6, linoleic 6.1, myristic 0.3, palmitic 7.2, stearic 42.5, and arachidic 0.3.

The fat contained 2.7 per cent of fully saturated glycerides, about 45 of oleo-disaturated, and about 50 of dioleo-saturated glycerides. The small quantity of linoleic acid present is included with the oleo-glycerides mentioned above.

Other fats and oils from the seeds of *Garcinia* species, natural order *Guttiferae*, are as follows: The seeds of the *G. balansae* yield a liquid oil which has been examined by C. Grimme [*Analyst*, **36**, 21 (1911)]. The seeds, which weigh 2 to 3 grams, contain over 60 per cent of oil that gave the following characteristics: Sp. g. at 15° C. 0.913; $N_D^{40°}$ 1.4682; Sap. V. 176.3; Unsap. 4.2%; Iod. No. 86.2; Sol. Pt. 8.6°; Titer 30.3°.

Ran and Simonsen [*J. Soc. Chem. Ind.*, **41**, 912A (1922)] found that the seeds of *G. cambogia* contained 31 per cent of a solid fat similar to those from some of the other species. The seeds of the *G. echinocarpa* yield a viscous oil which is used in India as an illuminant and vermifuge. The oil from *G. canranana* has also been examined by the Imperial Institute (*Bull. Imp. Inst.*, **1912**). These oils are produced and used only by the natives.

Jojoba Seed Oil. This oil, which is a liquid wax, amounts to about 50 per cent of the seed of *Simmondsia californica*, belonging to the *Buxaceae* (boxwood family). In various localities it is also known as the pig, sheep, goat, and quinine nut. The plant is an evergreen shrub ranging in height from 3 to 15 feet. It is found growing in arid regions on hillsides and mountains in southern Arizona, Lower California, and western Mexico. Being one of the few green plants in these localities, it is freely eaten by sheep, goats, and other browsing animals. Rodents feed on the seeds.

The plant bears both staminate and pistillate flowers. The mature fruit is a thin, brown, 3-valved, capsule which contains a single seed having a tough, reddish brown testa. The seeds (about 12 mm. x 8 mm.) vary in weight from 0.4 to 1.4 grams.

R. A. Greene and E. O. Foster [*Botanical Gazette*, **94**, 826 (1933)] were the first to discover that the oil was a liquid wax and contained no detectable quantity of glycerides. Their qualitative tests suggested that it might consist largely of fatty acid esters of decyl alcohol. The characteristics reported by them are as follows: $N_D^{25°}$ 1.4650; Sap. V. 95; Iod. No. (Hanus) 88.4; Acetyl V. 6.8; R.M.V. 0.70; Pol. No. 0.31; Unsap. 37.6 per cent; Solid. Pt. 10-12°.

Insofar as the writer is aware, there is no record of any other seed containing wax esters in place of glycerides. Subsequent investigations have shown that the composition of this liquid seed wax is unique as far as waxes of vegetable origin are concerned.

R. S. McKinney and Jamieson [*Oil and Soap*, **13**, 289 (1936)] investigated the oil extracted with petroleum ether from 25 pounds of seed from the state of Sonora, Mexico, which was sent to us by L.

Kishlar, St. Louis, Mo. The seed contained 4.7 per cent of moisture and 51.2 per cent of oil. This oil, like that expressed later from a larger sample of seed, was a beautiful golden liquid. When it is heated for a short time at about 300°, the color disappears completely and does not return. The characteristics are as follows: Sp. g. 25/25° 0.8642; $N_D^{25°}$ 1.4648; Iod. No. (Hanus) 81.7; Sap. V. 92.2; Unsap. 48.3 per cent; Acid V. 0.32; Sat. acids (Bertram) 1.64 per cent; Acetyl V. of Unsap. 171.8 and Iod. No. (Rosenmund-Kuhnhenn) 77.2.

The percentages of the acids and alcohols in the oil are as follows: saturated 1.64, palmitoleic 0.24, oleic 0.66, eicosenoic 30.30, dicosenoic 14.20, eicosenol 14.60 and dicosenol 33.70 per cent. Simultaneously, T. G. Green, T. P. Hilditch and W. J. Stainsby [*J. Chem. Soc.* **1936,** 1750] made an investigation of the oil extracted from seeds sent from Arizona by R. A. Greene. Oils from seeds, labelled 1935 and 1936, gave oils with an iodine number of 83.4 and 83.1, saponification equivalents of 594.3 and 590. The iodine numbers of the respective acid constituents were 79.8 and 80.71, and of the alcohol fractions 80.8 and 81.5. They found that the chief constituents of the wax esters were C_{20} and C_{22} unsaturated acids and unsaturated alcohols, along with unusually small quantities of oleic and palmitic acids. The C_{20} components were identified as $\Delta^{11:12}$ eicosenoic acid and the corresponding alcohol as $\Delta^{11:12}$ eicosenol; the C_{22} as $\Delta^{13:14}$ dicosenol; the higher acid is probably dicosenoic. For details of this extensive investigation, the original paper should be consulted.

For certain purposes this liquid wax could be used as a lubricant, if it should be produced on a commercial scale. It has been used by several chemists in melting point apparatus in place of sulfuric acid. Under the date of September 15, 1936, United States Patent 2,054,283 was granted to C. Ellis, covering jojoba oil factice for use in the manufacture of floor coverings such as linoleum. It would be interesting to find out whether or not the seeds of other *Buxaceae* plants such as *Stylocereae laurifolium, S. columnare* and *S. kunthianum* of South America, or the *Ticera citrifolia* of Cuba, contain a liquid wax.

Kurrajong Oil. This oil is obtained from the seeds of the tree *Brachychiton populneum* (*Sterculia divesifolia. F. Don*). The tree, which grows in Eastern Australia, reaches a height of 60 feet. The seeds contain 25 to 27 per cent of fat, which has been examined by F. R. Morrison [*Bull. Imp. Inst.,* **24,** 691 (1926)], with the following results: Sp. g. at 30° C. 0.908; $N_D^{20°}$ 1.4676; Sap. V. 198; Iod. No. (Wijs) 101.3; M. Pt. 30° C.; Acid V. 65.

When extracted, a moderately viscous red oil was obtained, but in a few days it became semi-solid. A second sample of seeds gave an oil with an acid value of 42.7, and this remained liquid.

Lamy, Kanga or Sierra Leone Butter. This fat is obtained from the seeds of the large tree *Pentadesma butyracea* of the *Guttiferae*, which is native to tropical West Africa. There it is known as the butter or tallow tree. The seeds are enclosed in large, fleshy fruits.

Depending upon the moisture content, the large irregular kernels contain from 36 to about 50 per cent of fat. The following characteristics have been reported by various investigators: Sp. g. at 100/15° C. 0.857 to 0.860; $N_D^{40°}$ 1.4563; Sap. V. 186 to 199; Iod. No. 42 to 47; R.M.V. 0.3; Unsap. 0.9 to 1.7%; M. Pt. 33° to 42° C.; Titer 51° to 55°.

T. P. Hilditch and S. A. Saletore [*J. Soc. Chem. Ind.*, **50**, 468T (1932)] examined kernels from Sierra Leone, Africa. They contained about 41 per cent of fat. The solvent-extracted fat gave a saponification equivalent of 294.7, an iodine number of 42.9, an acid value of 12.5, and contained 0.5 per cent of unsaponifiable matter. The fat melted 33.5-34°. The mixed fatty acids consisted of the following percentages of constituents: palmitic 5.4, stearic 46.1, and oleic 48.5. From their investigation, it would appear probable that the fat consisted very largely of mono-oleo-disaturated and di-oleo-monosaturated glycerides. About 3 per cent of the glycerides was found to be fully saturated.

E. D. G. Fralm [*De Ingenieur (Netherlands Indies)* **8**, 87 (1941), *Analyst*, **67**, 25 (1942)] has made an investigation of this fat. The mixed acids from the fat contained the following percentages of constituents. Palmitic 7.3, stearic 38.5, oleic 47.5, and linoleic 1.58. The iodine number of the fat was 46.6 and the saponification value was 190.

The expressed fat is pale yellow and usually somewhat brittle. After refining it can be used for edible purposes, providing care is taken to remove foreign seeds, which may be poisonous, prior to the extraction of the fat. The crude product is suitable for making soap. References to this fat are as follows: *Analyst*, **34**, 164 (1909); **36**, 21 (1911); **39**, 134 (1914); **43**, 352 (1918).

Laurel (Bay) Berry Fats. These fats are found in the pulp and seed of the fruit from the southern Eurpoean tree *Laurus nobilis*, belonging to the *Lauraceae*. The berries consist of about 30 per cent of pulp and 70 of seed. The pulp contains from 35 to 37 and the kernels from 14 to 17 per cent of fat.

The commercial fat is obtained either by pressing or boiling the crushed berries in water. As prepared, it contains more or less aromatic essential oil constituents. It is used for making soap and as a veterinary medicine.

A sample of the fat was examined by Mathes and Sander [*Arch. Pharm.*, **246**, 165 (1908)] with the following results: $N_D^{40°}$ 1.4643; Sap. V. 200.9; Iod. No. (Hübl) 82.4; Unsap. 1.0%; R.M.V. 3.2; Pol. No. 2.8; Acetyl V. 15.2; Acid V. 9.4; M. Pt. 32 to 36° C. The following results were by various observers: Sp. g. at 15° C. 0.933 to 0.953; Sap. V. 198 to 201; Iod. No. 75 to 82; Titer 15 to 19° C.

Collin and Hilditch [*J. Soc. Chem. Ind.*, **49**, 141T (1930)] found that the berries which they examined consisted of 70 per cent seed and 30 per cent pericarp. The kernels contained about 17 per cent of a pale yellow, solid fat, whereas the pericarp had 35 to 37 per cent of a dark green oil. The mixture of kernel and pericarp commercial oil, extensively investigated after the removal of essential oil by these

workers, had the following characteristics: Iod. No. 86.4; Acid V. 9; Unsap. 6.2%; Solid Acids 50.7; Liquid Acids 40.3. The mixed fatty acids consisted of lauric 35, palmitic 9.7, oleic 36.6 and linoleic acid 18.7 per cent.

G. Collin [*Biochem. J.*, **25**, 95 (1931)] has examined both the pulp and kernel fats. The fat extracted from the pulp was a dark green liquid which gave a saponification value of 196.4 and an iodine number of 113.1. The extracted kernel fat was a light brown solid. It gave a saponification value of 217.6 and an iodine number of 84. The percentage composition of the mixed fatty acids of the pulp fat is as follows: lauric 2.4, palmitic 18.3, oleic 56.9, linoleic 12.6, and unsaponifiable matter 9.8.

The mixed fatty acids from the kernel fat contained the following percentages of constituents: lauric 33.2, palmitic 4.8, oleic 24.9, linoleic 14.2, and unsaponifiable matter 22.9.

The investigation of the glyceride structures of these fats indicated that the one from the pulp was a normal specimen of its class, but the kernel fat possessed one of extreme heterogeneity instead of the usual "even mixed" structure. This fat contains about 24 per cent of the trilaurin. The original article should be consulted for other details and data concerning the glyceride structures of these fats.

Locust (Carob Bean) Seed Oil. This oil is found in the seeds of the *Ceratonia siliqua*. A. L. Williams [*Analyst*, **53**, 411 (1928)] examined the extracted oil with the following results; Sp. g. at 15.5° C. 0.951; Sap. V. 198 to 205.5; Iod. No. (Wijs) 98.5 to 99; R.M.V. 1.8; Pol. No. 0.8; Unsap. 2.86%; Titer 25°. The extracted meal contained 12 per cent of moisture, 15.12 of proteins, 1.8 of oil, 6.1 of fiber and 62.1 of carbohydrates.

Macadamia (Queensland) Nut Oil. This oil is found in the nut of the tree *Macadamia ternifolia*, native to the coast district of Queensland and the north coast district of New South Wales, Australia. Seeds of this tree were introduced into Hawaii about 1883.

According to C. A. Lothrop [*J. Oil and Fat Ind.*, **2**, 44 (1925)], who examined the nuts and oil with the results given below, this is one of the most promising nuts for commercial cultivation within the tropics and subtropics. The very ornamental tree, which attains a height of about 35 feet, bears the nuts singly or in clusters containing up to 8 nuts. The trees often begin to bear when three years old. When the nuts have matured, they fall from the trees. The nuts have shells 3 mm. thick and are difficult to crack. They consist of 29 per cent of kernels and 71 of shells. The kernels contain about 76 per cent of oil. The oil has a slight nutty flavor and would be a delicious salad oil, if produced commercially.

The kernels were analyzed with the following results: Moisture 3.1, fat 76.5, fiber 1.7, proteins 8.6, carbohydrates 8.2, and ash 1.9 per cent. Characteristics of expressed oil: Sp. g. at 15.5° C. 0.9141; $N_D^{15.5°}$ 1.4698; Sap. V. 193.7; Iod. No. 74.2; Unsap. 0.32%; Acid V. 0.2; Sol. Pt. —12.2° C.

A. and F. Morrison [*J. Soc. Chem. Ind.*, **43**, 915B (1924)] found the following range of characteristics: Sp. g. at 15° C. 0.912 to 0.915 $N_D^{40°}$ 1.4602; Sap. V. 195.6; Iod. No. 74 to 76; Unsap. 0.1 to 0.2%.

Macasser (Kussum) Oil. This oil is obtained from the seeds of the paka or kussum tree, *Schleichera trijuga* of the *Sapindaceae*, which is found in India, Ceylon and East Indies. The reddish brown seeds weigh from 0.5 to 1 gram each and contain about 60 per cent of kernel. The oil content of the kernels varies from 60 to 72 per cent. The oil is chiefly used as an illuminant but is employed to some extent in India as an edible and soap oil. Bolton and Jesson [*Analyst*, **40**, 3 (1915)] examined a sample of the oil with the following results: Sap. V. 227; Iod. No. 54.5; R.M.V. 16.0; Pol. No. 0.3; Kirch. V. 15.5; Titer 52°; $N_D^{40°}$ 1.4597. Lewkowitsch reported the following results: Sap. V. 215 to 230; Iod. No. 48 to 69; R.M.V. 9; Titer 52°; Unsap. 3.1 per cent.

Poleck [*Pharm. Centr.*, **32**, 396 (1891)] found that the fatty acids of the oil contained 5 per cent of palmitic, 25 of arachidic, 70 of oleic, and small quantities of acetic acid.

D. R. Dhingea, T. P. Hilditch, and J. R. Vickery [*J. Soc. Chem. Ind.*, **48**, 281T (1929)], who made an extensive examination of the oil, found that the unsaponifiable matter varied from 1.5 to 7.2 per cent, and that acetic acid was present to the extent of 1 to 2 per cent, but probably not in the form of glyceride; contrary to previous statements, they found no lauric acid. They found the composition of the mixed fatty acids to be approximately as follows: oleic 60 per cent, linoleic 3 to 4, arachidic 20 to 25, palmitic 5 to 8, stearic 2 to 6, and myristic acid about 1 per cent. They state that the general structure of the glycerides appears to be that of other kernel fats, namely, a more or less even distribution of all the acids present among the glyceride molecules and possibly also some triolein, and that triarchin occurs only in very minute quantities. The oil also contained more or less resinous substances.

Unless the oil is properly refined, it is not considered suitable for edible purposes. Cyanogenetic glucosides may or may not be present in the seeds. This requires further investigation, particularly before the seeds or oil cake are fed to animals.

Mafura Oil and Tallow. These products are obtained from the nut-like fruits of the tree *Trichilia emetica*, belonging to the *Meliaceae*, found on the East African Coast. The small red or brown, ovoid fruits, depending upon the source, weigh from 0.3 to 1 gram, and depending upon the variety, the shells constitute from 12 to 42 per cent of the fruit. The shells contain from 30 to 50 per cent of oil and the kernels, 45 to 65 per cent of tallow. The natives boil the fruits in water and remove the oil by skimming, the better grades of which are said to be used in cooking. The tallow which is extracted from the kernels is considered poisonous by the natives and is used as an ointment. The crude tallow has a bitter taste. The commercial product is usually a mixture of oil and tallow and is used chiefly for making soap.

For many years, the seeds have been exported to France [Amanor and Vinlet, *J. Soc. Chem. Ind.*, **34**, 288 (1915)] for the manufacture of candles and soap from the tallow. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.931; $N_D^{20°}$ 1.4695; Sap. V. 195 to 202; Iod. No. 66 to 70; Unsap. 0.6 to 0.8%; Sol. Pt. 6° C.; Titer 44°. Tallow: Sp. g. at 40° C. 0.902; $N_D^{40°}$ 1.4583; Sap. V. 201; Iod. No. 43 to 49; Unsap. 1.2 to 1.4%; M. Pt. 33° to 41° C.; Titer 51° to 52°.

Mahuba Rana Fat. This fat is probably obtained from the seeds of one or more species of *Acrodiclidium* (belonging to the *Lauraceae*) indigenous to Brazil. The seeds, which weigh from 2 to 3 grams, contain about 90 per cent of kernels. The kernels contain from 63 to 70 per cent of a pale yellow fat. Bolton reports the following characteristics: $N_D^{40°}$ 1.4535; Sap. V. 245.1; Iod. No. 21; Unsap. 4%; M. Pt. 40° to 44° C. The fat, if available in quantity, could be used in the manufacture of soap and candles.

Malabar or Piney Tallow (Dhupa Fat). This product is obtained from the seeds of the large evergreen tree *Vateria indica (Dipterocarpaceae)*, native to the East Indies. The tree is abundant on the Malabar Coast and in the region from Kanâr to Travancore. It is also the source of the Indian copal resin of commerce. The seeds, which are enclosed in a thick, hard husk, contain usually from 22 to 27 per cent of the tallow which, in consistency, is similar to cacao butter and has usually but little odor or taste. When they are freshly extracted, the color is greenish yellow, but it is readily bleached by sunlight. In India it is used for edible purposes, the manufacture of candles and soap, and for sizing cotton yarn in place of tallow. It is also used in Europe by candle and soap makers.

The characteristics are as follows: Sp. g. 100/100° C. 0.890; $N_D^{40°}$ 1.4574 to 1.4590; Sap. V. 187 to 192; Iod. No. 36 to 41; Unsap 1.2 to 2.5%; M. Pt. 30° to 40° C.; R.M.V. 0.2 to 0.4; Titer 53° to 55°. A sample of Indian press cake contained the following: Moisture, 10.5, oil 7.7, crude proteins 7, carbohydrates 66, and crude fiber 5.6 per cent. The cake has a very bitter taste and is suitable for use only in supplying humus to the soil. Reference to kernels and fat: *Bull. Imp. Inst.*, **28**, 279 (1930).

T. P. Hilditch and S. A. Saletore [*J. Soc. Chem. Ind.*, **50**, 468T (1932)] examined a sample of the fat furnished by the Government Soap Factory at Bangalore. It gave a saponification equivalent of 303.5, an iodine number of 42.8, an acid value of 8.8, and contained 1.4 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: oleic 47.8, palmitic 10.2, stearic 38.9, and arachidic acid 3.1.

Mammy Apple Seed or Sapote (Sapucyul) Oil. This oil is obtained from the seeds in the fruit from the tree *Calocarpum mammosum* of the *Sapotiaceae*, formerly known as *Sideroylum sapotum*, *Achras mammose*, *Lucuma mammose* and *Vitellaria mammosa*. The tree, which grows from 30 to 90 feet high, is native to Central America.

The fruit is globose to fusiform in shape and varies in length from 8 to 20 cm., and is 6 to 12 cm. in diameter. The pulp is used for making jelly, marmalade and a beverage. The brown or yellow seeds are about 6 to 8 cm. long and 2 to 3 cm. at the largest diameter. Locally, the seeds are used for lubricating irons for ironing clothes.

Jamieson and McKinney [*Oil Fat Ind.*, **8**, 255 (1931)] made an analysis of the seed and investigated the expressed oil. The seeds (kernels), which were received from Honduras, were found to contain 57 per cent of oil and 9.4 of moisture. The expressed oil gave the following characteristics: Sp. g. at 25°/25° C. 0.9105, $N_D^{25°}$ 1.4652; Sap. V. 189.5; Iod. No. (Hanus) 70.2; R.M.V. 0.15; Pol. No. 0.30; Acetyl V. 12.2; Unsap. 1.39%; Sat. Acids 30.37%; Unsat. Acids 63.73%.

The oil contained the following percentages of fatty acids: oleic 52.15, linoleic 12.88, palmitic 9.40, stearic 20.95, and arachidic .02.

The expressed oil had a slight almond-like odor and a very mild, pleasant taste. When cooled to 15° C. it solidified. The oil could be used as a cooking and salad oil in tropical countries, and for the manufacture of soap.

Maroola Nut Oil. This oil is obtained from the kernels of the fruit of the *Sclerocarya coffra*, a small tree belonging to the *Anacardiaceae*, which is found in Natal and the Transvaal. The fruit is a drupe about the size of a small hen's egg, and is yellow. The thin pericarp surrounding the nut has a flavor somewhat like the mango, but is much more acid. The nuts, which weigh about 5 grams, contain from 1 to 3 kernels. The kernels amount to about 10 per cent of the nut and contain about 56 per cent of oil, which has been examined by the Imperial Institute, [*Bull. Imp. Inst.*, **18**, 481 (1920)] with the following results: Sp. g. at 15° C. 0.9167; $N_D^{40°}$ 1.460; Iod. No. 73 to 76; Sap. V. 193.5; Unsap. V. 0.6%; R.M.V. 0.1; Pol. No. 0.45; Acid V. 3.7.

"In view of the difficulty of cracking the nuts and separating the kernels, it is unlikely that the nuts could profitably be used as a source of oil."

Mung Bean Oil. This oil is found in the Asiatic bean *Phascolus mungo*, which belongs to the *Leguminosae*. The beans contain about 9 per cent of oil. S. Miki and S. Sera [*J. Agr. Chem. Soc., Japan*, **8**, 1313 (1932), *Chem. Absts.*, **27**, 2054 (1933)] examined the extracted oil, which was a semi-solid green fat, with the following results: Sap. V. 173.3; Iod. No. 81.6; Unsap. 16.55 per cent. The solid acids, which amounted to 39 per cent, were separated by the lead salt method; they contained approximately 70 per cent of palmitic, 20 of stearic, and traces of arachidic acid. The unsaturated acids contained approximately the following percentages of constituents: oleic 30, linoleic 65, and linolenic acid 5.0.

Myristicaceae. These are tropical trees, the fruits of which enclose seed that are surrounded by arils. The nutmeg *(Myristica fragrans)* is the most important member of this family from a com-

mercial standpoint. In a number of cases confusion apparently exists in regard to the botanical nomenclature and it would appear desirable to have the botanists re-examine the *Virola bicuhyba,* the *V. venezuelensis,* the *V. surinamensis* and the *V. guatamalensis* and determine whether or not these trees are to be classified as different species, or simply different varieties of the same species. Also it is desirable that the fats should be examined more thoroughly because in a number of cases, the data available are meager.

The fats from the seeds of these trees are characterized by large quantities of glycerides of myristic acid. Most of the fats are quite hard, and with few exceptions, contain more or less essential oil as well as resins. Many of the fats are colored various shades of brown, the color coming from the ramifications of the inner seed coat in the form of irregular dark bands extending through the kernels.

Nutmeg Butter. This product is obtained from the seeds of the tropical tree *Myristica fragrans (officinalis)* indigenous to the Banda Islands, Java, Moucca, Sumatra, and neighboring regions. It is cultivated now in many parts of the tropics. The seeds contain about 40 per cent of fat and essential oil. The fat, which is usually expressed but sometimes extracted by solvents, contains from 6 to 13 per cent of essential oil, to which it owes its characteristic odor. The product exported from the East is in the form of bricks weighing 1 to 1½ pounds. That from the English colonies is yellowish red, fine-grained, marbled cakes, while that from the Dutch colonies is more coarsely grained and of lighter color. The fat prepared in the East and in Europe is obtained from nutmegs that are not suitable for exportation for one reason or another. It is used for medicinal purposes and for a flavoring. Power and Salway [*J. Chem. Soc.,* **93,** 1653 (1908)] examined the butter from Aylong nutmegs with the following results:

Fat	Expressed	Extracted	Expressed, Free from Essential Oil
Melting point	48° C.	50° C.	49° C.
Density 50/50° C.	0.9399	0.9337	0.9443
Acid value	11.2	12.9	14.0
Sap. value	174.6	180.5	199.6
Iodine number	57.8	45.7	35.7

The approximate composition of the expressed fat was as follows: essential oil 12.5, myristin 73, olein 3, linolein 0.5, resins 2, and unsaponifiable constituents 8.5 per cent. A previously unknown compound ($C_{18}H_{22}O_5$), which is a viscous liquid, was isolated from the unsaponifiable constituents, as well as myristicin ($C_{11}H_{12}O_3$). The former, which amounts to about 5 per cent or more of the unsaponifiable matter, has one ethylenic linking and an iodine value of 79.9.

The usual range of the characteristics is as follows: Sp. g. at 15° C. 0.945 to 0.960, at 100° C. 0.8840; $N_D^{40°}$ 1.4662 to 1.4704; Sap. V. 168 to 180; Iod. No. 45 to 59; M. Pt. 42° to 52° C. Sometimes, the commercial product gives lower saponification and higher iodine values than those given.

Collin and Hilditch [*J. Soc. Chem. Ind.*, **49**, 141T (1930)] investigated the composition of nutmeg butter with regard to the fatty acids and their glycerides, [*Biochem. J.*, **23**, 1273 (1929)]. The sample had an iodine number of 61 and contained 17.7 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: lauric 1.5, myristic 76.6, palmitic 10.1, oleic 10.5, and linoleic 1.3. The refined fat contained 58.6 per cent of fully saturated glycerides, corresponding to a saturated glyceride content of 71 per cent on the fat actually present, and with an "association ratio" in the non-fully saturated glycerides of the latter of 1.6 mols of saturated per mol of oleic acid, thus conforming to the general rule of even distribution of the fatty acids between the glycerides of kernel fats. For further details, the original references should be consulted.

Ucuhuba Butter. It was formerly believed that this fat was obtained from the seeds of the fruit from the tree *Virola bicuhyba,* which is found in southern Brazil, but according to Paul Le Cointe, Director of the commercial museum at Belem, Para, Brazil, the fat of commerce is from the seeds of the trees *Virola surinamensis* and *sebifera.* These trees grow in the Amazon River region. The spherical seeds of these 3 species are similar in appearance and weigh from 1 to 3 grams. They have thin, easily removable shells. The kernels, which constitute 82 to 88 per cent of the seeds, contain from 65 to 76 per cent of fat, and resins (6 to 7 per cent). The usual range of the characteristics is as follows: $N_D^{40°}$ 1.4559 to 1.4607; Sap. V. 218 to 228; Iod. No. 10.5 to 18; Unsap. 1.1 to 3.2%; M. Pt. 40 to 47° C.

A. Steger and J. van Loon [*Rec. trav. chim.*, **54**, 149 (1935)] have made an extensive investigation of the commercial fat before and after purification, as well as of that extracted with petroleum ether from the ground seeds from *Virola surinamensis.* The characteristics of these fats are as follows: Commercial fat: Sp. g. at 78/4° C. 0.9016; $N_D^{70°}$ 1.4445; Sap. V. 221; Iod. No. (Wijs) 17.0; SCN V. 10.4; Acid V. 26.5; R.M.V. 1.5; Pol. No. 3.9; M. Pt. 47° C. Purified commercial fat: Sp. g. 78/4° 0.8855; $N_D^{70°}$ 1.4431; Sap. V. 229; Iod. No. (Wijs) 12.3; SCN V. 8.6; Acid V. 20.7; R.M. V. 1.5; Pol. No. 40; M. Pt. 47° C. Fat extracted from seed of *V. surinamensis*: Sp. g. at 78/4° 0.8882; $N_D^{70°}$ 1.4446; Sap. V. 224; Iod. No. (Wijs) 10.9; Acid V. 8.4; R.M.V. 1.6; Pol. No. 4.0; M. Pt. 51° C.

The percentages of the constituents in the mixed fatty acids from the petroleum-ether soluble fat were as follows: lauric 12.6, myristic 63.2, palmitic 8.4, stearic 1.5, oleic 6.3, linoleic 2.8, and resins 5.2.

For other data, details, and references to earlier investigations, the original article should be consulted.

A. Atherton and M. L. Meara [*J. Soc. Chem. Ind.*, **58**, 353 (1939)] examined the "nuts" from Brazil and the oil. The nuts consisted of 83 per cent of kernel and 17 of shells. The kernels contained 71 per cent of fat, which gave an iodine number of 14.5, a saponification equivalent of 249, and contained 17.2 per cent of free fatty acids as

oleic acid. The neutral or refined fat, which gave an iodine number of 9.9 and a saponification equivalent 246.1 was used for the investigation. The mixed fatty acids contained the following percentages of constituents: capric 0.5, lauric 19.8, myristic 72.5, palmitic 4.9, oleic 6.0, and a trace of tetradecenoic acid. Unsaponifiable matter amounted to one per cent.

The free fatty acids: capric 0.2, lauric 11.5, myristic 58.1, palmitic 9.1, oleic 17.7, and unsaponifiable matter (resins) 3.4 per cent.

Locally, the fat is used for making candles and soap, and that exported is very largely used by soap manufacturers. Although the press cake does not appear to be poisonous, unless it is mixed with other substances, neither guinea pigs nor rabbits will eat it.

Characteristics for the fat from *Virola sebifera* seeds could not be found, except that it melts 45–50° C.

Fat from Seeds of Virola Venezuelensis. The seeds consist of 83 per cent of kernel and 17 of shell. The kernels contain about 75 per cent of a hard, yellow-brown fat. Grimme [*Chem. Rev.*, **17**, 324 (1910), *J. Soc. Chem. Ind.*, **29**, 1318 (1910)] reported the following characteristics: Sp. g. at 50° C. 0.8996; $N_D^{40°}$ 1.4541; Sap. V. 221.5; Iod. No. 12.4; Unsap. 0.9%; M. Pt. 47° C.; Titer 39.5° C.

Fat from Seeds of Virola guatamalensis. From the following characteristics, it will be observed that this fat is similar to that from ucuhuba seeds, but the iodine number is usually lower: $N_D^{40°}$ 1.4600; Sap. V. 223 to 230; Iod. No. 11 to 18; R.M.V. 1.1; Pol. No. 5.9; M. Pt. 41° C.

Fat from Seeds of Myristica Platysperma. The seeds from the tree *Myristica platysperma*, native to Brazil, contain about 55 per cent of kernel having 55 to 60 per cent of a hard, almost white fat with but little odor. Jesson [*J. Soc. Chem. Ind.*, **34**, 499 (1915)], and Bolton and Hewer [*Analyst*, **42**, 35 (1917)] examined this fat with the following results: $N_D^{40°}$ 1.4502; Sap. V. 240; Iod. No. 5.0; M. Pt. 42° to 43° C. It will be observed that this fat is characterized by having a very low iodine number and probably consists largely of the glyceride myristin.

Ochoco Butter. This fat is obtained from the seeds of the West African tree *Scyphocephalium ochocoa*, belonging to the *Myristicaceae* family. The kernels weigh from 5 to over 12 grams, according to Lewkowitsch [*Analyst*, **33**, 313 (1908)], who found that they contained about 59 per cent of fat. Unless the dark-colored bands passing through the kernels are removed, the extracted fat is colored dark brown. Characteristics: Sp. g. at 60° C. 0.8899; $N_D^{40°}$ 1.4496; Sap. V. 238.5; Iod. No. 1.72; R.M.V. 0.65; Pol. No. 4.0; Unsap. 0.37%; M. Pt. 45° to 48° C. It will be observed that this fat contains even less unsaturated acids than those described above. It is said to contain no essential oil.

Fat from Seeds of Myristica Canarica. The kernels contain 60 to 65 per cent of fat. The extracted fat is a light brown crystalline solid.

Characteristics: $N_D^{40°}$ 1.4600 to 1.4697; Sap. V. 203 to 206; Iod. No. 19 to 27; R.M.V. 0.6 to 0.7; Pol. No. 5.8; Unsap. 2 to 3.5%; M. Pt. 37° to 39° C.; Titer 34°.

Kombo Butter. This fat is obtained from the seeds of the tropical tree *Pycnanthus kombo (Myristica angolensis),* which is found in West Africa, where it is known by various native names, depending upon the region. The seeds, which weigh about 4 grams, have the appearance of nutmegs, but unlike the latter, they contain no essential oil. The kernels contain about 55 per cent of fat, for which the following characteristics have been reported [*Bull. Imp. Inst.,* **6,** 378 (1908)]: Sp. g. 99/15° C. 0.887; Sap. V. 255; Iod. No. 65.4; Titer 37°.

A. Atherton and M. L. Meara [*J. Soc. Chem. Ind.,* **58,** 353 (1939)] found that the "nuts" from Sierra Leone consisted of 86 per cent of kernel and 14 of shell. The kernels contained 61.6 per cent of fat, which gave an iodine number of 67, a saponification equivalent of 249.9, and contained 18.7 per cent of free fatty acids as oleic acid. The refined (neutralized) fat gave an iodine number of 32.3, a saponification equivalent of 238.3, and contained 0.7 per cent of unsaponifiable matter. The mixed fatty acids from the refined oil contained the following percentages of constituents: lauric 5.4, myristic 60.8, palmitic 3.6, tetradecenoic (myristoleic) 23.4, oleic 5.6, and unsaponifiable matter 1.2. The composition of the free fatty acids was as follows: lauric 2.6, myristic 39.7, palmitic 3.7, tetradecenoic 26.3, oleic 11.4, and non-fatty substances 16.3 per cent.

Fat from Seeds of Myristica Malabarica. The seeds contain about 41 per cent of fat and resins for which the following characteristics are given: $N_D^{40°}$ 1.4580 to 1.4587; Sap. V. 189 to 192; Iod. No. 50.4 to 54; M. Pt. 31° to 32° C.

Collins and Hilditch [*J. Soc. Chem. Ind.,* **49,** 141T (1930)] found the following percentages of acids and resins in the mixed fatty acids: myristic 22.3, palmitic 7.6, other saturated acids 1.3, oleic 25.1, linoleic 0.6, and resins 43.1.

"The fat as refined, was found to contain 10.4 per cent of fully saturated glycerides, corresponding to a fully saturated glyceride content of 18 per cent on the fat actually present which leads to an 'association ratio' in the non-fully saturated glycerides of the fat itself, of 1 mol of saturated per mol of oleic acid: the fat is therefore apparently somewhat of an exception to the principle of even distribution of the fatty acids in the glycerides of kernel fats."

Otoba Butter (American Nutmeg or Mace Butter). Otoba butter is obtained from the seeds of the *Virola otoba,* a tree which grows in the mountainous regions of Colombia, South America. The seeds are spherical and about 2 cm. in diameter. They consist of about 30 per cent of shell and 70 per cent of kernels. The kernels examined at the Imperial Institute [*Analyst,* **46,** 51 (1921)] gave about 7 per cent of a colorless volatile oil by steam distillation, and the dried residue contained 67.3 per cent of fat. The fat has long been used by the

Colombian natives to treat skin diseases of domestic animals.

E. Uricoccha [*Ann.*, **91**, 369 (1854)] made a cursory examination of otoba butter and stated that it resembled nutmeg butter and consisted of the glycerides of myristic and oleic acids, with a considerable amount of unsaponifiable matter, but made no mention of the volatile oil.

Baughman, Jamieson, and Brauns [*J. Am. Chem. Soc.*, **43**, 199 (1921)] made an extensive investigation of a sample of otoba butter received from Colombia through the Office of Foreign Seed and Plant Introduction, United States Department of Agriculture. It contained 9.3 per cent of volatile oil (chiefly sesquiterpenes) and 20.4 per cent of unsaponifiable matter. The fixed oil consisted of the glycerides of lauric 15.1, myristic 52.2, palmitic 0.2 and oleic acids 3.9 per cent. The unsaponifiable constituents of the fixed oil consisted of a yellow, viscous mass (11.0%) and of the isomeric otobite and isotobite $C_{20}H_{20}O_4$ (9.4%). Otobite crystallized from alcohol in beautiful large, silky, orthorhombic prisms which melt at 137° to 138° C. The isotobite, which is much more soluble in alcohol than otobite, separated in the form of small, needle-like prisms. It melts at 106° to 108° C. Both compounds give a pink coloration with sulfuric acid; this becomes very intense and persists for several days. These substances can neither be acetylated nor methylated. Fusion with potassium hydroxide is without effect. Otobite contains one methoxyl group, but iso-otobite none. Both give penta-bromides ($C_{20}H_{20}O_4Br_5$) which melt at 190° to 191° C.

The characteristics of this sample are: Sp. g. 20/20° C. 0.9293; $N_D^{40°}$ 1.4710; M. Pt. 34° C.; Sap. V. 185; Iod. No. (Hanus) 54; Volatile Oil 9.3, and Unsap. V. 20.4. The fat examined at the Imperial Institute: M. Pt. 37.8° C.; Sap. V. 198.9; Iod. No. 20; Titer 37.2°.

Myrobalans Oil. This oil is found in the seeds of the tree, *Terminalia chebula,* of the *Combretaceae* of India. The oil has been studied by S. R. Sunthankar and S. K. K. Jatkar. [*J. Ind. Inst. Sci.*, **21A**, 149 (1938); *Brit. Chem. Absts.*, **B1938**, 1446] with the following results: Sp. g. 25/25° C. 0.9132; $N_D^{25°}$ 1.4700; Sap. V. 190.2; Iod. No. 105.1. The oil contained 78.8 per cent of unsaturated and about 17 per cent of saturated acids.

Neem or Margosa Oil. This oil is in the seeds of the tree *Melia azadirachta* of the *Meliaceae*. This large evergreen tree is found growing in India, Ceylon and some parts of South America.

The kernels, which amount to about 25 per cent of the whole fruit, contain from 43 to 44.5 per cent of oil. Both the fruit and kernel oil have a strong garlic odor. The odoriferous and bitter constituents of the oil have been investigated by Watson, Chatterjee, and Mukerjii [*J. Soc. Chem. Ind.*, **42**, 387T (1923)].

The oil has been used for centuries in India and Ceylon on account of its medicinal properties, and it has been suggested as a preventive of blow-fly attacks on sheep.

The oil has received some attention on the part of various inves-

tigators, and an extensive study of it has been made by R. Child and S. Ramanathan [*J. Soc. Chem. Ind.*, **55**, 124T (1936)]. The kernel content of the small seeds (0.17 to 0.22 g.) ranged from 50.8 to 60 per cent. The oil content of the kernels from one lot of seed was 33 per cent, and from two other samples (each from a different locality) 42.8 per cent. The range of the characteristics for nine samples of the oil is as follows: Sp. g. 30/30° C. 0.9159 to .9182; $N_D^{40°}$ 1.4616 to 1.4623; Sap. V. 198.5 to 204.1; Iod. No. 69.3 to 71.9 (one oil 75.2); SCN V. 54.3 to 57.3; R.M.V. 1.7 to 3.8; Pol. No. 1.2 to 3.5; Unsap. 0.7 to 1.1 per cent; soluble acids as butyric 2.1 to 4.0 per cent; insoluble acids 90.4 to 93.3 per cent. The mixed fatty acids from a commercially expressed oil were found to contain the following percentages of constituents: palmitic 13.6, stearic 19.1, arachidic 2.4, oleic 49.1, and linoleic 15.8.

The molar ratio of saturated to unsaturated acids was found to be approximately 1:1.8. Less than one per cent of fully saturated glycerides were present in this oil. It should be mentioned that these investigators held their oils for 3 months, and then decanted them from the resinous substances which had separated, before undertaking their investigation; this may account for the small quantities of unsaponifiable found in contrast to those (up to 7.7%) previously reported by other observers.

The fatty acids and glycerides of the oil have been more recently investigated by T. P. Hilditch and K. S. Murti [*J. Soc. Chem. Ind.*, **58**, 310, 1939)]. The characteristics of the oil were as follows: Sap. Equiv. 284.8 (Sap. V. 197.0); Iod. No. 67.9; Acid V. 36.0; Unsap. 1.7 per cent. The mixed fatty acids contain the following percentages of constituents: oleic 61.9, linoleic 7.5, palmitic 14.9, stearic 14.4, and arachidic 1.3. Composition of the free fatty acids: oleic 62.2, linoleic 9.4, palmitic 14.8, stearic 12.4, and arachidic acid 1.2 per cent.

The molar percentages of the probable component glycerides of the oil are as follows: palmitostearins 0.6, oleodipalmitins 5.0, oleopalmitostearins 12.3, palmitodi "oleins" 26.0, stearodi "oleins" 33.6, and tri-"oleins" 22.5. For other details the original should be consulted.

In India, the oil has long been used for the treatment of skin diseases. More recently, it has been used in the manufacture of medicated soap. The oil's therapeutic properties are attributed to the various resinous and bitter constituents which are present in the crude product.

Niam (Meni) Oil. This oil is found in the seeds of the tree *Lophira alata (Ochnaceae)*, native to central and west Africa along the coastal districts. The kernels which amount to 61 to 63 per cent of the seeds contain, depending upon their source, from 31 to 43 per cent of oil. The product prepared by the natives of the Sudan is usually liquid, but that extracted from seed from other localities by different investigators is a soft solid which melts at about 24° C. According to Lewkowitsch, the oil has the following characteristics: Sp. g. at 40° C. 0.9016 to 0.9044; Sap. V. 182 to 195; Iod. No. 70 to 72.5; R.M.V.

0.8 to 0.9; Unsap. 0.5 to .9 per cent; Titer 47° to 49° C. The oil from the Sudan contains about 1.4 per cent of unsaponifiable matter.

Pickles and Heyworth [*Analyst,* **36,** 493 (1911)] examined the oil from Sierra Leone seed and found that it contained about 50 per cent of saturated acids, from which they separated and identified arachidic and palmitic acids. The unsaturated acids consisted of oleic and linoleic acids. In some localities the natives prepare the oil and use it for culinary purposes and as a hair oil.

Ochna Pulchra Oils. The ochna pulchra is a tree of moderate size (15 to 20 ft.) indigenous to the Transvaal and southern Rhodesia, [*Bull. Imp. Inst.,* **23,** 1 (1925)]. The small, kidney-shaped, berry-like fruits consist of an oily pericarp which has an unpleasant odor similar to valeric acid, and a yellowish brown kernel which amounts to 43 per cent of the fruit. On a moisture-free basis, the pericarp contains 34.6 and the kernel 37.2 per cent of oil. The pericarp oil is a dark green semi-solid and the kernel oil is a yellowish brown liquid. The oils have the following characteristics:

	Pericarp Oil	Kernel Oil
Sp. g. at 100/15° C.	0.8611	0.8615
$N_D40°$	1.4590	1.4600
Sap. V.	197.7	197.1
Iod. No. (Hübl)	58.5	74.3
R. M. V.	0.6	0.3
Pol. No.	0.5	0.45
Acid. V.	16.3	21.5

The oils may be used for soap making. Because of the difficulty of separating the pulp from the kernels, it would be necessary to express or extract the pulp and kernel oils together. The meal or cake, on account of the odor and taste, cannot be used for feeding stock.

Nasturtium Seed Oil. This oil is from the seeds of the tropical perennial nasturtium *Tropaeolum majus,* the *T. minus,* and possibly *T. lobbianum,* belonging to the *Tropaeolaceae.* The seeds contain usually from 6 to 7 per cent of oil, for which the following characteristics have been reported: Sap. V. 172.6 to 178.6; Iod. No. 75 to 78.5; Unsap. 1.1 to 1.8 per cent.

This oil is of interest on account of the large quantity of erucic acid present. Gadamer [*Arch. Pharm.,* **237,** 471 (1899)] reported that the oil consisted almost entirely of trierucin. However, Sudborough, Watson, Ayyar and Damle [*J. Indian Inst. Sci.,* **9A,** 65 (1926)] found that the oil also contained small quantities of other saturated and unsaturated acids. They isolated 35 per cent of trierucin from the oil. Hilditch and Meara (*J. Chem. Soc.,* **1938,** 1610) examined the oil from seeds collected from the garden. The extracted greenish oil gave the following characteristics: Sap. V. 160.1; Iod. No. 75.1; Acid V. 4.0; Unsap. 4 per cent. The mixed fatty acids contained the following percentages of constituents: erucic 81.8, linoleic 1.2, oleic 16.0, behenic 0.8 and palmitic 0.2. The oil contains almost 40 per cent of trierucin and probably over 50 of oleodierucin.

These investigators called attention to this oil containing a much larger quantity of erucic acid than the *Cruciferae* seed oils.

Okra Seed Oil. The seed of the various varieties of okra (*Hibiscus esculentus, Malvaceae*), according to Halverson and Naiman [*J. Oil Fat Ind.*, **3**, 386 (1926)], contain from 15 to 22 per cent of oil and from 19.8 to 26 per cent of protein. These authors state that the okra plant is prolific and a vigorous grower in the United States cotton belt. The seeds have possibilities of economic importance due to their oil content and to the feeding value for animals of the high-protein meal remaining after the oil is extracted.

Jamieson and Baughman [*J. Am. Chem. Soc.*, **42**, 166 (1920)] examined several samples of okra seed oil which was expressed in their laboratory by means of an expeller. The seeds were grown on Avery Island, La. The oil had a fine, greenish yellow color and a slight but distinct fragrant odor. The variation in the characteristics of the four samples was as follows: Sp. g. at 25/25° C. 0.9160 to 0.9187; $N_D^{25°}$ 1.4692 to 1.4702; Sap. V. 195.2 to 195.5; Iod. No. (Hanus) 93.2 to 100.3; Acid V. 0.34 to 1.42. One sample with an Iod. No. of 95.2 contained 29.22% Sat. Acids and 67.33% Unsat. Acids. The insoluble acids had a neutralization value of 210.6 and a titer of 38.5°. The oil was found to contain the following percentages of acids: oleic 41.86, linoleic 25.47, palmitic 25.82, stearic 2.62 and arachidic 0.05.

Olive Oil. Olive oil is obtained from the fruit of the tree *Olea europaea*, of which there are about 300 varieties. Some varieties are specially grown for oil or for picking the fruit, but some serve both purposes. Olive oil has been used for edible and other purposes by southern European and Asiatic peoples since the beginning of historical time. Olives are grown in nearly all the countries bordering on the Mediterranean sea, Australia, California, South Africa, Mexico, and, to less extent, in several South American countries. The oil content of olives, which varies greatly, depends not only upon the variety, but also upon soil and climatic conditions. In European countries, the olives cultivated for oil usually contain from 14 to about 40 per cent of oil. The olives grown in North and South America and Australia seldom contain as much as 30 per cent of oil. Climatic conditions affect the quality of the oil to the extent that in a given region, the olives may yield a fine oil one season and the crop of the next may yield an inferior oil. Also the quality of the oil is lowered by the ravages of the olive fly and other insects, as well as by diseases which attack the trees. Much low-grade oil is produced in some regions and this is often largely due to the improper handling of the fruit and crude methods used in the expression and storage of the oil. Sound fruit of the proper maturity and extreme cleanliness of the oil mill and equipment, together with proper treatment of the oil, are prerequisites for the production of good oil. In many localities more attention is now being paid to these facts.

The world production of olive oil has until recently been about two billion pounds per year. Spain, which for some years was the largest

producer, had over 4 million acres planted to olives. The annual production of oil was between 6 and 7 hundred million pounds. Much oil is still produced by small mills in a primitive manner, but enough sizable modern mills have been established so that the average quality of Spanish olive oil has been improved. Spain's fine oils rank with the best of those of France and Italy. The growing tendency to establish cooperative mills with modern equipment along with cooperative marketing organizations, particularly in northeast Spain, is of benefit to these olive growers; besides, the oil now produced in this region is much improved in quality. In Spain, it is estimated that the yield per acre is from 500 to 1200 pounds of olives. In addition to olives grown for oil, large quantities are produced for pickling.

Italy ranks second in the production of olive oil, although she has over 5.6 million acres planted to olives. Prior to Spain's leadership in the production of oil, Italy ranked first for over 1000 years. Two-thirds of the acreage in Italy is used to produce other crops in addition to olives. The trees are planted farther apart when intercropping is practiced and this accounts for the relatively low yield of olives per acre. The annual production of oil has been about 526 million pounds. About one-fifth of this oil is produced in Sicily where climatic conditions are especially favorable for olive culture. Many of the olive growers press their own fruit, but in some sections cooperative oil mills have been established for many years.

Up to recently, Greece ranked third in the production of olive oil. It is estimated that there are about 8,900,000 acres on which olive trees are growing. The area devoted to cultivated olive trees is about 1,300,000 acres. The annual production of oil (from wild and cultivated fruit) amounts to 220 million pounds but in very favorable years it is larger. About nine-tenths of the oil is from olives grown in Crete, the Peloponnesus, the Aegean and Ionian Islands, and Euboca. Although during rather recent years, nearly a hundred cooperative oil mills have been established, much oil is still produced by the small primitive mills. As extensive planting of the trees is being made in various localities, this will eventually result in a large increase in the production of olive oil.

Portugal ranks fourth in the production of olive oil. She has about 850,000 acres planted to olives. The annual production of olive oil ranges from about 180 to 196 million pounds. Tunis ranks fifth, and has about 600,000 acres of olive trees and is planting more every year under the encouragement of an interested government. The annual production is about 85 million pounds of oil. A considerable proportion of the oil is produced in modern mills. Large quantities of high-grade oil come from central and southern Tunis, some of which is exported to the United States.

Algeria in 1929 had about 211,000 acres planted to olives. It is estimated that there were at this date 14,668,723 trees, of which 7,696,591 are in bearing. The annual production of oil is now about 6.5 million gallons, a part of which is exported to the United States.

Turkey has about 1,860,000 acres, of which 400,000 are devoted to cultivated olive trees. The annual production of oil from cultivated and wild fruit varies from 43 to over 77 million pounds. In recent years, a considerable number of modern olive oil mills have been established, as well as a number of solvent extraction plants for the recovery of the oil from the press cake.

France has about 300,000 acres planted with olive trees and has an annual production of about 45 million pounds of olive oil. To meet her demands, much olive oil is imported. A blend consisting of 75 per cent of peanut oil and 25 of olive oil has become popular; consequently, France is less dependent upon imported olive oil. Much of the French oil is expressed in cooperative mills and the quality is much improved over that formerly produced in those localities in antiquated individual mills of the growers.

Syria is another important olive-growing country. The trees are found in nearly all sections, but the most important producing states are Lebanon, 31,369 acres; Alointes, 25,194 acres; and Syria, 118,194 acres. These states contain 12 million bearing trees. The annual production of oil amounts to about 20 million pounds. Both the fruit and oil are important parts of the Syrians' diet.

Olives are grown in the states of California and Arizona. California is the chief producer and has over 1.25 million trees. The larger part of the crop is pickled. For the most part, the oil is expressed from the undersized, bruised or over-ripe olives which are not suitable for canning. When this fruit is pressed before it deteriorates, as is now customary at the larger mills, oil of good quality is obtained.

In the Argentine provinces Mendoza, La Rioja, Entre Rios, and other localities, the cultivation of olives and the production of oil is increasing.

Some olives are also grown for the production of oil in Chile, Peru, and Uruguay.

The percentage of the 1936 world production of olive oil for the more important olive growing countries is as follows: Spain 38, Italy 25, Greece 14, North Africa 9, Portugal 5.8, Turkey 4.8, and France 2.

Harvesting of Olives. Depending upon the latitude in which the olives are grown and on the condition of the crop, harvesting begins from the latter part of October to December. For the production of the finest oil, the olives should be hand-picked just before complete maturity and pressed without delay. If the fruit is too immature, the yield of oil is poor and it has a bitter taste (*Brit. Chem. Absts.*, B, **1926**, 677). However, comparatively little fruit is hand-picked for the expression of oil. A common practice is to knock off the fruit with light poles or rakes. In some cases, sheets of burlap or canvas are placed under the trees to receive the olives. Before harvesting by any method, it is customary to gather all the fallen fruit and press it separately, as it yields oil of inferior quality on account of its damaged condition. The olives are collected in bags, baskets or loaded into ox carts and transported to the mills. It should be observed that the practice of

knocking off the fruit with poles or rakes not only injures the fruit but also injures more or less the bearing wood of the trees.

Storage. With the exception of comparatively few large modern mills that can press the fruit as it is received, it is necessary to resort to storage. The common practice at the older mills is to use deep bins in which the olives soon begin to ferment and rot. The same result is obtained where it is the practice to leave the fruit in the sacks sent from the orchards. When the fruit is stored in very shallow bins, trays, or shallow baskets and kept dry and well ventilated, spoilage is reduced to a minimum. For a long period of storage it is recommended that the olives be placed under a 6 per cent brine solution.

Crushing and Pressing. The equipment and methods employed vary greatly even in the same country. In some regions the same equipment is now used that was in use centuries ago.

The olives, after being freed from leaves and other foreign matter, are commonly crushed in various sizes of stone "edge runners" operated by animal, steam or electrical power. Also, rolls and other types of crushing machinery are used in some places. At most mills, the pits are not crushed to any extent prior to the first and second pressings. The crushed fruit is placed in cloths of fiber, esparto grass, or hair, (scourtins, capachos, etc.) and formed into cakes. The cakes are piled on top of one another until the capacity of the press had been reached. Modern mills use various types of hydraulic presses, while many of the older mills use screw and beam presses. When the press is filled, the pressure is gradually applied, which in the case of the hydraulic press amounts finally from 300 to 500 pounds per square inch. Then, depending upon the type of press (hand or power), the pressure is maintained from about 1 to 12 hours. This first pressing removes most of the juice together with a small portion of the oil. The oil from the first pressing, which is considered the best, is often called "virgin" or "superfine" oil, and in Europe it is customary to keep it separate from that of the second pressing. In France, some of the mills make only two pressings. The press cakes from the low-pressure press are transferred to another press where a very high pressure is gradually applied, with the result that the press cake contains only about 8 per cent of oil. With few exceptions, in other countries, it is customary to grind the press cake, usually with the addition of a small quantity of water and make a second pressing, but at a much higher pressure than that used for the first pressing. Many mills make a third and some a fourth pressing. Before making the third pressing, it is customary to crush the press cake (breaking the pits) and mix it with a small quantity of warm water. As would be expected, the oil is decidedly inferior to that of the first and second pressings. The final press cake, depending upon the equipment and method used, contains from 8 to 20 per cent of oil. The average oil content is probably about 15 per cent. In some localities, the press cake is ground under water and a further recovery of oil is obtained by flotation, but it is more customary to extract the residual oil from the cake with volatile solvents. Carbon disulfide is the solvent

still most commonly employed. Gasoline, benzol, di- and trichloroethylene are also used. In the case of halogenated ethylenes, it is important not to heat or distill them in contact with any alkali, otherwise explosions and fire are the usual result [*Chem. Age* (New York), **32**, 264 (1924)]. The extracted oil has long been called "sulfur olive oil," but in the United States it is known as "olive oil foots." Most of the press cake, which is also called "pomace" or "marc," is used to supply humus to the orchards, for which it is well adapted. In some localities, the fresh, unextracted cake is fed to hogs or other livestock; in others, more or less of the cake is burned under the boilers.

A process for the expression of olive oil has been developed and patented by the California Packing Corporation. The olives are crushed without breaking the pits with an "edge runner" and gradually fed into a continuous working screw press, specially designed for this purpose. Only one pressing is made and the press cake is reported to contain 4 per cent or less of oil. The oil is separated from the juice, after the addition of some water, by repeated treatment in a centrifugal separator, and finally filtered. Sound olives are used and the resulting oil has a fine yellow color. It contains very little free fatty acids.

The Acapulco process for the extraction of olive oil is based upon rubbing the finely crushed olives previously freed from pits against a fine screen of copper or nickel wire supported in a horizontal cylinder, by means of revolving rubber-tipped brushes. The oil, together with more or less fine pulp, is pressed through the screen. Several ways have been suggested for the separation of the foots from the oil, but probably this can best be effected by the centrifuge. It is claimed that a high yield of oil can be obtained [J. Bonnet, *Chem. Absts.*, **23**, 5053 (1929)].

The so-called "Leon Process" is based on crushing the whole fruit by means of high-speed steel beaters in a suitable container, the pulp being forced through a grating or screen. Part of the oil and much of the juice is separated by passing the mass between laminated rollers, after which the pomace is broken up and heated somewhat without the addition of water, and again pressed in hydraulic presses. It is claimed that the equipment is very compact, requires much less power than other processes, effects a greater saving in press cloth, and yields more oil. As yet this is not extensively employed.

Separation and Clarification. At most mills, the oil and juice from each pressing are collected in separate tanks or vats. When the oil has separated, it is skimmed or drawn off. The practice of separating the oil from the juice by centrifuges, immediately after expression, is being adopted by the more progressive mills. In California a number of plants use continuous washers for this purpose, while in other regions the washing is done in tanks. A large number of the manufacturers, however, do not wash the oil, as they consider that this treatment impairs the flavor. Space does not permit of a detailed description of various methods employed for the separation of juice and water from the oil; but, to prevent spoilage, it is very important to remove them

before the oil is stored. Glass, glazed tiled, or tin-lined tanks are best for storage. Large quantities of oil are adversely affected by storage in defective underground cisterns or reservoirs and porous jars. The oil is stored for several months or longer to improve its flavor.

Filtration. For the removal of dissolved moisture and the final clarification of the oil, a great many types of filters are used. Many of the simpler types of filters expose the oil to the air for a comparatively long time, which causes a loss of flavor and often the absorption of undesirable odors. The more progressive plants commonly employ capillary filters, of which there are several types. One of the best is the vertical cylindrical French filter which contains a series of removable units. Each unit is filled with circular filter papers. The oil is either pumped or allowed to flow from tanks, elevated so as to give the desired pressure, on the upper unit, being finally discharged at the bottom of the filter. When any of the units become clogged, they are replaced by others without interrupting the filtration. These filters hold up to 500 sheets of paper. This final filtration is usually made just before the distribution of the oil to the trade.

Some oil is produced perfectly clear by allowing it to stand a month or longer in one tank, then transferring it in such a way as not to disturb the sediment and separated water, to another tank where it remains for a month. This treatment is repeated until the oil is brilliant.

Some of the African olive oils contain a large quantity of saturated acid glycerides, which cause them to tend to solidify at much higher temperatures than do the European oils; consequently, it is customary to "winter" or "demarginate" them. These oils are cooled until a sufficient quantity of the "stearin" has crystallized (as determined by experiment), and filtered.

Refining. Ordinarily, the refining of olive oil refers to the treatments described above for the clarification of the oil, and in certain cases it may also refer to "demargination." However, in comparatively recent years, inferior grades of olive oil, particularly those received from the antiquated mills of individual olive growers, have been refined by the caustic soda process; in the case of very bad oils, this is followed by treatment with bleaching earth or carbons and deodorization, in a manner similar to that employed for refining crude cottonseed oil. Quite a number of these refineries have been established in southern Europe. This product, which is commonly called "neutralized olive oil," is mixed with a sufficient quantity of unrefined oil to make it palatable. In countries where the oil is chemically refined, it is compulsory to sell it as "refined olive oil" to the consumer. Often this refined oil is not permitted to be sold by dealers who handle the unrefined oil, to prevent unlawful substitution.

Blending. In order to satisfy customers, olive oil which is sold under trade names must be maintained as nearly uniform as possible in flavor and appearance. Because of the seasonal variation of the oil, this can be accomplished only by mixing two and often more oils in such proportions as will give the desired characteristics of the brands in

question. Not infrequently, the blender has to find new sources of supply in order to maintain the desired uniformity on account of either the poor quality or scarcity of the oils formerly used. The successful blender must have a keen taste and much practical experience in judging olive oils as well as in their blending. The blending, after preliminary experiments have shown the best proportions of the oils to be used, is usually conducted in plants especially equipped for the purpose. Often oils having a strong or harsh flavor are mixed with very mild-flavored oils, so that the former can be sold for edible purposes. Blending is also practised for purposes other than that of maintaining the uniformity of established brands. Oils from one region or country are imported into another and mixed with oil of domestic production, then sold under the local name.

Uses. The edible grades are chiefly used as salad and cooking oils. Olive oil is used in limited quantities as a lubricant, for which it is well adapted, providing that it is low in free fatty acids. Some is used in canning sardines and for medicinal purposes. Inedible olive oil, including that extracted by solvents from the press cake, is chiefly used in making soap. Inedible oil is usually required to be "denatured" by the addition of rosemary oil or other substance before it can be exported, to prevent its use by unscrupulous dealers for edible purposes.

Composition. Myddleton and Barry (Fats: "Natural and Synthetic," p. 107) give the following data: palmitic 14.6, oleic 75.4, and linoleic acid 10.0 per cent. Lapworth and Mottram [*J. Chem. Soc.*, **127**, 1628 (1925)]: oleic 72, linoleic 12 to 13, saturated acids 14 to 15, and unsaponifiable 1.4 per cent. Eibner and Rasquin [*Chem. umschau.*, **33**, 29 (1926)]: palmitic 5.5, stearic 3.4, oleic 79.7, and linoleic acid 6.7 per cent. Taufel and Saria [*Anales. soc. espan. fis. quim.*, **24**, 25 (1926)]: Spanish oil, palmitic 7.5, stearic 2.3, oleic 83.9, linoleic 0.5, and unsaponifiable 0.8 per cent.

Representative authentic samples of Californian, Italian, Spanish, and Tunisian olive oils have been examined by Jamieson and his associates [*Oil and Fat Ind.*, **2**, 40, 110 (1925); *Ibid.*, **4**, 63 and 426 (1927)] with the following results:

	Characteristics			
	Californian	Italian Bitonto	Spanish Borjas	Tunisian Sousse
Sp. g. 25°/25° C.	0.9119	0.9120	0.9116	0.9131
Refrac. index (20° C.)	1.4690	1.4690	1.4689	1.4700
Acid V.	1.5	1.8	1.8	1.9
Iod. No.	85.1	84.4	83.7	86.0
Sap. V.	190.6	190.6	192.4	193.6
Unsap.	1.0	1.1	0.8	0.8
Sat. Acids	8.9	10.9	10.7	16.5
Unsat. Acid	85.2	83.3	83.6	77.6

	Composition			
	Californian	Italian	Spanish	Tunisian
	Per Cent			
Oleic acid	84.4	83.1	80.5	69.1
Linoleic acid	4 6	3.9	6.9	12.0
Myristic acid	tr.	tr.	0.2	0.1
Palmitic acid	6.9	9.2	9.4	14.4
Stearic acid	2.3	2.0	1.4	2.4
Arachidic acid	0.1	0.2	0.2	0.3

T. P. Hilditch and E. C. Jones (*J. Chem. Soc.*, **1932**, 805) found that the mixed fatty acids from Tuscan olive oil, giving an iodine number of 83.6, contained the following percentages of constituents: myristic 1.1, palmitic 9.7, stearic 1.0, arachidic 0.9, oleic 79.8, and linoleic 7.5.

T. P. Hilditch and H. M. Thompson [*J. Soc. Chem. Ind.*, **56**, 434 (1937)] examined an olive oil from Palestine which gave an iodine number of 84 and contained 1.1 per cent of unsaponifiable matter. The mixed fatty acids were found to contain the following percentages of constituents: myristic 0.5, palmitic 10.0, stearic 3.3, arachidic 0.1, oleic 77.5, and linoleic 8.6.

These investigators have shown that olive oils also contain about one per cent of hexadecenoic (palmitoleic) acid. It was found that the oils which have been investigated contained 2 per cent of tripalmitin and about 50 per cent of triolein, which is notably less than that formerly believed to be present. For other information and details concerning the investigation of the glyceride structure of the oil and the hydrogenated product, the original papers should be consulted.

References: "Chemical Composition of The Oil in Relation to The Morphological and Physiological Characters of the Plant," S. Fachini and G. Dorta [*Chem. Absts.*, 23, 3117 (1929)]. "Iodine Value in Relation to Origin and Age of Olive Oil," *Brit. Chem. Absts.*, B, 1929, 402.

"The Mixed Unsaturated Glycerides of Liquid Fats III Low Temperature Crystallization of Olive Oil," T. P. Hilditch and L. Maddison, [*J. Soc. Chem. Ind.*, **60**, 258, (1941)]. Turkish, Palestine and Italian olive oils examined, were found to contain 30 and ±5% of triolein, 25 and 45% of glycerides containing linoleic acid (chiefly linoleo-di-olein).

Characteristics of Olive Oil. Sp. g. at 15° C. 0.9145 to 0.9190, at 25° C. 0.9100 to 0.9150; Sap. V. 185 to 200; Iod. No. 77 to 94; R.M.V. 0.3 to 0.6; Unsap. 0.6 to 1.3; Crismer V. 69°; Acetyl V. 4 to 12; $N_D^{15°}$ 1.4670 to 1.4675, at 25° C. 1.4660 to 1.4680, and at 40° 1.4606 to 1.4633. The unsaponifiable matter in extracted oil ranges from 1.5 to over 3 per cent. The iodine number of the unsaponifiable from olive oil (expressed) ranges from 150 to over 200. With the exception of some of the African oils, those of edible grade usually have iodine numbers from 78 to 86. The saponification value usually varies from 188 to 196. Tolman and Munson [*J. Am. Chem. Soc.*, **25**, 954 (1903)] give a large number of analyses of authentic Californian oils which were obtained from all parts of the state in which olives are grown. The iodine numbers ranged from 78.5 to 89.8, the average being 85.1. The United States Pharmacopoeia, Eleventh Edition, specifies that the iodine number by the Hanus method shall be not less than 79 nor more than 88; the saponification value shall be not less than 190 nor more than 195; the specific gravity at 25° C. shall be from 0.910 to 0.915. The British Pharmacopoeia gives the following specifications: Sp. g. 0.915 to 0.918; Sap. V. 188 to 197; Iod. No. 79 to 87; $N_D^{40°}$ 1.4605 to 1.4635; Acid V. not over 6.

Conno and Rago [*Ann. chir. applicata.*, **19**, 98 (1929)] state that the iodine number of olive oil decreases to a marked extent during the

first six months of storage. This decrease is particularly noticeable for the summer months; from then on the reduction is slight.

Lewkowitsch states that olive oils of high specific gravity usually have a dark color and that a light-colored oil with a gravity above 0.918 (at 15° C.) is to be looked upon with suspicion. Also as a rule, the iodine number is between 81 and 85, and the more mature the fruit the higher is the iodine number of the oil.

Adulterants and Tests. At various times, many different oils have been used to adulterate olive oil. The more common oils used for this purpose are cottonseed, corn, peanut, poppyseed, rape, sesame, soybean, sunflowerseed and teaseed. The addition in any applicable quantity of corn, cottonseed, poppyseed, sesame, sunflowerseed or soybean oils will increase the iodine number and the specific gravity. Rape and mustard oils will lower the saponification value and increase somewhat the iodine number. Peanut and teaseed oils have iodine numbers and saponification values similar to those of olive oil.

When testing a suspected sample of olive oil, it should be kept in mind that the adulterator has kept up with the progress of analytical methods and is said to use a mixture more often than a single oil, as was the former practice.

See Chapter VI for the Halphen and Millan tests for cottonseed oil, the Renard test for peanut oil, and the Villavecchia test for sesame oil.

Fachini and Dorta [*Chem. Absts.*, **21**, 506 (1927)] have further studied their method [*Analyst*, **39**, 122 (1914)] for the detection of peanut oil and have extended the method to include the approximate quantitative determination of peanut oil in the presence of olive oil. The method is rapid and can detect the presence of 5 per cent of peanut oil. The test can be made as follows: Separate the fatty acids from 20 grams of the sample to be tested, in the usual manner, and dehydrate them completely by heating for several hours in an oven heated to 110 to 115° C. Weigh 5 grams of the acids into a 150-cc. Erlenmeyer flask, add 50 cc. of acetone and warm to 55 to 56° C., until the acids are dissolved. Stopper the flask with a cork through which a thermometer is inserted so that its bulb will be in the solution. When the solution has cooled to 20° C., add 10 cc. of 0.1 *N* aqueous solution of potassium hydroxide and mix by rotating the flask. A milkiness or precipitate indicates peanut oil. For the quantitative test, the following procedure may be used. Collect the precipitate on a filter and wash with small quantities of anhydrous acetone. Dissolve the precipitate and wash the filter with warm water into a 500-cc. separatory funnel. Add 5 cc. of hydrochloric acid and cool the mixture. Add 75 cc. of ether and shake. After the layers have separated, withdraw the acid solution and wash with four 25-cc. portions of water. Transfer the ether to a weighed 200-cc. flask. Distill the ether and dry the acids and flask to a constant weight in an oven heated to 110 to 115° C., weigh the mixture of arachidic and lignoceric acids, and calculate the approximate quantity of peanut oil. As the author has not had an opportunity to test this method he cannot make any comments.

The Thomas and Yu [*J. Am. Chem. Soc.*, **45**, 113 (1923)] method is based upon the precipitation of the magnesium salts of the saturated acids from an alcoholic solution and the weight of the mixture of arachidic and lignoceric acids separated by crystallization from 90 per cent alcohol by volume. Olive oil containing 10 to 15 per cent of peanut oil gave reasonably good results; but with larger percentages of peanut oil, our results as well as those of our collaborators were unsatisfactory. However, the method is satisfactory for the detection of peanut oil when present from 5 to 15 per cent or more. "A New Method for Determination of Peanut Oil in Olive Oil," by Jaffe [*Chem. Absts.*, **23**, 100 (1929)], depends upon the lithium salt of peanut fatty acids separating from alcohol at a higher temperature than those from olive oil.

Teaseed Oil. A number of color tests have been proposed for the detection of teaseed oil, but the investigation of H. A. Caulkin [*Pharm. J.*, **118**, 769 (1927)] has shown that these methods are not satisfactory for testing the purity of olive oil in which only refined, deodorized teaseed oil would be used. On account of the strong, disagreeable taste of crude teaseed oil, it would not be so used. The proposed tests in some cases failed even when applied to the crude oil.

J. Fitelson [*J. Assoc. Offic. Agr. Chem.*, **19**, 493 (1936)] has developed the following method for the detection and the approximate determination of teaseed oil: Place in a test tube, approximately 18 x 150 mm., exactly 0.8 cc. acetic anhydride, 1.5 cc. chloroform, and 0.2 cc. concentrated sulfuric acid. Mix and cool the solution in a water bath at 25° C. Then add 7 drops (about 0.22 g.) of the oil to be tested from a glass tube with an inside diameter of about 2 mm. Mix contents of test tube and return it to water bath. If the solution is turbid after the addition of the oil, add a drop of acetic anhydride and shake the solution. Repeat this treatment, if necessary, to remove the turbidity. Allow the mixture, which becomes green, to remain in the water bath for five minutes. Add 10 cc. anhydrous ethyl ether and mix contents immediately. Within a minute or two, teaseed oil gives an intense red color, which soon begins to fade. Olive oil usually gives a brownish gray at this stage of the test, but some samples give a faint pink.

The approximate quantitative determination of teaseed oil is made as follows: Follow the above directions before the addition of ether. While the solution is being cooled in the water bath, cool the 10-cc. portion of anhydrous ether in an ice-water bath. At the end of the five minute period, place the test tube containing the oil and reagents in the ice-bath for one minute, then add the ether, mix, and add the solution to the ice bath. The color will develop slowly. It reaches a maximum intensity in about five minutes, and does not noticeably begin to fade for five and sometimes more minutes. The maximum color is compared with that of "standards" containing known quantities of teaseed oil in olive oil, the color of which has been developed simultaneously with the color of the oil being tested.

Ten per cent or more teaseed oil in olive oil can be approximately

determined, provided the method is conducted exactly as it has been described.

The Olive Oil Committee of the American Oil Chemists' Society [*Oil and Soap,* **16,** 181 (1939)] investigated the Fitelson method and recommended cooling the mixture of acetic anhydride, chloroform and sulfuric acid to 5°, adding the oil to be tested and cooling again to 5° before the cooled anhydrous ether is added.

The Bolton and Williams method [*Analyst,* **55,** 5 (1930)], which was given in the first edition of this book, has been omitted as it has not been found as useful as hoped for the detection of teaseed or other oil in mixture with olive oil. [See Jamieson and McKinney, *Oil and Soap,* **10,** 69 (1933)].

Rape Oil. Rape oil can be detected by means of the iodine number of the saturated fraction of the fatty acids of the sample to be tested, which has been obtained by the lead-salt-ether method described elsewhere. The test depends upon the separation of the larger part of the erucic acid of the rape oil along with the saturated acids. For this test, 20 grams of the oil should be taken and when the lead-salt-ether method is properly conducted, in the absence of rape oil, the resulting solid acid fraction will have an iodine value of 8 or less; but in the presence of 10 per cent of rape oil, it will have an iodine value ranging from 10 to 13. It should be noted that large quantities of rape oil will lower the saponification value and raise the iodine value of olive oil.

Kreis and Roth [*Analyst,* **38,** 114, 434 (1913)] state that as little as 5 per cent of rape oil in olive oil can be detected by the following method. Separate the fatty acids from 20 grams of the sample to be tested, in the usual manner and after dehydration, dissolve them in 100 cc. of 95 per cent (by volume) alcohol. Heat to boiling and add 1.5 grams of lead acetate dissolved in 50 cc. of alcohol. Cool and let stand at 15° C. for 12 hours. Filter and wash the precipitate 3 times with alcohol. Transfer the insoluble lead salts to a separatory funnel and shake with 50 cc. of 1 : 1 warm hydrochloric acid until the salts are completely decomposed. Cool and add 80 cc. of ether, 50 cc. of water, and mix by rotating the separatory funnel. After the mixture has stood for 10 minutes or longer, withdraw the aqueous solution and lead chloride. Wash the ether with 3 successive 75-cc. portions of water. Transfer the ether to a 200-cc. Erlenmeyer flask and distill. Dissolve the residue of acids in 100 cc. of hot alcohol and add 1 gram of lead acetate previously dissolved in 50 cc. of alcohol. Boil, cool and let stand for 12 hours at room temperature; then filter off the precipitate and evaporate the filtrate to dryness in a 150-cc. flask. Heat the residue with 20 cc. of 1 : 1 hydrochloric acid until the fatty acids melt and collect at the surface of the solution. Cool until the acids are solid and decant the solution. Wash and remelt the acids with water, cool, and separate the solid acids from the water; then allow them to stand for 12 hours or longer and take the melting point. In the case of pure olive oil, this fraction of acids will melt at about 47° C., but in the presence of rape oil, the melting point will be considerably lower.

R. S. McKinney, after investigating the various methods that have been proposed for the detection of rape in admixture with olive oil, developed a modification of the magnesium-soap method proposed by R. Kerr [*Ind. Eng. Chem.*, **8**, 904 (1916)] and extended by Thomas and Yu [*J. Am. Chem. Soc.*, **45**, 113 and 129 (1923)]. The method is as follows:

Reagents. *Alcoholic Potassium Hydroxide.* Dissolve 50 grams of the alkali in 1000 cc. of alcohol (95 per cent by volume) and filter. *Alcoholic Magnesium Acetate.* Dissolve 50 grams of magnesium acetate in 100 cc. of hot water, filter, and cool. Mix the cold solution with 3 volumes of 95 per cent alcohol.

Alcoholic Acetic Acid. Mix 20 cc. of glacial acetic acid with 80 cc. of 95 per cent alcohol. *Ninety Per Cent Alcohol.* Mix 900 cc. of 95 per cent alcohol with 50 cc. of water. *Hydrochloric Acid 1:1.* Dilute 500 cc. of the concentrated acid to one liter.

Method. Weigh 10.00 grams of sample into a 250-cc. Erlenmeyer flask. Add 50 cc. of the alcoholic potash and 50 cc. of 95 per cent alcohol. Boil for 30 minutes with the flask connected to a reflux condenser. Cool the mixture somewhat and neutralize the excess of alkali with the alcoholic acetic acid, using phenolphthalein as indicator; then add sufficient alcoholic potash to produce a distinct pink color. Add 25 cc. of the magnesium reagent and heat the mixture to boiling. Cool and place in a refrigerator at 10° C. over night. Decant the cold solution onto a filter in a 7.5-cm. Büchner funnel rinsing flask, precipitate and filter with small quantities of 90 per cent alcohol. Return any precipitate on the filter to the flask, add 100 cc. of 90 per cent alcohol, boil, cool, and place in a refrigerator overnight. Then decant the alcoholic solution onto the same filter, wash the flask, precipitate, and filter with a small quantity of 90 per cent alcohol. Drain the flask as completely as possible, and continue the suction until the filter paper is dry. Transfer any precipitate on the filter to the flask, washing the paper and funnel with a fine stream of hot 1 : 1 hydrochloric acid by means of a small wash bottle (containing 50 cc. of the acid), and then again with hot water, collecting all the washings in the flask. Add any unused acid in the wash bottle to the flask and boil until the magnesium soaps are completely decomposed. Cool until the fatty acids are solid. Decant the solution onto a filter in a Büchner funnel and wash the fatty acids in the flask, and filter until the washings are neutral to methyl orange indicator. Break the cake of fatty acids and wash them with cold water onto the filter. Continue the suction until the filter is dried; then transfer the acids to a weighed 150-cc. beaker, rinsing the filter, funnel and flask with hot 95 per cent alcohol. Evaporate the alcohol without loss of acids and dry the residue to a constant weight in a vacuum oven heated to 70° C., or an oven heated to 110° C., with an atmosphere of carbon dioxide.

Determine accurately the saponification value in the usual manner with alcoholic potash and standard acid, as this is preferable to the determination of the neutralization value by the titration of the acids

(in alcohol) with alkali. When comparatively small quantities of acids (0.5 to 1 gram) only are available for this determination, it is necessary to use an alcoholic solution containing about 15 grams of potassium hydroxide per liter and a 0.1 N acid solution for the determination. Calculate the saponification value, then the molecular weight by the following formula: $M=\frac{56110}{S}$, in which M is the molecular weight of the fatty acids, and S the saponification number. The percentage of rape oil may be approximated by the formula $x=1.3\ (M-275)$, in which M is the molecular weight of the fatty acids, 275 represents the molecular weight of olive oil fatty acids, and 1.3 is the percentage of rape oil equivalent to each unit of molecular weight above that normal for olive oil.

Olive oil that gives an iodine number over 90 and a saponification below 189 is to be suspected of containing rape or similar oil, but oils giving lower iodine numbers and low saponification values are not above suspicion. Erucic acid ($C_{22}H_{42}O_2$, Mol. Wt. 338.3) is present in rape oils to the extent of about 45 or more per cent, and the larger part of the acid is separated as the magnesium salt along with the saturated acids. Consequently, the acids from rape oil by the magnesium salt separation would give a comparatively large iodine number (71 to 74).

When the method is properly conducted, it is possible to detect (and to determine approximately) about 8 per cent of rape oil in the presence of olive oil. It is believed that the method is superior to any that have as yet been proposed.

Tests for Extracted Olive Oil. S. Fachini (*Brit. Chem. Absts.*, -B, **1926**, 592) states that the presence in expressed oil of even a small proportion of oil, either extracted with solvents or extracted from the marc and then refined, may be detected by the following method: Heat 3 cc. of the sample to be tested and 3 cc. of acetic anhydride in a test tube for 10 minutes, while shaking over a free flame. When cool, filter through a small filter paper previously moistened with acetic anhydride. Place a few drops of the filtrate in a small porcelain dish or crucible and add a few drops of concentrated sulfuric acid. A cherry red coloration results if extracted oil is present. When a small quantity of water is added, a more or less intense fugitive green coloration appears.

M. Lauro [*Oil and Fat Ind.*, **4**, 324 (1927)] has proposed the following delicate test for the detection of oil which has been extracted by carbon disulfide. By means of an oil bath, heat 5 cc. of the sample to be tested in a test tube with about 0.02 gram of finely powdered silver benzoate to 150° C. for 10 minutes; then note the color of the oil, after shaking the mixture. Do not heat above 155° C. nor longer than 10 minutes. A brown or black color indicates extracted oil. Expressed olive oil sometimes darkens when first heated, but in the absence of extracted oil, this disappears within less than 10 minutes. The silver benzoate can readily be prepared by dissolving 10 grams of sodium benzoate in 30 cc. of hot water and adding an excess of 20 per cent solution of silver nitrate. When the solution has cooled to room tem-

perature, the silver benzoate is filtered by suction, washed with small quantities of cold water and dried in a desiccator.

It is stated that oil extracted by trichloroethylene or other halogenated solvent can be detected by heating in a flame a clean copper wire which has been dipped into the sample. A green-colored flame is the test. Expressed oils and those extracted by carbon disulfide give no green flame test.

Detection of Refined Olive and Other Oils. The method is based on exposing the samples in quartz tubes (or glass bottles which give no fluorescence) to the ultraviolet light which is filtered through a Woods' screen of nickel oxide glass as described by Baud and Courtois [*Chem. Absts.*, 22, 1051 (1928); *Analyst*, 53, 164 (1928)]. These authors placed 2 or 3 cc. of the sample in a small quartz test tube and placed it in a dark chamber in front of the Woods' screen through which waves of 3650 Angström units were obtained from a mercury-arc lamp. The tube, which should be corked, is turned so that the oil is spread all over the internal surface of the tube. This increases the intensity of the colors. Refined oil gives a blue fluorescence and the virgin oils which were tested gave a yellow or yellowish brown color. Further study of this method has been made by Marcille [*Chem. Absts.*, 22, 3310 (1928)], Stratta and Mangini (*ibid.*, 22, 3794), and others.

K. S. Gibson of the United States Bureau of Standards examined many samples of virgin and refined olive oils using colorless glass bottles. Green olive oils gave an intense orange or red fluorescence. Other virgin oils gave a yellow color, but one California oil gave a pale bluish fluorescence like that given by refined oils. This oil was obtained by a new method in which, by one pressing, the press cake contained only about 4 or 5 per cent of oil.

The method in its present form cannot be used to detect refined oil in mixture with greenish virgin oils, because the red fluorescence given by the chlorophyll marks that given by the refined oil. It may be added that refined oils other than olive give violet or blue fluorescences of varying intensities.

Attention is directed to the following references:

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"Is the Fluorescence of Refined Olive Oils under the Ultraviolet Rays Sufficient to Distinguish Them from Oils Extracted by Pressure," C. C. Buzi and L. Sommaini, *Olive Oil* (Pub. of Am. Olive Oil Assoc.), 3, No. 9 (1930).

Buzi and Sommaini point out that refined olive oil may be treated with small quantities of vegetable pigments so that it gives a yellow fluorescence like the virgin oil. This discovery, which has recently become common knowledge here and elsewhere, obviously renders the ultraviolet test of little or no use for regulatory examination of olive oils.

Two methods have been proposed by S. Kaloyereas, W. V. Cruess, and B. C. Lesly [*Fruit Products J.*, 8, No. 5, 20 and No. 6, 27 (1929)] for the determination of the oil in olives which are based on the

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Olive Kernel Oil. Olive kernel oil is obtained from olive pits either by expression or extraction by solvents. The kernels contain from 25 to 28 per cent of oil. The expressed oil has a yellow color and a sweetish taste somewhat resembling almond oil, but is lacking in the fruity flavor which is characteristic of the pulp oil. In other respects, it closely resembles olive oil. The expressed oil has the following characteristics: Sp. g. at 15° C. 0.9184 to 0.9191; Sap. V. 182.3 to 183.8; Iod. No. 86 to 87; $N_D^{25°}$ 1.4682 to 1.4690.

Palms: Pulp and Kernel Oils. A considerable number of palms produce fruits that yield oils, several of which have become of great economic importance. Without doubt, the oils of other palms, particularly some of those from Central and South America, will in time become important commercial products.

It should be observed that in numerous cases, much confusion still exists both in the botanical classification and that caused by giving the same common name in various localities to different species of palms. Often the common name simply refers to the color or shape of the fruit, or even the seeds or "nuts." For example, the name, "Corozo," which means red, is applied to the fruits from several different palms, and similarly, the word "coquito," meaning a little coconut, is applied. The confusion in the botanical nomenclature is due partly to the lack of agreement among botanists and partly to the attempted identification of the palms when only the fruit or seed is available; this, in many cases, is impossible because of the similarity of these products from closely related species. Although an attempt has been made to give the correct botanical classification of those mentioned, further investigation may necessitate changes in certain cases.

The fleshy portion of the fruits from a number of different species of palms contains notable quantities of oil. With few exceptions, these "pulp" oils are more or less semi-liquid, highly colored products. On the other hand, the oils from the fruits of various species of *Oenocarpus* and the segen palm (*Jessenica polycarpa*) are liquid and resemble olive oil in many respects. The most important pulp oil is the "palm oil" of commerce, from the fruit of the *Elaeis guineensis*. These oils differ in composition and properties from those of the palm kernels which are pale-colored or white solid fats, and are characterized by consisting largely of glycerides of the saturated fatty acids. Of these, the most important are coconut and palm kernel oils.

The pulp and kernel oils of many of the numerous species found growing in tropical America remain to be investigated or studied further, but this should be done only after the species of each source of oil has been properly identified.

Palm Oil. Palm oil is obtained from the fleshy portion of the fruit from numerous varieties of the palm *Elaeis guineensis,* of tropical West Africa. The palm is extensively cultivated in the Dutch East Indies, British Malaya and on a smaller scale elsewhere. Before Sumatra and Malaya became important producers of palm oil, it was available only from the wild palms in West Africa.

In West Africa, the palm is found from 12° South to 16° North latitude; from Angola to Gambia. It is largely confined to a 300-mile wide belt along the coast, but is common in the forest region of middle Congo to the southern frontier of Wadai, Ubangi, the Upper White Nile and the Albert Nyanza, and in Belgian Congo to the north and northeast shores of Lake Tanganyika, on the Zambesi, and as far south as Bandawe on the west shore of Lake Nyosa.

In East Africa, the palm occurs in Uganda, Tanganyika and Zanzibar, where it is less common and less productive than on the West Coast.

The more important producing sections of West Africa are Angola, the Cameroons, Belgian and French Congo, the Gold Coast, Dahomey, Sierra Leone, Nigeria, and Togoland. Nigeria produces the largest quantity. Other producing regions are the Ivory Coast, the French colonies of Senegal, Guinea, and Gaboon, Gambia and Portuguese Guinea. In Liberia, it is estimated that there are at least 40 million mature palms which form forests so dense that production of the fruit is seriously interfered with. The thinning of these forests, would eventually cause Liberia to become an important producer of this oil.

This palm has also been introduced into Ceylon, Indo- and Cochin-China, and British Guiana. It was brought to or from Brazil many years ago by slave ships.

It should be observed that this palm is essentially a light-demanding species. Those found in dense jungles have been sown by birds. These stragglers are usually stunted and often sterile. They grow well on a variety of soils. They require deep soils. The productive soils are often poor in lime and not rich in either phosphates or potash, but are usually rich in humus. The palms do not flourish on heavy soils or on swampy land. It is stated that the soil must be neutral or alkaline. According to the Imperial Institute [*Bull. Imp. Inst.*, **18**, 209 (1920)], the most favorable conditions for the cultivation of the oil palm are to be found in the Niger delta, Ivory Coast, San Thorné, the lower Congo, the Seychelles, East Sumatra, the low-lying parts of the Federated Malay States, Java, Borneo, Brazil and British Guiana, with the possibility of certain parts of the Philippines.

The palm may attain a height of 60 feet, but usually the height is nearer 30 feet for the mature trees. Depending upon the locality and elevation, the palms begin to fruit from the fourth to the eighth year.

As these palms, like some others, do not at first grow tall, it is possible to gather the fruit from the ground until after they are 10 or 12 years old. The fruit is borne in bunches (called "cones," "hands," or "heads") which, as the palms reach maturity, become fewer in number and contain up to a thousand or more fruits. The number as well as the size of the bunches or "heads" of fruit found per season depends for the most part upon the age and the location of the palms. In the case of those growing in dense stands or in localities deficient in rainfall, if they bear at all, the bunches are usually very small. Mature palms usually bear from 2 to 6 bunches of fruit, which usually weigh

from 10 to 35 pounds apiece; but sometimes they weigh much more. The bunches contain from about 60 to 65 per cent of their weight of fruit, the remainder being stems and bracts.

The fruits, which are oval and pointed at the apex, vary from one to two inches long and are from three-quarters to an inch and a half in diameter. When mature, depending upon the variety, they are yellow, orange, reddish brown or nearly black, and weigh from 3 to about 25 grams. The average weight is from 6 to 8 grams. In the outer fleshy portion of the fruit, containing more or less fiber in longitudinal strands, the palm oil is located. In the center of the fruit is the seed which is commonly called the "palm nut," the kernel of which yields the palm kernel oil of commerce. The oil content of the fleshy part of the fruit ranges from about 30 to about 70 per cent. The proportion of flesh to the seeds or nuts is also subject to great variation. The large-fruited varieties cultivated in Sumatra contain about 60 per cent of pericarp and 8 per cent of kernels. The seeds of the different varieties differ much in size as well as in the thickness of their shells. Some have very thick, and others very thin shells. Usually, the fruits contain one seed, but some contain two and a few contain three seeds.

Professor O. Beccari [*L'Agricoltura Coloniale Italiano,* 7, 5, 108 (1914)] gives a very complete description of 18 varieties of this palm and their fruits, which should be consulted by those interested. Also, the various native names have been correlated with Beccari's varieties in *Kew Bulletin* **1914,** 285.

Sumatra Palm Oil Industry. The oil palm was first introduced from West Africa into the Dutch East Indies in 1848, but it was not until 1910 that the present industry in Sumatra had its beginning. There the palm is chiefly cultivated in the Province of Sumatra, East Coast. Some plantings were made also in South Sumatra, particularly in Lampong Province. During the first 4 years, 6500 acres were planted; then owing to the war of 1914-18, further planting was delayed until about 1918, when it was resumed on such a large scale that the acreage now exceeds 100,000. The experimental stations of the Sumatra East Coast Planters' Association and individual companies have made extensive selection experiments along with propagation and cultivating studies in order to develop a palm which will breed true to type and yield the maximum quantity of oil. Improved types have been planted on a large scale. Under the highly favorable climatic and soil conditions, the palms begin to bear after the fourth year, and when 8 years old they produce a full-sized crop of fruit. In 1932 the production of palm oil in Sumatra amounted to 85,000 tons and in 1937 it was 197,000 tons. For additional information, the following references may be consulted:

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Extraction of Palm Oil. Formerly, all the African palm oil was obtained by the crude, inefficient native methods, but serious attempts are being made in the Belgian Congo, Nigeria, and other regions to introduce modern equipment and methods in order to meet the competition of Sumatra in the world markets for this product. A few modern mills have been established which are producing oil of good quality.

The extraction of palm oil has been practised by the natives for centuries. The methods employed vary in details according to the locality. The best oil extracted by native methods, which is not produced in a quantity which permits of export, is prepared by selecting the thoroughly mature but not overripe fruits and boiling them in water until soft. Then they are removed from the water and washed by pounding until the seeds or nuts can be readily removed. The pulp is placed in boiling water and when the oil rises to the surface it is skimmed off and clarified by various means. All this oil is used for edible purposes by the natives and is vastly superior to that prepared for export by other methods which permit of a larger yield. In some localities this export oil is prepared as follows:

The fruits, after being cut from the bunches or heads, are placed in leaf-lined holes in the ground, moistened, and covered with leaves.

There they remain for two weeks or longer. The fleshy parts, softened by fermentation, are then placed in a hole lined with stones and beaten with long stout poles. The crushed fruit is transferred to another hole. the sides of which are lined with a mixture of palm oil and wood ashes, and left for about a week. Some of the oil drains from the pulp to the lower part of the hole. The nuts are removed, and a further yield of oil is obtained by boiling the pulp in water. Another method is to place the fermented pulp in a bag and squeeze out the oil. The crude methods of extraction account in large measure for the large quantity of free fatty acids present in the exported oil.

The consistency of commercial palm oil varies from that of soft butter to that of tallow. Its color ranges from orange yellow to dark red. In trade, the following grades of African palm oil are recognized: soft oils—Lagos, Calabar, Opobo, Bonny; hard oils—Congo, Niger, Old River, Liberia, Gold Coast; mixed oils—Gold Coast and Niger. The harder the oil, the larger the quantity of free fatty acids. All of the oil prepared for export by native methods is characterized by containing large quantities of free fatty acids; and some of the harder kinds of palm oil contain up to 50 per cent or even more.

A. C. Barnes [*Chem. Absts.*, **19**, 1956 (1925)] states that sound, mature palm fruit will keep satisfactorily for about a week in a dry, well-ventilated place, but that the immature fruit does not keep so well. It is extremely difficult to gather the fruit without bruising it to some extent. To prevent rapid deterioration of the fruit with the splitting of the oil into free fatty acids several methods of treatment have been proposed. Steam sterilization [*Bull. Imp. Inst.*, **22**, 497 (1924)] of the bunches or separated fruit in specially designed equipment appears most effective to inhibit the action of the enzymes which liberate the free fatty acids from the oil. Heating the fruits for 10 minutes at 55° C. is said to be sufficient to stop the action of these enzymes. Also, heating the extracted oil to 110° C. for a short time prevents further development of acidity.

Within recent years, a number of methods have been more or less developed for the more efficient extraction of the oil. The Nigerian Products Co., Ltd., employ the following equipment and method: About 3000 pounds of palm fruit are charged into a steam pressure digester which is provided with an agitator for stirring the fruit during the cooking. After steaming for a half hour, the charge is transferred by an automatic conveyor to a centrifuge, which contains a removable, perforated metallic basket having a capacity of 500 pounds of fruit. Each charge is centrifuged for about ten minutes, during which time steam is admitted to facilitate the separation and expulsion of the oil through the perforations in the basket. The oil is discharged through a pipe in the outer casing of the centrifuge into a tank from which it is pumped to the settling tank. The settled oil is then withdrawn to the storage tanks. After centrifuging, the basket is lifted by chains from the centrifuge, transported by an overhead runway to a hopper, and dumped. The hopper feeds a long, inclined rotary drier which is

heated by the flue gases from the boiler fires. Within 20 minutes, the dried fiber and nuts are discharged from the drier to an elevator which raises them to a rotary screen which separates the nuts; the latter pass to the nut crackers which deliver the product to a screen for the separation of any uncracked nuts. The cracked nuts fall into a salt solution, the gravity of which is adjusted so that the shell fragments sink and the kernels float. The separated shells and kernels are collected and then centrifuged to remove the brine, which is returned to the tank. The fiber and the shells are burned under the boilers. The kernels are dried and bagged for export. A plant with three full-sized centrifugals can handle 20 or more tons of palm fruit a day. Most of the operations of this process are automatic. When sound fruits are used, the oil contains but little free fatty acid, usually well under 5 per cent and sometimes only about 2 per cent. This process gives a high yield of oil.

Some of the "central" mills or factories employ a combination of centrifuges and hydraulic presses for extraction of palm oil, but the yield of oil does not appear to be any larger than that by the process of the Nigerian Products Co. The separation of the pulp by various "depericarpers," as practiced at some plants prior to the extraction of the oil, is apparently not so satisfactory as when the nuts are not separated, particularly with the centrifugal process.

In Sumatra, several of the more modern methods are employed on the various oil palm estates, but it may require some years of further experimentation before either the method or equipment will become standardized and generally adopted there and elsewhere.

At the present time, many are of the opinion that palm oil is most satisfactorily obtained by means of hydraulic presses which permit of a higher recovery of oil than the centrifugal equipment. Some mills grind the press cake and extract it with solvents for a further recovery of oil.

In England and on the Continent, a number of firms are engaged in manufacturing complete plants for the extraction of palm oil and the preparation of kernels for export. As space does not permit a description of the equipment or methods of operating it, the reader is referred to the comprehensive article entitled "Machinery for Use in Palm Oil Industry" [*Bull. Imp. Inst.*, **24**, 223-43 (1926)], which also mentions the names of various manufacturers. It may be added that machines are made for the separation of the palm fruit from the bunches, and also equipment for the separation of the kernels from the broken shells of the nuts to take the place of the salt solutions or clay suspensions now employed for this purpose.

"Palm Fruit," by R. A. Bellwood [*Oil and Fats Record*, **3**, 144 (1922)], discusses in considerable detail machinery and methods used in the preparation of palm oil and kernels. Also see *Bull. Imp. Inst.*, **15**, 57 (1917) and later references listed below.

In Brazil, the palm is called Dende. Although Bolton and Hewer [*Analyst*, **42**, 35 (1917)] state these palms are found in the Amazon

Valley, over a million of them are now in the state of Baia, where particular attention is being given to their propagation and cultivation. It is estimated that Itaparica Island, which is a few miles from Sao Salvador, contains about 300,000 of the palms. Of these, 17,000 belong to the Baia Palm Experiment Station, which has an oil expeller, which is used at times for expressing the palm oil.

In Brazil, some of the Dende palm oil produced is used for making soap, but apparently the larger part of it, after refining (and wintering, in some cases), is sold to the retail trade and used as a cooking oil in the home. The kernel oil is used chiefly by soapmakers.

Refining of Oil. Increasing quantities of the better grades of the crude oil are being refined for edible purposes. The oil is refined by caustic soda in a manner similar to that used for cottonseed oil. This treatment does not remove the color. The product, after deodorization at a low temperature, is used in the manufacture of margarine. Considerable quantities of the oil, after the caustic soda treatment, are bleached by bleaching agents and high-temperature deodorization (about 250° C.), and used in the manufacture of uncolored margarine.

On account of excessive refining losses, it does not appear feasible to attempt to refine palm oil that contains much over ten per cent of free fatty acids.

Characteristics and Composition. The range of the characteristics reported by various observers is as follows: Sp. g. at 15° C. 0.9209 to 0.9250; $N_D^{40°}$ 1.4531 to 1.4580, at 60° 1.4451 to 1.4518; Sap. V. 196 to 205; Sap. Equiv. 268.9 to 279.3; Iod. No. 48 to 60; Unsap. 0.2 to 0.5%; Titer 38 to 47° (usually between 42° and 44°); R.M.V. 0.1 to 0.2; Pol. No. 0.2 to 0.3.

T. P. Hilditch and associates [*J. Soc. Chem. Ind.*, **49**, 363T (1930); **50**, 171T (1931); **54**, 77T (1935)] have examined 16 samples of palm oil from important producing regions of West Africa, as well as from Malaya and Sumatra. In each case they have determined the more important characteristics and the component acids in connection with their extensive investigations on the glyceride structures of the oils.

The percentage compositions of the mixed acids from some of these oils are as follows:

Oils	Myristic	Palmitic	Stearic	Oleic	Linoleic
Belgian Congo	1.1	41.1	4 2	38.4	10.7
Cameroons (soft)	1.3	38.3	5.3	40.8	9 8
Grand Drewin, Ivory Coast	2.3	34.3	5.6	49.5	8 3
Malaya	2.4	39.0	3.5	43.1	7 5
Sumatra	2.5	41.7	4.2	42.0	9 3
Lagos, Nigeria	1.1	39.5	5.8	42.3	10 9
Freetown, Sierra Leone	2.0	35.7	6.0	47.8	8 0
Sherbo, Sierra Leone	1.6	34.9	5.3	50.0	7.9

T. P. Hilditch and H. Jasperson [*J. Soc. Chem. Ind.*, **57**, 84 (1938)] have shown that palm oil fatty acids contain about one per cent of hexadecenoic acid.

Hilditch and Jones concluded from their investigation of four dif-

ferent palm oils that the mode of arrangement of the fatty acids as glycerides in palm oils differs from the seed oils examined, but is analogous to that in certain of the animal fats, notably tallows and milk fats. Allowing for the different proportions of the acids in palm oil as compared with tallow, these two classes of fats have a great deal in common. They stated that the percentage of fully saturated glycerides present in palm oil appears to vary according to the ratio of saturated to unsaturated acids in the whole oil, and that of the quantity (7 to 10%) found in these oils, between 70 and 80 per cent was tripalmitin. By far the larger part of the oil consists of mono-unsaturated-disaturated and di-unsaturated-monosaturated glycerides in which oleopalmitins predominate.

A. Banks, H. K. Dean and T. P. Hilditch [*J. Soc. Chem. Ind.*, **54**, 77T (54)] have made further progress with the investigation of the glyceride structure of palm oils through the use of progressive hydrogenation, for details of which the original article must be read. For this investigation they selected two oils (a native Cape Palmas, Liberia and a Belgian Congo plantation oil) which represented the extremes in fatty acid composition of those studied. The characteristics of these oils are as follows:

	Cape Palmas Oil	Belgian Congo Oil
Saponification Equivalent	283.8	280.1
Iodine number	60.0	54.1
Acid Value	3 5	3.9
Unsaponifiable matter (%)	0.4	0.3
Setting point of fatty acids (°C.)	40.2°	45.3°

The Cape Palmas and Congo oils were found to contain the following percentages of glycerides, in which the term "olein" includes not only oleic acid but also linoleic acid, the total quantity of which is small compared with the former:

Cape Palmas oil: Approximately 2 of tripalmitin, 1.5 of dipalmito-stearin, 16.5 of dipalmito-"oleins," 66 of monopalmito-di-"oleins," including any palmitostearo-"olein," and 14 of tri C_{18} glycerides (tri-"olein" or stearodi-"oleins").

Belgian Congo oil: Approximately 5.5 of tripalmitin, 1 of dipalmito-stearin, 29.5 of dipalmito-"oleins," 58 of monopalmito-"oleins" (including any palmito-stearo-"olein") and 6 of tri C_{18} glycerides (tri-"olein" or stearodi-"oleins").

From this investigation it was concluded that both α- and β-palmito-di-C_{18}-glycerides and both forms of mono-C_{18}-dipalmitins are present. The symmetrical forms (β-palmitodi-"olein" or β-"oleo"-dipalmitin) predominate, but evidence was obtained of increasing proportions of the unsymmetrical α-palmitodi-"olein" or α-"oleo"-dipalmitin, as the total quantity of palmitic acid and C_{18} acids in the palm oil approached equality. The proportion of the unsymmetrical glycerides is distinctly larger in the Belgian Congo oil than in that from Cape Palmas.

It is of interest to note that Hilditch and his associates have found that the composition of native West African palm oils varies to some

extent according to their source. The oils from the coastal regions of Liberia and the Ivory Coast contain the smallest quantity of palmitic acid (32.3 to 35.3 per cent of mixed fatty acids), whereas the acids from the oils from Nigeria, the plantation oils from the Belgian Congo, Malaya, and Sumatra contain from 43 to 45 per cent of this acid.

From the investigations which have been made it appears that the variations found in the composition of the oils are due largely to the inherent varietal characteristics of the palms themselves rather than to differences of their environments.

Properties. The oil at ordinary temperatures varies from a soft butter to the hardness of tallow. The higher the percentage of free fatty acids, the harder is the oil. The color varies from pale yellow to a deep orange and sometimes it is dark brown. Oil of the better qualities has a pleasant odor and taste, in marked contrast to that imported from Africa which has been extracted by native methods.

Most palm oil can be bleached readily by heating it to about 100° C. and blowing air through it. The oil can also be bleached by treatment with dichromate and hydrochloric acid for technical use at a slightly elevated temperature as well as with other oxidizing agents. It is stated that the oil refined by the caustic soda method has excellent keeping qualities, and the same is probably true of the high-grade crude oil obtained by modern methods. Palm oil has a flash point of about 187° C. and a burning point of about 210° C.

No specific test has as yet been found for palm oil. Gill (*Analyst*, **42**, 216) has shown that the test proposed by Crampton and Simons [*Analyst*, **30**, 250 (1905)] which depends upon the formation of a green color when the oil is treated with acetic anhydride and a little sulfuric acid is given by other oils.

Uses. Large quantities of palm oil are used in making soap and by the tin plate industry for protecting the cleaned iron surfaces before coating them with tin. Increasing quantities of the high-grade refined oil are being used in the manufacture of margarine and vegetable shortenings. In Africa, the natives use the oil for edible and some other purposes. In the Belgian Congo and elsewhere, palm oil is used in trucks provided with a Diesel type of motor.

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"Palm Oil Carotenoids," H. Wilkenson, *Biochem. J.*, **35**, 824 (1941); *Chem. Absts.*, **36**, 2172 (1942).

Palm Kernel Oil. Palm kernel oil is obtained from the kernels of the fruit from which the palm oil of commerce is extracted. The kernels are obtained from the so-called palm nuts by machinery designed for the purpose at the established modern palm oil mills, or from the African natives who crack the nuts by hand. Many thousands of tons of the kernels are exported annually to America and to Europe where the oil is expressed or extracted by solvents. The oil content of the kernels ranges from 44 to about 53 per cent.

At the oil mill, the kernels are passed over screens to clean them and over magnets to separate any scrap iron present. They are crushed by oil rolls, heated to about 50° C., pressed, the press cake ground and heated to about 60° C. and pressed again. In the United States, M. Neumunz [*Cotton Oil Press*, **4**, (No. 10), 48 (1921)] stated that as early as 1913, he made a single hot pressing of palm kernels heated to about 80° C. in 3 high 72-inch cookers, in a cage hydraulic press and obtained a press cake which contained from 5 to 6 per cent of oil. He

stated that the cage type of press was well adapted for pressing palm kernels. The solvent extraction of the oil is conducted in England and on the Continent. Also, considerable oil is obtained in these countries by expression. The press cake and meal are used for feeding cattle [*Analyst*, **43**, 63 (1918); **44**, 204 (1919); **46**, 138 (1921)], for which it is well adapted. The European oil cake contains about 16 per cent of protein, 10 of oil, and 38 of carbohydrates, while the extracted meal contains about 2 per cent of oil, 19 of protein, and about 48 of carbohydrates.

The oil which is to be used for edible purposes is refined and deodorized in the same manner as coconut oil.

Composition and Characteristics.—Bömer [*J. Soc. Chem. Ind.*, **42**, 1232A (1923)] Bömer and Schneider [*Ibid.*, **43**, B478 (1924)] isolated and identified the following glycerides: Caprylo-myristo-olein M. Pt. 13.9° C.; myristo-di-laurin M. Pt. 33.4° C.; lauro-di-myristin M. Pt. 40.0° C.; palmito-di-myristin M. Pt. 45.2° C.; and myristo-di-palmitin M. Pt. 51.4° C. They were unable to detect either caproic or stearic acids in the sample of oil which they examined.

G. Collin and T. P. Hilditch [*J. Soc. Chem. Ind.*, **47**, 261T (1928)] have investigated the glycerides of palm kernel oil using the permanganate-acetone method. The sample of oil was found to contain the following percentages of fatty acids: caprylic 2.5, capric 6.6, lauric 44.4, myristic 13.3, palmitic 8.4, stearic 1.2, oleic 17.5, and linoleic 0.6 per cent.

The fully saturated glycerides amounted to 63 per cent, of which di-lauromyristin was the most abundant. The mixed saturated and unsaturated glycerides, which amounted to 37 per cent of the oil, consisted of 26 per cent of oleo-disaturated acid and 11 per cent of dioleo-mono-saturated acid glycerides. Little or no triolein was present.

Oudemans [*J. Prakt. Chem.*, **2**, 11,393 (1870)] detected caproic, caprylic, capric, lauric, myristic, palmitic, stearic, and oleic acids. Valenta [*J. Soc. Chem. Ind.*, **8**, 806 (1889)], with the exception of stearic acid, found the same acids present as Oudemans. Elsdon [*Analyst*, **39**, 78 (1914)] examined palm kernel oil with the following results: caproic 2, caprylic 5, capric 6, lauric 55, myristic 12, palmitic 9, stearic 7 and oleic acid 4 per cent. E. F. Armstrong and J. Allan [*J. Soc. Chem. Ind.*, **42**, 207T (1924)] investigated palm kernel oil (No. 1) and again with W. Moore [*Ibid.*, **44**, 143T (1925)] No. 2, with the following results:

Acids	No. 1	No. 2
	Per Cent	
Caproic	None	traces
Caprylic	3.0	3.0
Capric	6.0	3.0
Lauric	50.0	52.0
Myristic	16.0	15.0
Palmitic	6.5	7.5
Stearic	1.0	2.5
Oleic	16.5	16.0
Linoleic	1.0	1.0

The different results obtained by Elsdon and the other investigators are due in part to variation in the oils from different sources. Without doubt Elsdon isolated a sizable fraction of caproic ester and this acid, as well as all the others mentioned, is probably present in all palm kernel oil, but in varying quantities, depending upon the source of the oil and its method of extraction. The solvent-extracted oil is reported to contain more of the higher melting acids as glycerides than that expressed in Europe. If this is true, then it would be desirable for the same investigators to determine the composition of authentic samples of expressed and solvent-extracted oil obtained from a given shipment of palm kernels from a known locality. For purposes of comparison, other investigations should be undertaken to determine the variation in composition of oils from widely different but known sources.

Salway [*J. Soc. Chem. Ind.*, **36**, 1184 (1917)] found that part of the characteristic odor of this oil is due to methylnonylketone, which he separated to the extent of 0.1 per cent.

The characteristics are as follows: Sp. g. 99°/15° C. 0.873, at 40°/15.5° C. 0.9119; Iod. No. 16 to 23; Sap. V. 244 to 255; R.M.V. 4.8 to 7; Pol. No. 9.4 to 11; $N_D^{60°}$ 1.4430 to 1.4435, at 40° C. 1.4492 to 1.4517; Titer of fatty acids 20° to 25° C.; M. Pt. of fat 24° to 30° C. R. H. Ellis and E. M. Hall [*J. Soc. Chem. Ind.*, **38**, 128T (1919)] examined over 1000 samples of oil by the Wijs method and the average iodine number was 18.6.

Characteristics of palm kernel oil "stearin" determined by Sachs [*Analyst*, **33**, 124 (1908)]: Iod. No. 8; Sap. V. 242; R.M.V. 2.2; M. Pt. 31° to 32° C.; Titer of fatty acids 28.5°. The fatty acids of the "olein" have a titer of 16° to 18°.

Uses. Palm kernel oil, which in composition is similar to coconut oil, is used for the same purposes, chief of which is the manufacture of margarine and soap. The "olein" is used in soap making while the "stearin" is used either as a substitute for cacao butter under the name of "chocolate fats" or for manufacture of margarine. Sometimes the "stearin" is employed in making solid lubricants.

Properties and Tests. The crude oil is white, pink or light brown, depending upon the quality and method of extraction. The best grade has an agreeable odor and taste, and is low in free fatty acids. This oil, which is practically indistinguishable in appearance as well as in properties from coconut oil, can be refined and deodorized in the same manner. It should be observed, however, that palm kernel oil does have somewhat lower Reichert, Meissl and Polenske values than coconut oil. Oil of good quality has excellent keeping properties. Like coconut oil, palm kernel oil is characterized by its high saponification and low iodine values as well as by the notable quantities of volatile fatty acids.

The oil is now seldom adulterated with other oils, which is also true of coconut oil. On account of the similarity of coconut and this oil, it does not appear worth while to attempt to detect the presence of the former in mixtures. Those interested in this should consult "Edible Oils and Fats" by G. D. Elsdon. There is no color test for this oil.

The following additional references may be noted: "Differentiation of Coconut Oil and Palm Kernel Oil," G. D. Elsdon, *Analyst,* **42,** 298 (1917); "The Crushing of Palm Kernels," J. H. Shrader, *The Cotton Oil Press,* **4** (No. 7) 51 (1920); "Palm Nut Cracking Machines," *Bull. Imp. Inst.,* **24,** 234 (1926).

Areca (Betel) Nut Fat. This oil is obtained from the kernels of the seed from the fruit of the palm *Areca catechu,* native to the Malay Peninsula; it is cultivated in many tropical regions of Asia, the Philippines and East Indies for its nuts, which after special treatment are chewed. The fruits of this palm which reaches a height of about 50 feet, are about the size of hen's eggs and grow in clusters on 8 or 9 broad fronds. The nuts or seeds contain about 16 per cent of fat. A. Rathje [*Arch. Pharm.,* **246,** 692 (1908)] reported the following characteristics for the fat extracted by petroleum ether: Sp. g. at 15° C. 0.973; Sap. V. 234.6; Iod. No. 12.3; Acetyl V. 18.2; R.M.V. 4.2; M. Pt. 36° to 38° C.; Unsap. about 1 per cent.

The pale yellow fat has but slight odor, whereas that obtained by ethyl ether is reddish brown and possesses a nutmeg-like odor. No information has been found in regard to the fat content of the kernels and it apparently is not produced on any commercial scale.

The Palm Elaeis Melanococca (Noli Palm, Coquito de Aceite, etc.), the American relative of the African oil palm, grows on the low lands of the coast and river valleys in Mexico, Central America, and in South America to the Amazon and the Madeira. In Colombia it is known as the Noli palm and in the state of Jalisco, Mexico, Coquito de Aceite. It is a dwarf palm with a short trunk or stem. The fruits are borne in erect racemes which can be reached from the ground. The fruits consist of 16 per cent of pulp, 62 of shell, and 22 of kernel. The pulp contains about 30 per cent of an orange semi-liquid oil which has an odor and taste similar to that of African palm oil. This oil is not produced on a commercial scale. The characteristics of the pulp oil are as follows: Sp. g. at 100°/15° C. 0.8636; Sap. V. 199; Iod. No. 83.5; Unsap. 0.7%; R.M.V. 0.7; Pol. No. 0.5; Titer 33.6°.

The kernels contain about 50 per cent of oil, which is stated [*Bull. Imp. Inst.,* **17,** 196 (1919)] to be very similar to that of African palm kernel oil. It has an iodine number of about 28 and a saponification value of 234. At times small quantities of the kernels are exported from Mexico to the United States where the oil is expressed. The oil can be used for edible purposes or soap making.

The palm Acrocomia vinifera, which is known as the coyol palm, grows in Nicaragua, Costa Rica, Guatemala and Panama. The "nuts" produced by this palm are so hard and tough that to date no machine has been devised to crack them for the separation of the kernels which contain 48 to 50 per cent of oil. Consequently, the oil is not produced commercially. The characteristics are as follows: Sp. g. at 25° C. 0.9136; Iod. No. 25; Sap. V. 246; R.M.V. 5; M. Pt. 25° C. The oil has a pleasant taste and is somewhat similar to coconut oil.

The palm Acrocomia sclerocarpa, commonly known as the Paraguay

palm, is widely distributed in tropical South America, the West Indies and the Leeward Islands. In Trinidad, this palm is called the gru-gru according to A. W. Knapp [*J. Soc. Chem. Ind.*, **33**, 9 (1914)], but Bray and Elliott [*Analyst*, **41**, 29 (1916)] believe that the gru-gru is not identical with *A. sclerocarpa*. Evidently further study is necessary to settle this question definitely. *A. sclerocarpa*, which forms large forests in Paraguay, reaches a height of 30 feet in favorable localities and has somewhat the appearance of the coconut palm. The fruits, which are borne in bunches, are inclosed in smooth, shells amounting to about 28 per cent of the fruit, which weigh about 30 grams. The pulp, which constitutes about 24 per cent of the fruit, contains about 60 per cent of a yellow oil of a consistency similar to that of palm oil. Bolton and Hewer [*Analyst*, **42**, 35 (1917)] gave the following characteristics: Sap. V. 189.8; Iod. No. 77.2; $N_D^{40°}$ 1.4527; Sol. Pt. 24.9° C.

The kernels, which are almost spherical and weigh about one gram each, contain from about 53 to 65 per cent of oil, which is considerably softer than that of either coconut or palm kernel. This product is known as Mocaya oil or butter. Characteristics: Sp. g. at 100°/15° C. 0.865 to 0.868; Sap. V. 237 to 246; Iod. No. 16 to 28; R.M.V. 6.5; Pol. No. 10.2; Unsap. 0.3%; Titer 21°. Bray and Elliott [*Analyst*, **41**, 298 (1916)] examined gru-gru kernel oil with the following results: Sp. g. at 100°/15° C. 0.868; Sap. V. 254-255; Iod. No. 16.2 to 21.0; R.M.V. 5.7 to 6.8; Pol. No. 10 to 12; Unsap. 0.4 to 0.5%; Titer 20.5°.

G. Collin [*Biochem. J.*, **27**, 1366 (1933)] examined a sample of the palm nuts from Trinidad. They contained 26 per cent of kernels which had 44.4 per cent of oil. The characteristics were as follows: Sap. Equiv. 222.3; Iod. No. 17.1; Acid V. 0.6; Unsap. 0.45%; M. Pt. 24°. The mixed fatty acids contained the following percentages of constituents: caprylic 7.8, capric 5.6, lauric 44.9, myristic 13.4, palmitic 7.6, stearic 2.6, oleic 16.5, and linoleic 1.6. An examination of the oil indicated that it contained 64.5 per cent of fully saturated glycerides, the remainder consisting of mixed saturated-unsaturated glycerides.

In the state of Minas Geraes, Brazil, this palm is called Macaúba. Although large numbers of these palms are found in certain localities of this state, comparatively little of the available fruit is collected as yet for processing. The pulp oil produced is used chiefly for making soap, but some is refined, winterized and sold to the retail trade for use as a cooking oil. The kernel oil is used chiefly for soap manufacture. Aceite de Macaúba is discussed also by M. Silva [*Industria y Química (Argentina)* **3**, 39 (1940)].

The palm *Manicaria saccifera* is indigenous to Central America and Brazil. G. Collin [*Biochem. J.*, **27**, 1366 (1933)] found that nuts from Trinidad contained 15 per cent of kernels which had 57.7 per cent of oil. The characteristics were as follows: Sap. Equiv. 221.8; Iod. No. 10.7; Acid V. 0.6; Unsap. 0.05%; M. Pt. 27°. The percentages of constituents in the mixed fatty acids are as follows: caproic, a trace, caprylic 5.3, capric 6.6, lauric 47.5, myristic 18.9, palmitic, 8.2, stearic 2.4,

oleic 9.7, and linoleic 1.4. Fully saturated glycerides in oil amounted to 79.5 per cent.

The palm Astrocaryum vulgare, which is known as the tucum or aouara, is found in Central and South America. It should be noted that the names tucum and tucan are applied in different localities to various species of *Astrocaryum* and *Bactris.* The fruits of the *A. vulgare,* which weigh from 15 to 20 grams, consist of 30 per cent of pulp, 50 of shell, and 20 of kernel. The pulp contains 35 to 38 per cent of oil and the kernels from about 45 to 48 per cent. The pulp oil is yellow and has a faint pleasant odor. Depending upon its quality, it can be used for edible purposes or making soap. Characteristics: Sap. V. 220; Iod. No. 46.4; Unsap. 0.75%; M. Pt. 27° to 30° C.; $N_D^{40°}$ 1.4610.

The kernel oil is a somewhat brittle, firm, creamy-white solid which resembles commercial palm kernel oil in its properties and can be used for the same purposes. When refined, it is an excellent edible oil with the following characteristics: Sp. G. at 100°/15° C. 0.867; Sap. V. 240 to 249; Iod. No. 11 to 14; R.M.V. 3.8; Pol. No. 5.9; Unsap. 0.3%; M. Pt. 30° to 32° C.; Titer 26° to 27°; $N_D^{40°}$ 1.4497 to 1.4505.

References: Bray and Elliott [*Analyst,* **41,** 299 (1916)]; Bolton and Hewer [*Analyst,* **42,** 35 (1917)]; *Bull. Imp. Inst.,* **15,** 40 (1917); H. Junnelle [*Mat. grasses,* **12,** 5507 (1920)] F. Michotte [*Mat. grasses,* **15,** 6354 (1923)]; E. W. S. Ventriss [*Oils and Fats Record,* **3,** 8 (1921)].

The palm *Astrocaryum aculeatum* is found in the Guianas, Brazil, and elsewhere. It is known in various localities as the aouara, maraja, tucum, tucumce, besides other names (*cf. A. vulgare*). The pulp of the fruit, which is sweet and succulent, is eaten by the natives. The fruit consists of 23.3 per cent of pericarp, 52.5 of shell, and 24.2 of kernel. The pulp contains from about 34 to 41.6 per cent of an orange or brownish-colored oil. Characteristics: M. Pt. 18° to 23° C.; Sap. V. 184.

The kernels contain about 25 per cent of oil. Characteristics: Sap. V. 211 to 214; Iod. No. 9.5 to 10; Unsap. 0.6%; M. Pt. 32° C.

The palm Cocos syagrus, which is known as the piririma, is found in the Para Valley, Brazil. Bolton and Hewer examined the fruits from two varieties of this palm and give the following information: "Two distinct types of fruit have been examined, the more common being a blunt form, which consists of a hard shell sparsely covered with fiber, enclosing a tough, white kernel covered by a brown, woody skin. The pointed kernels are similar in every way except shape. The structure of both the long and blunt kernels, is strikingly characteristic in that they have three points of attachment, close together in the former, and widely apart in the latter."

	Blunt Fruits	Pointed Fruits
Kernels	40% Oil	41% Oil
Sap. V.	252.2	—
Iod. No.	12.5	13.4
M. Pt.	23°–28.7° C.	22.2°–26.1° C.
Acid. V.	6.4	5.9

The palm *Astrocaryum tucuma* is found in Brazil, the Guianas, Venezuela, and other tropical regions of South America. It is known by various names including tucuma, tucum, tucumaly, gru-gru, chambira, and cumaix. The fleshy portion of the fruit, which is edible, contains an oil, but to date no figures for the characteristics have been found. It is stated that this oil can be used for edible purposes and soap making.

The kernels contain about 52 per cent of oil, for which the following characteristics have been reported: Sp. g. 100°/15° C. 0.867; Sap. V. 240; Iod. No. 11.6; R.M.V. 3.8; Pol. No. 5.9; Acid V. 2.1; M. Pt. 30.5° C. The press cake contained the following constituents: moisture 8.4, crude protein 10, fat 7, carbohydrates 62.9, and crude fiber 9.5 per cent.

The Guere palm of Colombia [*Bull. Imp. Inst.*, **19**, 293 (1921)] is probably *A. tucuma*. The nuts examined at the Imperial Institute averaged 8 grams in weight and consisted of 40 per cent of kernels and 60 of shell. The kernels weighed about 3 grams and contained about 38 per cent of fat, which is harder than that from *A. vulgare*. Characteristics: Sp. g. at 100°/15° C. 0.864; Sap. V. 249.6; Iod. No. 9.4; M. Pt. 35.5° C.; Acid V. 1.7; Titer 29.7°.

G. Collin [*Biochem. J.*, **27**, 1366 (1933)] found that kernels from nuts grown in Malaya contained 39.8 per cent of oil for which the following characteristics were reported: Sap. Equiv. 230.3; Iod. No. 15.8; Acid V. 1.8; Unsap. 0.4%; M. Pt. 30.3°. The percentage composition of the mixed fatty acids was as follows: caprylic 1.3, capric 4.4, lauric 48.9, myristic 21.6, palmitic 6.4, stearic 1.7, oleic 31.2, and linoleic 2.5. The oil contained 69.7 per cent of fully saturated glycerides, the remainder being saturated-unsaturated glycerides.

Murumuru Oil. This oil is obtained from the kernels of the fruit of the *Astrocaryum* murumuru, which is found growing in certain parts of Brazil. The pointed hard-shell nuts are characterized by being sparsely covered with fiber which yields no oil. The kernels contain from 36 to 42 per cent of oil for which the following characteristics are reported: $N_D^{40°}$ 1.4499 to 1.4507; Sap. V. 237 to 247; Iod. No. 10.8 to 13; Unsap. 0.7%; M. Pt. 33° to 35° C. This hard white fat has little odor or taste.

M. Saraiva [*Mem. inst. chim. Rio de Janeiro*, 1929, No. 2, 5-19; *Chem. Absts.*, **24**, 3663 (1930)] has examined the fat from the kernels of the fruit of a palm in Brazil classified as *Astrocaryum murumuru*. The kernels contained 39.7 per cent of fat which has the following characteristics: $N_D^{40°}$ 1.4540; Iod. No. 11; Sap. V. 242; R.M.V. 2.8; Acid V. 14.5; Unsap. 0.26%; M. Pt. 32° C. The oil was reported to contain the following percentages of acids: caprylic 1.03, capric 1.47, lauric 39.92, myristic 34.55, palmitic 4.26, stearic 2.01, linoleic 0.38, oleic 10.13.

The Awarra palm, Astrocaryum jauari, is a native of the Guianas, South America The fruits, which weigh about 14 grams, vary in color from light to a dark reddish brown. They consist of about 37 per cent of fibrous red orange pericarp, about 40 of shell and 23 of kernel. The

nuts average about 9 grams and the kernels 3 grams in weight. The nuts contain one and sometimes two kernels. The pericarp contains about 45 per cent of an orange-red oil which is partially solid at ordinary temperatures. The kernels contain about 36 per cent of a hard, cream-colored fat with a slight odor similar to that of coconut oil. These oils can be used for the same purpose as the palm and palm kernel oil of commerce. According to *Bull. Imp. Inst.*, **26**, 413 (1928), these oils have the following characteristics: *Pulp or pericarp oil:* Sp. g. at 100°/15° C. 0.8573; $N_D^{40°}$ 1.458; Sap. V. 195.8; Iod. No. 68; R.M.V. 0.4; Pol. No. 0.2; Unsap. 0.5%; Titer 36.7°. *Kernel Oil:* Sp. g. at 100°/15° C. 0.8660; $N_D^{40°}$ 1.4505; Sap. V. 242; Iod. No. 13 to 14.6; R.M.V. 2.4; Pol. No. 6.8; M. Pt. 31° C.; Unsap. 0.5 to 0.7%; Titer 23.5° to 27°.

Ouricury Palm Kernel Oil. This oil is obtained from the kernels of the Brazilian palm *Syagrus* (or *Cocos*) *coronata*. The thin-skinned, fibrous fruits, which have the appearance of small plums, average 6.5 grams in weight. They consist of 47.5 per cent of pulp and fibers and the so-called palm "nut" accounts for the remaining 52.5 per cent of the fruit. The pulp contains 3 per cent of red oil, or 1.4 per cent on the basis of the whole fruit, and is of no economic importance. The seed or nut consists of 23.8 per cent of kernel and 76.2 of shell. They have the appearance of miniature coconuts.

McKinney and Jamieson [*Oil and Soap*, **15**, 172 (1938)] received from the Franklin Baker Company, Hoboken, N. J., 25 pounds of the kernels. These contained 2.4 per cent of moisture and 69.7 of oil. The expressed oil was slightly yellow. It appears to have a lower solidification point than any other commercial palm kernel oil. Only a very small quantity of "stearine" was deposited when the oil was cooled to 18° C.

The characteristics were as follows: Sp. g. at 25/25° 0.9221; $N_D^{25°}$ 1.4543; Sap. V. 256.9; Iod. No. (Hanus) 14.7; SCN V. 12.8; R.M.V. 5.93; Pol. No. 18.38; Unsap. 0.27 per cent; Sat. acids 78.2 per cent; Unsat. acids 14.2 per cent.

The oil contained the following percentages of acids: caproic 1.66, caprylic 9.10, capric 7.64, lauric 42.70, myristic 8.43, palmitic 7.15, stearic 2.15, arachidic .09, oleic 12.18, and linoleic 2.1.

For some years, the kernels were exported from Brazil to Marseilles, France, but more recently, shipments of them have been made also to the United States. Here it is understood that the oil is much appreciated by margarine manufacturers. As with other palm kernel oils, it can be used by soap makers.

The palm wax and kernel oil are discussed in "Licuri (cocos coronata) Na Bahia," G. Bondar, Boletin No. 11, Instituto Central de Fomento Economico da Bahia, 1942. 86 pages.

Cera e Oleo de Licuri, Moacyr Silva, Instituto Nacional de Technologia, Rio de Janeiro 1940. 22 pages.

Cocos Pulposa Palm Kernel Oil. The palm is found in Uruguay

and in Brazil. The average weight of the nuts from Uruguay was 3.8 grams. Each nut contained three kernels and the individual weight of these ranged from 0.20 to 0.55 gram. The kernels were found to contain 4.8 per cent of moisture and 59.5 of oil. G. S. Jamieson and W. G. Rose [*Oil and Soap,* 17, 144 (1940)] examined the oil which they expressed with the following results: $N_D^{26°}$ 1.4554; Sap. V. 260.3; Iod. No. (Hanus) 24.6; SCN V. 22.4; Acid V. 1.7; R.M.V. 7.1; Pol. No. 24.8; Unsap. 0.44 per cent; Sat. acids 68.02 per cent; Unsat. acids 24.80 per cent. The melting point of the oil was between 17 and 18° C. The oil was found to contain the following percentages of acids: caproic 1.47, caprylic 9.40, capric 13.23, lauric 34.39, myristic 6.59, palmitic 1.78, stearic 1.31, oleic 22.4, and linoleic 2.4.

Cohune Oil. Cohune oil is obtained from the kernel of the seed of the nut from the fruit of the palm *Attalea cohune* which grows in the well-drained, rich, tropical lowlands in the southern part of the Yucatan peninsula in Mexico, British and Spanish Honduras, Guatemala, and some other regions. The fruit, which is borne in bunches ranging in weight from 30 up to 200 pounds, requires a year to reach maturity. The palms bear from 1000 to 2000 fruits a year. The brown, matured fruits are rounded at the base and pointed at the apex. They range from 2 to 3 inches in length and from 1.25 to 2 inches in diameter, and weigh from 45 to 50 grams. The tough, outer fibrous layer enclosing the nut is about one-eighth of an inch thick and usually contains from 8 to 10 per cent of oil, but sometimes considerably more. The seed or nut, which contains one and sometimes two kernels, has an exceedingly hard shell from 0.25 to about 0.5 inch thick. The kernels, which are 1 to 1.25 inches long and 0.5 to 0.6 in diameter, weigh about 5 grams and contain from 65 to 71 per cent of a solid white fat resembling coconut oil in appearance and odor. The fibrous portion ranges from about 15 to 34 per cent, the nut from 58 to 71, and the kernel from 8 to 11 per cent of the fruit. A ton of kernels is obtained from about 10 tons of nuts.

Although cohune oil is similar in composition and properties to coconut and palm kernel oils, and can be used for the same purposes, its commercial production has not reached anything like the proportions that naturally would be expected in view of the extensive area in which the palms grow. Unfortunately, there have been many failures in attempts to advance this industry. Most of these failures have been due to lack of sufficient capital, accurate knowledge of the conditions in these tropical regions, misleading reports in regard to the actual number of fruiting cohune palms in a given area, and to the difficulty of collecting the nuts. To establish this industry firmly on a profitable basis will probably necessitate, in most localities, the cultivation of these palms; but where the palms are particularly numerous, by clearing the ground of other trees and undergrowth, and by giving the palms the necessary care for the maximum production of fruit, it might be possible to operate a plant at a profit.

For many years, repeated attempts have been made to devise a

machine satisfactory for cracking the nuts. Several machines, most of which are of a centrifugal type, have been invented, which are claimed to operate satisfactorily. Also, machines for separating the nuts from the husks have been placed on the market.

The oil can be obtained from the kernels either by expression or solvent extraction. The press cake is of value for feeding stock. The chief use of the shells is for fuel, but a carbon can be prepared from them comparable in value to that from coconut shells. Unless a solvent extraction plant were established in the cohune region, primarily to treat the kernels, it would not pay to attempt the extraction of the oil in the husks, which, in most cases, could be used only for soap making.

In southern Mexico and Central America, considerable quantities of the kernels are obtained by the natives, who crack the nuts by hand. The natives extract the oil, which they use for edible purposes, as an illuminant, and for making soap. In some places sizable soap works are in operation. Large quantities of the kernels are fed to cattle and hogs, while some are used in the preparation of sweetmeats.

Composition and Characteristics: T. P. Hilditch and N. L. Vidyarthi [*J. Soc. Chem. Ind.*, **47**, 35T (1928)] have determined the composition of cohune oil, which gave the following characteristics: Iod. No. 9.8; Sap. V. 251; Acid V. 0.9; Usap. 0.47%; Titer of fatty acids 21.2°. This oil, which was extracted by the authors, had the following composition: Percentages of fatty acids: caproic, trace; caprylic 7.5; capric 6.5; lauric 46.5; myristic 16; palmitic 9.5; stearic 3.0; oleic 10; linoleic 1.

The characteristics are as follows: Sp. g. 100°/15.5° C. 0.868 to 0.971; Iod. No. 10 to 14; Sap. V. 252 to 256; R.M.V. 6.8 to 8.3; Pol. No. 12.5 to 15.4; Unsap. 0.2 to 0.5%; M. Pt. 18° to 20° C.; $N_D^{15.5°}$ 1.4510; Titer of fatty acids 19.8° to 21.2°.

The *Bull. Imp. Inst.*, **12**, 237 (1914) gives the following data for the oil extracted from the outer fibrous portion of the fruit: Sp. g. at 100°/15.5° C. 0.848 to 0.855; Sap. V. 197.4 to 203.1; Iod. No. 65.4 to 75.1; R.M.V. 1.65; Unsap. 0.95%. The acid value of the two oils examined was 121.3 and 162.0. As would be expected, this oil is of entirely different character from that obtained from the kernel. In all cases, the oil is dark green, but most of this color is removed by treating the oil with animal charcoal.

Attention is called to the following references:

"The Globulin of the Cohune Nut," C. O. Johns and C. E. F. Gersdorff, *J. Biol. Chem.* **45**, 57 (1920).

"Coconut and Cohune Production in Mexico," E. F. Feeley, *The Oil Miller*, **12**, No. 4, 32 (1920).

"Cohune Nut in Malaya," *Oils and Fats Record*, **3**, No. 5, 83 (1921).

"An American Palm Oil Industry," H. Wadell, *Oil and Fat Ind.*, **4**, 217 (1927).

"The Cohune Palm in British Honduras," N. S. Stevenson, *Tropical Woods*, No. 30, 3 (1932).

"The Cohune Nut Industry (British Honduras)," *Bull. Imp. Inst.*, **22**, 409 (1934).

The palm Arecastum romanzoffianum. The fruits of this palm, which is called "plumy coconut," weigh about 6 grams apiece. They

consist of 23% of pulp, 69% of shell, and 8% of kernel. G. N. Pulley and H. von Loesche [*Oil and Soap,* **18,** 251 (1941)] found that the kernels contain 52.2% of oil. The characteristics of this oil are as follows: $N_D^{20°}$ 1.4580; Sap. V. 239.5; Iod. No. (Hanus) 28.4; SCN V. 24.5; Unsap. 0.41; Sat. acids 68.1%; Unsap. 27.2%.

The palm Attalea gomphococca. The kernels of this palm, which is common in certain parts of Mexico and Central America, contain from 63.5 to 67 per cent of oil. R. C. Fernandez [Bol. Tec. No. 35 (1941) Dept. Nacl. Agr., Costa Rica; *Chem. Absts.,* **35,** 3840 (1941)] reported the following characteristics for the oil: $N_D^{20°}$ 1.4560; Sap. V. 249.6 to 255.2; R.M.V. 5.8 to 7.4; Pol. No. 5.7 to 6.4; M. Pt. 23.5° C.

The palm Attalea spectabilis, known as the curua palm, grows in Brazil. The fruits, which weigh about 35 grams, consist of 15.5 per cent of fibrous pericarp, 71.3 of shell (nut) and 13.2 of kernel. The nut contains one kernel. The shell of the nut is thick and very hard. The kernels, which weigh about 5 grams, contain 56 to 60 per cent of oil similar to that from the cohune. The fibrous pericarp contains from 3 to 15 per cent of oil which, when extracted by solvent, is a red or greenish semi-solid mass. It has not been examined.

The oil from the kernels has the following characteristics as reported by the *Bull. Imp. Inst.,* **18,** 172 (1920): Sp. g. at 100°/15° C. 0.8693; $N_D^{40°}$ 1.447; Iod. No. 8.9; Sap. V. 259.5; Unsap. 0.36%; R.M.V. 6.3; Pol. No. 15.6; M. Pt. 24° to 26° C.; Titer 24.6°.

The extracted meal had the following composition: Moisture 8.9; crude protein 16.8; carbohydrates 52.8; fiber 15.1; and ash 6.3 per cent.

The palm Butea (Cocos) bonneti, Becc. is being grown experimentally at Suchum in the Black Sea region, according to S. Ivanov and Z. P. Alissoya [*Chem. Umschau.,* **36,** 401 (1929); *Brit. Chem. Absts.,* -B, **1930,** 154] in their study of the effect of climate on the composition of oils of the *Palmae.* The kernels contain 64 per cent of a liquid oil which gave the following characteristics: Iod. No. 23.6; SCN V. 19.78; Sap. V. 259.6; Acid V. 0.7; Sat. Acids 77.9%. From this thiocyanogen value it was calculated that the oil contained 4.41 per cent of linoleic and 18.54 of oleic acid as glycerides. The authors state that these results illustrate the theory that the proportion of unsaturated glycerides increases with the severity of the climate. Suchum is the northern limit for this palm.

The oil can readily be hydrogenated to yield a solid fat, which may be used as a substitute for coconut oil.

Remarks: For many years the various species of *Butea,* natives of North and South America, have been cultivated as ornamental palms in California and many countries here and abroad. Much uncertainty still exists in regard to the botanical identity of the various species of Butea formerly grouped under cocos.

The palm Maximiliana caribaea is a native of Brazil and Central America. G. Collin [*Biochem. J.,* **27,** 1366 (1933)] was supplied with a sample of the nuts from Trinidad which upon examination were found to be immature. The kernels, which amounted to 59 per cent of the

nuts, contained only 4.8 per cent of oil. The following characteristics were determined: Sap. Equiv. 236.8; Iod. No. 22.7; Acid V. 20.2; Unsap. 0.23 per cent. The high acidity is characteristic of oil from immature seeds. The small quantity of oil obtainable accounts for the approximate percentages of acids in the mixed fatty acids, which are as follows: caprylic ?, capric 5, lauric 47, myristic 21, palmitic 9, stearic ?, and unsaturated acids 18.

Apparently the oil has not been previously examined.

Carnauba Palm Kernel Oil. The palm *Copernicia cerifera* of Brazil is the source of carnauba wax. The seeds are reported to contain about 14 per cent of oil. No information appears available on the oil content of the kernels or whether the "seeds" actually refer to the kernel itself. The characteristics of the fat are as follows: Sp. g. at 15° C. 0.9483; $N_D^{40°}$ 1.4291; Sap. V. 221.5; Iod. No. 23.3; R.M.V. 4.2; M. Pt. 27° C.; Unsap. 0.8%.

Date Pit (Stone) Oil. This oil is in the seed of the palm *Phoenix dactylifera.* R. G. Harry [*Analyst,* **61**, 403 (1936)] has examined three samples of date pits and their oils with the following results:

Sample	Moisture	Oil	Proteins	Carbohydrates	Fiber	Ash
Mixed Var.	7.96	6.77	5.25	65.53	13 60	0.89
Deglet Nour	9.82	7.39	5.30	58 53	18.10	0.86
Iraq	6.46	8.49	5.22	62.51	16.20	1.12

Characteristics of Extracted Oils

Samples	Sp. g. at 15.5° C.	$N_D^{40°}$	Sap. V.	Iod. No.	R.M.V.	Pol. No.	Acid V.	Unsap. %
Mixed Var. ...	0.9201	1.4580	206 1	54.5	1.0	3.0	1.0	1.98
Deglet Nour ...	0.9203	1.4574	212.6	50.2	0.9	2.7	0.4	0.51
Iraq	0.9207	1.4580	208.3	53 0	1.1	2.9	0.6	0.40

The oils were a pale, yellowish green liquid having a pleasant odor.

On account of the small oil content of date seeds, extraction of their oil does not appear to be of commercial interest to those firms that are selling pitted dates.

Of the Diplothemium species of palms, five of those growing in tropical South America have been identified as follows: *D. acaule, D. candescens, D. littorale, D. maritinum* and *D. umbircola.* The palm *D. littorale* produces fruit, the flesh of which is orange yellow and has a sweet, agreeable flavor. The "nuts" have a hard shell and the kernels contain about 55 per cent of oil. The oils from all these species remain to be investigated.

The palm Juboea spectabilis (J. Chinensis), commonly known as the Chilean molasses or honey palm, is native to certain portions of Chile. It does not thrive near the sea. The palm grows from 30 to 40 feet high and has the general appearance of the coconut tree except that the trunk is much thicker and the leaves are somewhat shorter. The fruit, which is borne in bunches of about 50, have the appearance of diminutive coconut fruits. The nuts, which weigh between 6 and 7 grams, are

hollow like coconuts but contain no milk. The kernels, which amount to 40 per cent of the nuts, contain, when mature, about 68 per cent of oil which, unlike coconut oil, remains liquid at ordinary temperatures. The oil has a more delicate and sweeter odor and taste than coconut oil.

Locally, the immature fruits are sold for consumption. Also the sap from the palm is concentrated to a syrup and sold in Chile, whence the name "molasses palm."

C. A. Lathrop [*The Cotton Oil Press,* **6,** No. 8, 32 (1922)] examined a sample of the oil, which he extracted with the following results: Sp. g. at 25°/15.5° C. 0.9243, at 40°/15.5° C. 0.9143; N_D at 25° C. 1.4541, at 40° C. 1.4482; Acid V. 0.4; Iod. No. (Wijs) 12.7; Sap. V. 273.7; R.M.V. 8.8; Pol. No. 25.5; Unsap. 0.24%; Sol. Pt. 8° to 10° C.; Titer 18.7°.

The palm Oenocarpus bataua, which is known locally as pataua, is found in Brazil, chiefly in the regions of Para and Maranhao. The oil extracted from the fleshy part of the fruit by the natives has but little odor or taste and varies in color from yellowish green to green. The oil is known as Batava, Coumou, and Patua. The pulp contains about 24% of oil. The seeds (kernels) contain so little oil (0.3 to 1%) that they are of no interest. The samples examined by Bolton and Hewer [*Analyst,* **42,** 35 (1917)] were very low in free fatty acids and bore a striking resemblance to olive oil. Except for a slightly lower iodine number and a distinctly lower index of refraction, the characteristics were strikingly similar. These authors state that the oil is an excellent edible oil. J. B. DeM. Carvalho [*Oil and Fat Ind.,* **6,** No. 9, 11 (1929)] states that the oil is prepared on a small scale in Para, where it is in much demand as a salad and cooking oil.

Characteristics. Sap. V. 190 to 191.8; Iod. No. 78.2 to 80; Sol. Pt. −7° C.; Acidity (as oleic) 0.48%; Unsap. 1.1%; Titer 17° to 18°. Grimme (*Chem. Rev. Fett Harz Ind.,* **1910,** 233) examined a sample of this oil with the following results: Sp. g. at 15° C. 0.9248; Sap. V. 190.5; Iod. No. 80.0; $N_D^{15°}$ 1.4691; Sol. Pt. −9° C.; Titer 17.9°.

Jamieson and McKinney [*Oil and Soap,* **11,** 207 (1934)] investigated a large sample of expressed patau palm fruit oil received from J. B. De Moraes Carvalho, Rio de Janeiro, Brazil. The fruits from which this oil was obtained were collected in the vicinity of Belem, State of Para. The characteristics of the oil are as follows: Sp. g. at 25/25° C. 0.9118; $N_D^{25°}$ 1.4662; Sap. V. 190.4; Iod. No. (Hanus) 75.4; SCN V. 72.8; R.M.V. 0.33; Pol. No. 0.19; Acid V. 3.0; Acetyl V. (Andre-Cook) 10.4; Unsap. 0.48%; Sat. Acids 14.45%, and unsaturated acids 79.94%.

The oil contained the following percentages of fatty acids: oleic 76.5, linoleic 3.4, palmitic 8.8, and stearic 5.6. A very small quantity (0.07 per cent of triacontanic acid ($C_{30}H_{60}O_2$) was found. The source of this acid is probably the wax on the exterior of the fruit which became dissolved in the oil during its expression.

The species *Oenocarpus distichus* and *O. bacaba,* like *O. bataua,* yield liquid oils from the fleshy portions of the fruits. Characteristics

reported for the pulp oil of *O. bacaba* are: Sap. V. 193.4; Iod. No. 81.5 and Unsap. 0.46 per cent. The kernels from these species contain only from 1 to 3 per cent of oil. Locally, the pulp of these various fruits is used to prepare a drink; that of *O. bacaba* is said to be superior to the others for this purpose.

Also the pulp oils from the *Euterpe oleracea, E. gissara, E. edulis* and *E. assahy* are liquid at ordinary temperatures and similar to those from the fruits of the *Oenocarpus.*

It is possible that some of the *Euterpe* species given may be found to be identical. The pulp oil from *E. oleracea* has an iodine number of 77 and a saponification value of 198.

The Segen or Unania palm, *Jessenica polycarpa,* found in Colombia, South America, yields a liquid oil similar in many respects to that from the fruits of the *Oenocarpus bataua.* The oil is used locally for cooking purposes. L. Bacarach [*Analyst,* **43,** 289 (1918)] examined samples of the oil with the following results: Sp. g. at 15°/4° C. 0.9161; Sap. V. 188.5 to 190.5; Iod. No. (Wijs) 73.5 to 74.8; Acid V. 3.8 to 4.

Babassu Oil. Babassu oil is obtained from the kernels of the seed or nut from the palm *Orbignya* (a Sub. Div. of *Attalea*) *speciosa,* which is abundant in some parts of Brazil. The fruits, which resemble those of the cohune, but are somewhat larger, are borne in bunches or "heads." Each palm bears from 2 to 4 of these very large bunches twice a year. Each bunch contains from 200 to 600 fruits. Not infrequently, a mature palm will yield a ton of nuts, which contains about 270 pounds of kernels. The outer tough, fibrous portion of the fruit, in contrast to many other palm fruits, contains only about 1 per cent of fat. Each nut contains from 2 to 6 kernels, 3 being the most common number. The kernels have a more elongated shape than those of the cohune and weigh about 3 grams each. They contain from 63 to about 70 per cent of oil, which resembles that from cohune kernels and coconut. Machines have been made to remove the husks from the nuts and for cracking the exceedingly hard, thick shells. However, the larger part of the kernels is still being obtained by hand labor. It is reported that a man can separate about 11 pounds of kernels per day. At the present time, large quantities of available nuts remain uncollected. With the establishment of central cracking plants, large quantities of shells will be available for use as fuel or for making charcoal which could be used in smelting ore.

From about 1915 to 1935 large quantities of the kernels were exported to Europe where the oil was either expressed or extracted with solvents. In recent years, considerable quantities of the kernels, as well as oil, have been exported to the United States, and less to Europe. The oil, after being refined in the same manner as coconut and other palm kernel oils, is used in the manufacture of margarine; the "stearine" obtained by "wintering" the oil is used by the confectionery and baking trades for the same purpose as coconut oil "stearine." In tropical regions, it is used as a cooking oil. The oil is also used for making soap.

According to R. Lüde [*Fettchem. Umschau.,* **41,** 51 (1934); *Chem.*

Absts., **28**, 392 (1934)], the press cake contains the following percentages of constituents: moisture 9 to 10, fat 4 to 16, proteins 20 to 23, fiber 15 to 18, and ash 4 to 6. The cake and meal are used as a feed for livestock.

A. Heiduschka and R. Agstin [*J. prakt. Chem.*, **126**, 53 (1930)] found that the mixed fatty acids contained the following percentages of constituents: caproic oil 0.1, caprylic 6.5, capric 2.7, lauric 45.8, myristic 19.9, palmitic 6.9, and oleic 18.1.

A. Bömer and H. Hüttig [*Z. Unters. Lebensm.*, **75**, 1 (1938)] found, as was to be expected, that the oil contained a small quantity of stearic acid. They were able to identify the presence of lauro-dimyristin, myristo-dilaurin, palmito-dimyristin and stearo-dipalmitin in the oil. These investigators also give analytical data for babassu kernels and press cake, as well as the characteristics of the oil which they used in their investigation.

Characteristics: Sp. g. at 15° C. 0.9240; $N_D^{40°}$ 1.4500; Sap. V. 246.9 to 251; Iod. No. 14 to 16.3; R.M.V. 5.8 to 6.2; Pol. No. 10.2 to 12.1; Acetyl V. (Andre-Cook) 3.1, Unsap. .03 to 0.7%; M. Pt. 22° to 26° C.

The babassu, which is known in Brazil by other names, including bassoba, baguassu, aguassu, uauassu and guaguassu, is still repeatedly quoted from earlier works as being the *Attalea funifera,* which is the well-known Brazilian fiber palm. There is the possibility at times, that kernels of the *A. funifera* may be found in shipments of babassu kernels. The following references may be of interest: *Bull. Imp. Inst.*, **22**, 39 (1924); Bray and Elliot, *Analyst,* **41**, 298 (1916); Monograph—"O Babassu," by E. Teixeira da Fonseca, Ministry of Agriculture, Rio de Janeiro, 1924-5 [*Bull. Imp. Inst.*, **23**, 357 (1925)], which states that the babassu palm is found from the Amazon to the Matto Grasso, and Bolivia. ["The Brazilian Babassu," A. P. Lee, *Oil Fat Ind.*, **7**, 91 (1930)].

"The Brazilian Babassu Nut," *Tropenpflanzer,* **32**, 516 (1929). "Some Notes on Babassu Oil," *Oil Col. Trds. J.*, **81**, 970 (1932). A 70-page monograph entitled "Babassu" by Instituto de Expansao Commercial, Rio de Janeiro, Brazil, 1930 (in English and Portuguese). "Babassu Oil," M. J. Hausman, *Soap,* **12**, 28 (1936).

The palm Maximiliana regia, which is known as the cokerite (kokerite) inaja, mareepa, and by other names, flourishes in the Guianas and Brazil. The fruit consists of about 17 per cent of pericarp, 12.4 of husk, 53.6 of shell and 17 of kernels. The pulp or pericarp contains about 15 per cent of semi-solid, orange-colored oil which has the following characteristics: Sap. V. 211.6; Iod. No. 51.4; Titer 25.5°.

The nuts usually contain 2 long, narrow, flattened kernels which are about an inch long and half an inch wide. The kernels contain from 56 to 60 per cent of a white solid fat having the consistency of lard, but showing a tendency toward brittleness. Characteristics: Sp. g. at 100°/15° C. 0.867; Sap. V. 242 to 253; Iod. No. 12 to 13; R.M.V. 3; Pol. No. 7; Unsap. 0.3%; M. Pt. 27° to 29° C.; Titer 24°.

The oil is similar to coconut oil, but contains smaller quantities of

volatile acids. The press cake (7% oil) contains about 15 per cent of proteins.

References: Bray and Elliot [*Analyst,* **41,** 298 (1916); *Bull. Imp. Inst.,* **8** (1916)]. Bolton and Hewer [*Analyst,* **42,** 35 (1917)]. H. Jumelle [*Mat. Grasses,* **12,** 5507 (1920)]. Kokerite Fruits from British Guiana [*Bull. Imp. Inst.,* **25,** 1 (1927)].

Mamarron (Nut) Oil. According to the Imperial Institute [*Bull. Imp. Inst.,* **20,** 147 (1922)], it was believed that mamarron nuts came from the palm *Scheela excelsa,* but later specimens, which also came from the Magdalena Valley, Colombia, were more like those from a species of *Attalea.* The fruits, which weigh about 48 grams, consist of 9.5 per cent of fibrous pericarp, 79.2 of shell and 11.3 of kernel. The seeds or nuts are light brown, ellipsoidal, bluntly pointed at the base, and sharply pointed at the apex. The nuts average 43 grams in weight. The kernels, which weigh slightly over five grams, contains about 70 per cent of a cream-colored fat with an odor like that of coconut oil. The characteristics are as follows: Sp. g. at 100°/15° C. 0.8679; $N_D^{40°}$ 1.4490; Sap. V. 251; Iod. No. 10.8; R.M.V. 8.6; Pol. No. 10.8; M. Pt. 24° C.; Acid V. 2.3; Unsap. 0.4%; Titer 23°.

It will be observed that the above figures are similar to those reported from babassu and cohune oils. The melting point and titer, which are somewhat higher than those of cohune oil, are the same for babassu oil.

The Cuban Royal palm, Roystonea regia (formerly named *Ceodoxia regia*), produces quantities of small, soft, almost black, berry-like fruits containing one seed. A sample of the ripe fruit was examined by the writer. The fleshy pericarp, constituting about half of the fruit, contains only about 3 per cent of oil and the little kernel about 18 per cent.

R. C. Stillman and R. M. Reed [*Oil and Soap,* **10,** 208 (1934)] examined the expressed kernel oil with the following results: Sap. V. 226.5; Iod. No. 39.8; Acid V. 28.2; Titer 20.5° C.; Sat. acids 61.5%; Unsat. acids 30.8%; Unsap. 0.5%. The mixed fatty acids contained the following percentages of constituents: capric 5.0, lauric 32.0, myristic 16.0, palmitic 7.5, and stearic acid 1.0. The mixed fatty acids gave the following characteristics: Iod. No. 42.5; SCN V. 33.9; Sap. V. 239.3.

Palma Real Kernel Oil. The name, in Ecuador, is applied to the palm *Ynesia colenda.* (O. F. Cook, Nat'l. Hort. Mag. 70, Apr. 1942). The average weight of the so-called nuts is 9.5 grams and that of the kernels is 3.3 grams. Usually each nut has one kernel. The kernels amount to about 35 per cent of the nuts. The kernels which were examined contained 51.74 per cent of oil and 4.28 of moisture. The oil gave an iodine number of 16.4 and a saponification value of 253.4.

Coconut Oil. Coconut oil is obtained from the kernels of the nuts of the palm *Cocos nucifera,* which grows along the coast-lines of practically all the tropical regions. Large forests of coconut palms are found in Ceylon, Java, Sumatra, Philippines, South Sea Islands, and East and West Africa. The trees grow best near the coast at low altitudes where the minimum rainfall is about sixty inches, with fairly uniform distribu-

tion throughout the year. Coconut trees which grow far inland in the tropics or those grown anywhere in subtropical regions bear few or no nuts. Since it has been shown in Puerto Rico [*Bull. Imp. Inst.*, **21**, 512 (1923)] that salt is beneficial, it is possible that coconut trees growing inland would fruit, if the soil about each tree was annually treated with three or four pounds of salt. The tree is very tolerant as to soil, except that it does not do well in very heavy soils, particularly in situations so low that the ground water remains stagnant.

The tree usually grows from 50 to about 100 feet high. The trunk terminates in a crown of about 20 pinnately compounded leaves from 12 to 15 feet long. The flowers are borne in spadices which appear in the axils of the leaves. The trees begin to bear nuts in the sixth or seventh year and they bear in quantity when 10 or 12 years old. Mature trees bear about 60 nuts. The ripening of the coconuts is not simultaneous, but extends over a long period of time. Under good agricultural practice, an acre planted to coconut palms will yield about 6000 nuts per year.

Three types of dwarf coconut palms are being cultivated in Malaya [*Malayan Agr. J.*, **12**, 371 (1924)]. These types are recognized by the color of the fruits, which are "apricot or red," "green," and "ivory yellow." The "ivory yellow" type is the most productive. The trees begin to bear when six years old. It has been found that an acre which contains 9- to 10-year-old trees, will yield 9000 coconuts or 2200 lbs. of copra, while an acre of ordinary trees yields about 1080 lbs. of copra. The trees are expected to be productive for about 30 years. For other details the original article should be consulted. Other, dwarf coconuts are known in the Philippines, Ceylon, and elsewhere.

The following references contain much information: "The Coconut Palm: The Science and Practice of Coconut Cultivation," by H. C. Sampson (J. Bale, Sons, and Danielson, London, **1923**). "Coconut Production in Latin America," *Bull. Pan. Am. Union*, Washington, **1918**. "Coconut Culture," by P. J. Wester, Phil. Bur. Agric., Circ. **39**, 1925. Also consult *J. Soc. Chem. Ind.*, **37**, 96A and 97A (1918); **33**, 1096 (1914). "Coconut Cultivation and Plantation Machinery," H. L. Coghlon and J. W. Hinchley (Crosby, Lockwood and Son, London, **1914**). "The Bud-Rot of the Coconut Palm," U. S. Dept. Agric., Bur. Plant Industry, Circ. 36. "The Coconut," J. S. Patel, Governor of Madras, India, 1938. A 313-page volume.

It has been estimated that Ceylon has 800,000, South America 500,000, Java and Sumatra 220,000, West Indies 110,000, African Coasts 100,000, Cochin China and Thailand 100,000, Philippines, Straits Settlements and New Guinea 260,000 acres of coconut trees. The annual world production of coconut oil is about 1.2 billion pounds.

Copra. Copra is the dried kernel of "meat" of the coconut from which the coconut oil of commerce is expressed. The methods employed for the preparation of copra vary in different localities, and much is still made by primitive methods. When the climate permits, the method of sun-drying, when properly conducted, gives an excellent product.

The nuts, separated from the husks, are split in half and after draining off the milk, they are exposed to the sun until the contraction of the "meat" permits of its ready removal from the shell. Then the separated meats are further dried. Unless the moisture of the copra is reduced below 8 per cent, it will mold and the oil will deteriorate. In some places, machines have been introduced which can split about a thousand coconuts per hour, but in many regions this work is still done by hand. Copra is also prepared by drying the pieces of coconut on bamboo grills over fires made from the husks and shells. This product is usually poorly dried and badly smoked, with the result that it yields oil of inferior quality. According to H. C. Brill [*Chem. Met. Eng.*, **24**, 567 (1921)], coconut meat arranged on trays is treated in a closed chamber for twelve hours with sulfur dioxide, then placed in sheds to dry for two weeks or longer. This treatment produces a light-colored, thoroughly dried product. The sulfur dioxide prevents the growth of microorganisms; it also softens the cell walls, which causes the coconut to dry more readily. Wells and Perkins [*J. Soc. Chem. Ind.*, **41**, 987A (1922)] recommend 1 kg. of sulfur burned to the dioxide for the treatment of 3000 nuts. Various other artificial driers have been designed. Hot-air kilns in India, Ceylon, Java, and elsewhere, are so arranged that the coconut is rapidly dried; this results in the production of a light-colored copra, some of which, on account of its fine quality, is used in confectionery. However, there are large quantities of hot-air or kiln-dried copra produced which is not nearly as good in quality as the better grade of the sun-dried product. If properly dried copra is kept in dark, rat-proof buildings which are dry and well ventilated, it will remain in good condition. Much good copra is damaged by improper storage, either in buildings or in ships. The following references may be of interest:

"Trinidad's Copra Crushing Industry" [*The Cotton Oil Press*, 2 (No. 8), 30 (1919)].
"Copra and Its Products," P. S. Tilson [*ibid.*, 2, (No. 1), 39].
"Problems in the Preparation of Copra and Coconut Oil," H. C. Brill [*Chem. Met. Eng.*, **24**, 567 (1921)].
"Trade in Copra and Coconut Oil," [*The Nat. Provisioner*, **64**, 33 (1921)].
"Copra Inspecting and Testing," P. W. Tompkins [*The Cotton Oil Press*, **4**, 53 (1920)].
"Copra Analyses," Allen and Auerbach [*J. Soc. Chem. Ind.*, **32**, 296 (1913)].
"Extraction of Copra Cake with Solvents," A. P. West [*Phil. J. Sci.*, **20**, 509 (1922); *Analyst*, **48**, 36 (1923)].
"Copra and Coconut Oil," Katherine Snodgrass, Food Research Institute, Stanford University, Cal. **1928.**
"Isolation and Identification of Some of the Sugars in Copra Meal and Coconut Water," E. M. Caray [*Chem. Absts.*, **19**, 547 (1925)].
"The Drying of Copra," A. C. Barnes, *Agric. J. Fiji*, **5**, 84 (1932).
"The Drying of Copra," G. De Belsunce, *Bull. mat. grasses inst. colonial Marseille*, **21**, 182 (1937).
"Ceylon Estate Copra," R. Child, *Tropical Agriculturist*, **88**, 137 (1937).
"Copra Manufacture," F. C. Cooke, *Malayan Agric. J.*, **24**, 167, 332 (1936).
"Copra Quality Under New Rules Importance of Sampling and Analysis," P. W. Tompkins, *Oil and Soap*, **18**, 103, (1941).

Fresh coconut contains 30 to 40 per cent of oil and 50 of water, while copra usually contains from 60 to 65 per cent, but some kiln-dried

copra contains over 70 per cent of oil. The yield of copra from whole coconuts ranges from 12 to 15 per cent. The nuts from about 2.5 acres of coconut palms in normal years are estimated to yield a ton of copra.

Coconut By-Product. The fiber from the husks of the coconut is made into brushes, mats, and coarse cloth. The shells are used for fuel, but some are converted into charcoal which is now well known for its adsorption properties, particularly of small quantities of rarefied gases.

Attention is called to the following references:

"The Destructive Distillation of Coconut and Palm Nut Shells," C. D. V. Georgi and T. A. Buckley, *Malay Agric. J.*, **17**, 398 (1929).

Coir: "Report on the Attributes and Preparation of Coconut Fiber," S. G. Barker, Empire Marketing Board Publication No. 71, London, 1933.

"Composition of Coconut Shells," L. C. Fleck, W. G. Van Beckum, and G. J. Ritter, *J. Am. Chem. Soc.*, **59**, 2279 (1937).

"Paper from Coconut Husks," *Chem. Trds. J.*, **101**, 550 (1937).

"Composition of Coconut Shells," R. Child and S. Ramanathan, *J. Am. Chem. Soc.*, **60**, 1506 (1938).

"Investigations on Coconuts and Coconut By-Products," F. C. Cooke, Bull. No. 8 (1932), Dept. Agric. S. S. and F. M. S. (Kuala Lumpur).

Coconut Oil. For centuries, the natives along the tropical coasts have boiled the crushed meats in water and skimmed off the oil as it floated to the surface. In this manner, a superior oil was obtained on the Malabar coast which was known in commerce as "Cochin oil," but now this name refers to the best grade of coconut oil rather than its source. The other grades in international commerce were called Ceylon and copra oil. Formerly, all the copra was exported from the tropics, but in recent years increasing quantities are being expressed locally. However, large quantities of copra are still exported to America and Europe, where the oil is expressed and the press cake is used for feeding stock. The lack of demand for the press cake has retarded to some extent the large-scale production of the oil in many parts of the tropics.

In the United States, the copra is unloaded from the ships by mechanical means. At one plant on the Pacific coast [A. W. Allan, *Chem. Met. Eng.*, **29**, 614 (1923)] the copra is removed from the ships by suction and delivered directly into the mill by an air blast system.

Because of the high oil content of copra, it is customary to make two pressings, neither being made cold. A number of mills grind, warm, and press the copra in oil expellers. Other mills "cook" the crushed copra and press it in cage hydraulic presses. In either case, the press cake is ground, heated, and pressed again in hydraulic presses under a pressure from 4000 to 5000 pounds per square inch. The second pressing is not made with the oil expeller as the cake is likely to be burned, because the friction due to its hard, fibrous character. A new type of expeller has been developed by the V. D. Anderson Co., which makes it possible to express the oil with a single pressing. The oil from the two pressings is combined and sent to the refinery. To produce high-grade oil, it is necessary not only to have good copra, but also to express and collect the oil in clean equipment. It is important to separate the foots (meal, etc.) from the crude oil as quickly as possible to prevent its deterioration, and this holds true for all oils. Settling tanks should

be frequently given a thorough cleaning. Neglecting to do this results in increased refining losses.

The press cake, which contains from 6 to 10 per cent of oil (modern mills), is sold as such or ground to a meal and sacked for shipment to cattle feed dealers. This product is recognized as a valuable feeding stuff. See the following references: "Nutritive Value of Coconut Globulin and Coconut Press Cake," Johns, Finks, and Paul, *J. Biol. Chem.*, **37**, 497 (1919); *J. Soc. Chem. Ind.*, **39**, 384A (1920). "Composition and Nutritive Value of Feeding Stuffs by Wood and Halman" (Cambridge Univ. Press, 24 pp.); "Analyses of Some By-Products of the Coconut Industry," A. W. R. Joachim and S. Kandish, *Tropical Agric.*, **78**, 15 (1932); *Chem. Absts.*, **26**, 3395 (1932).

Refining. Coconut oil is refined by the caustic soda process, using not over 0.2 per cent of alkali in excess of that required to neutralize the free fatty acids. Some add salt to the caustic soda solution to facilitate the separation of the soap stock. Owing to the presence in this oil of glycerides of fatty acids lower in the series than those present in the common seed oils, greater care is necessary in refining to prevent undue saponification of neutral oil. In some plants, it is customary to keep the oil warm until the soap stock has settled, forming a firm mass from which the neutralized oil can be readily withdrawn. If the soap stock is allowed to cool, it liquefies. After the removal of the oil from the refining kettle, it is necessary to wash it with warm water to remove the remainder of the soap stock. At other refineries, directly after the alkali treatment, the soap stock is removed by washing with warm water. This operation requires experience in order to avoid loss of oil through the formation of emulsions. The soap stock and wash waters are boiled and allowed to stand, and a further recovery of neutral oil is made. After the separation of this oil, the soap solution is acidified with sulfuric acid. The free fatty acids and entrained oil which rise to the surface are collected and shipped to the soap maker. The neutralized oil is dried in a vacuum drier or at atmospheric pressure in an open kettle, heated by steam coils, and then bleached while hot by agitation with a small percentage of activated carbon or a mixture of fuller's earth and carbon, the quantities required having been previously determined in the laboratory. The bleaching agents are removed by passing the hot oil through a filter press. After bleaching, unless the oil is to be stored some time, it is deodorized at once in a high vacuum deodorizer with superheated steam. See "Coconut Oil Refining," A. P. Lee [*Ind. Eng. Chem.*, **16**, 341 (1924)].

Some refiners "winter" the coconut oil. The separated stearine, which is known in the trade as coconut butter or "chocolate fats," is used in confectionery (candy, sweet fillings for wafers, etc.). The oleine is largely employed for cooking shelled nuts which are to be salted.

Crude coconut oil of good quality and the properly refined oil have good keeping qualities if stored in filled containers and protected from light and air.

Additional information will be found in the following references:

"Copra and Copra Oil," H. C. Brill, H. O. Parker and H. S. Yates [*Phil. J. Sci.*, **12**, 55 (1917)] "Methods of Production of Pure Coconut Oil," H. O. Parker and H. C. Brill (*ibid.*, p. 87); "The Rancidity of Philippine Coconut Oil," Brill and Parker (*ibid.*, p. 95); "Detection of Small Amounts of Fuel Oil in Coconut Oil," P. W. Tompkins and C. A. Lathrop, *The Cotton Oil Press*, **7**, No. 11, 33 (1924); "Copra and Coconut Oil," by Katherine Snodgrass, **1928**, a book published by Food Research Institute, Stanford University of California; "Keeping Qualities and Causes of Rancidity in Coconut Oil," H. S. Walker [*Phil. J. Sci.*, **1**, 117 (1906); *J. S. C. I.*, **25**, 381 (1906)].

One of the most important uses for refined coconut oil and coconut oil stearin is in the manufacture of vegetable margarines. Some is used in making vegetable shortening and for other minor purposes. Large quantities of the crude oil, as well as the soap stock from the refineries, are made into soaps of various kinds.

Grades of Coconut Oil. Choice crude coconut oil must be pressed and not extracted and shall not contain more than 3 per cent free fatty acid calculated as oleic acid, shall be free from moisture and impurities and shall have a color not greater than 12 yellow and 2 red.

Prime Crude Coconut Oil. Prime crude coconut oil shall be pressed and not extracted, and shall be free from moisture and impurities, and shall not contain more than 5 per cent of free fatty acids calculated as oleic acid, and shall have a color no deeper than 30 yellow and 5 red on Lovibond's Equivalent color scale: provided that any oil that tests in excess of 5 per cent free fatty acids and has less than 6 per cent and has a color darker than 30 yellow, 5 red, and not darker than 30 yellow and 6 red, shall not be rejected, but shall be reduced in price one-half of 1 per cent of the contract price for each 1 per cent excess fatty acid.

Off Crude Coconut Oil. Off crude coconut oil, neither choice nor prime, must be pressed and not extracted, and shall be called "Off Coconut Oil." When "Off" coconut oil is sold by sample, if it should refine at a loss exceeding the loss of the sample by not over 5 per cent, but otherwise equal, it is still a good tender at a reduced price in proportion to the excess loss.

Refined Coconut Oil. Refined coconut oil shall not contain free fatty acids in excess of one-tenth of 1 per cent, and shall be free from moisture and impurities, and shall not be darker than the combined standard glasses of 30 yellow and 3 red. If the oil tendered or delivered does not conform to these requirements, it may be rejected.

Refined Deodorized Coconut Oil. Refined deodorized coconut oil shall be free from moisture and impurities, sweet and neutral in flavor and odor, not in excess of one-tenth of 1 per cent free fatty acids, and shall not be darker than the combined standard glasses of 12 yellow and 2 red. If the oil tendered or delivered does not conform to these requirements, it may be rejected.

Characteristics of Coconut Oil. Sp. g. at 15° C. 0.926, at 25° C. 0.9188, and at 30° C. 0.9150; N_D at 25° C. 1.4530 to 1.4560, at 40° C. 1.4477 to 1.4495, and at 60° C. 1.4410 to 1.4420; Sap. V. 251 to 263; Iod. No. 8 to 9.6; R.M.V. 6 to 8; Pol. V. 15 to 18; M. Pt. 23° to 26° C.; Titer of fatty acids 20.4° to 23.5°. The completely hydrogenated fat melts at 44.5° C. (111° F.).

Characteristics of Coconut Stearine. Sap. V. 251 to 259; Iod. No. 3.8 to 7; R.M.V. 3.3 to 6; Pol. V. 11 to 12, and M. Pt. 27° to 32° C.

Characteristics of Coconut Oleine. Sap. V. 257 to 265; Iod. No. 13 to 15; R.M.V. 8 to 8.5; Pol. V. 23.2; M. Pt. 18° C., and titer of fatty acids 8° to 13° C.

Armstrong and Allan [*J. Soc. Chem. Ind.*, **43**, 212T; **44**, 63T (1924)]

have made an extended investigation of the oils from the skin or rind covering the coconut kernel and various palm kernels. They compared the characteristics of these oils with those of the corresponding oils extracted from the peeled kernels. The coconut skin oils gave saponification values 237 to 253 and iodine numbers from 25 to 59.7. The oil from the pared kernels gave a saponification value from 214 to 217.5 and iodine numbers from 7.2 to 9.6.

Composition of Coconut Oil. The glycerides of coconut oil which have been isolated and identified by Bömer [*Z. Nahr. Genussm.*, **40**, 97 (1920); *J. Soc. Chem. Ind.*, **33**, 756 (1914)] are as follows: caprylolauromyristin, laurodimyristin, myristodilaurin, palmitomyristin and stearodipalmitin. The unsaturated acid glycerides which are present in small quantities were not identified. The presence of small quantities of methylheptyl and methyl ketones was shown by Haller and Lassieur, *Analyst*, **35**, 356 (1910).

G. Collin and T. P. Hilditch [*J. Soc. Chem. Ind.*, **47**, 251T (1928)] have studied the character of the glycerides present in coconut oil using their permanganate-acetone method. The sample of oil contained the following percentages of acids: caproic, traces, caprylic 7.9, capric 7.2, lauric 48.0, myristic 17.5, palmitic 9.0, stearic 2.1, oleic 5.7, and linoleic 2.6 per cent. The saturated acid glycerides amounted to 84 per cent, in which probably dilauromyristin was the major constituent. The mixed saturated and unsaturated acid glycerides, which amounted to 16 per cent, consisted of 12 per cent of oleo (linoleo) disaturated acid glycerides and 4 per cent of dioleo (linoleo) monosaturated acid glycerides. No triolein or linolein could be detected.

A table gives the results obtained by several investigators.

No. 1, Elsdon [*Analyst*, **38**, 8 (1913)]. Nos. 2 and 3 Armstrong, Allan, and Moore [*J. Soc. Chem. Ind.*, **44**, 63T (1925)]. No. 2 oil was from pared coconuts and No. 3 was from the parings. Oils 4 and 5

COMPOSITION OF COCONUT OIL.

Acids	1	2	3	4	5
			Per Cent		
Caproic	2.0	0	0	0.2	0 2
Caprylic	9.0	9.5	2.0	7.4	7.2
Capric	10.0	4 5	2.0	9.5	10.7
Lauric	45.0	51.0	28.0	49.1	48.7
Myristic	20.0	18.5	22.0	17.6	17.5
Palmitic	7.0	7.5	12.0	4.3	5.4
Stearic	5.0	3.0	1.0	1.2	0.8
Oleic	2.0	5.0	23.0	10.3	9.0
Linoleic	...	1.0	10.0	...	...

were different samples examined by W. N. Stokoe [*Analyst*, **49**, 577 (1924)]. For details concerning these investigations, the original papers must be consulted. The quantitative determination of the acids present in coconut oil is exceedingly difficult, and this accounts in part for the variation of the results reported by different investigators. As in the case of other oils, some variation in composition would be expected in

coconut oils from widely different regions. E. R. Taylor and H. T. Clarke [*J. Am. Chem. Soc.*, **49**, 2829 (1927)] have shown definitely that coconut oil does contain caproic acid. They fractionally distilled 130 kilos of the methyl esters of the fatty acids from coconut oil and found the following percentages: caproic 0.46, carylic 8.7, capric 5.6, lauric 45, and myristic 16.5 to 18. They did not attempt to determine the other acids present as they were interested only in the determination of the acids below palmitic acid. More recently H. E. Longenecker [*J. Biol. Chem.*, **130**, 167 (1939)] examined the mixed fatty acids from a sample of coconut oil and found the following percentages of constituents: caproic 0.8, carylic 5.4, capric 8.4, lauric 45.5, myristic 18.0, palmitic 10.5, stearic 2.3, arachidic 0.4, hexadecenoic 1.3, oleic 7.5, and a trace of linoleic acid. For the occurrence of hexadecenoic acid in other vegetable fats, see T. P. Hilditch and H. Jasperon, *J. Soc. Chem. Ind.*, **57**, 84 (1938).

Hydrogenated Oil. When the oil is completely hydrogenated it melts at about 45° C. (the untreated oil melts at about 25° C.), but the solidification point was only about 7° C. above that of the original oil.

Tests. There is no color or other specific chemical test for coconut oil. The Polenske, saponification, and iodine values will in most cases indicate the adulteration of coconut oil. Coconut oil is now seldom adulterated. Palm kernel oils of either African or American origin, which are similar to coconut oil in many respects and are used for the same purposes, give higher iodine numbers and lower Polenske values than those of coconut oil. Various methods have been proposed for the estimation of coconut and palm kernel oils in mixtures. *See* Elsdon and Smith [*Analyst*, **50**, 53 (1925)], Bolton, Richmond, and Revis [*Analyst*, **37**, 183 (1912)], Stokoe (*J. Soc. Chem. Ind.*, **40**, 57T), Gilmour [*Analyst*, **50**, 119 (1925)], Elsdon [*Analyst*, **42**, 298 (1917)]. The detection of coconut oil in lard, margarine, and butter, L. Robin, *Analyst*, **32**, 47 and 168 (1907).

E. Hinks [*Analyst*, **32**, 160 (1907)] has devised the following microscopic test for the detection of coconut, particularly in admixture with butter. Five cc. of the melted and filtered fat is dissolved in 10 cc. of ether in a test tube which is then packed in ice. After half an hour much solid glyceride has separated out, leaving a clear ethereal solution above. The ether is poured onto a plaited filter and rapidly filtered. The ethereal solution is evaporated on a water bath and the residual fat poured into a test tube and boiled with 3 or 4 times its volume of alcohol (96 to 97% by volume). Complete solution takes place at the boiling point. The solution is allowed to cool to room temperature, when most of the fat separates. The test tube is then placed in water at 5° C. and kept at that temperature for 15 minutes. The alcoholic layer is rapidly filtered into another test tube which is then chamber-cooled to 0° C. A flocculent deposit soon separates. In this deposit are crystals which indicate the presence of coconut oil. This is examined microscopically after being kept at 0° C. for 2 or 3 hours. A portion is withdrawn by a wide-mouthed pipette, placed on a slide, and covered

without pressure. To view the crystals satisfactorily, a magnification of 250 to 300 is required. Pure coconut oil yields five needle-shaped crystals which are readily seen by magnifications lower than 250, but in the presence of butter a mixed deposit of granular butter spheres separates along with numerous very fine, almost feathery crystals of coconut fat, either alone, in clusters, or attached to the butter spheres. The presence of 5 per cent of coconut oil is stated to be readily detected by this method. The presence of 10 per cent of beef fat, cottonseed or sesame oils does not mask the test for coconut oil and the presence of these substances alone gives no positive microscopic results. The author states that the presence of lard does interfere. Lard yields stellate clusters of crystals readily differentiated from the characteristic appearance of coconut oil crystals and almost completely suppresses the granular appearance of butter. The identification of coconut oil in the presence of lard is more difficult, but the coconut oil crystals may in most cases be seen distinct from stellate lard crystals.

It should be observed that it is essential to make the examination of the crystals while the alcohol is cold; otherwise the crystals dissolve. Sometimes if the temperature of the room is high, it is necessary to place the slide on a clear piece of ice in a shallow glass dish while making the examination.

Attention is called to the following references:

"Trade in Philippine Copra and Coconut Oil," E. D. Gothwaite, Trade Promotion Series No. 11, U. S. Dept. Commerce, 1925.

"Coconuts: Localities Where Cultivated," B. Schmidt, *Allg. Oel Fett Ztg.*, **1932**, 437; *Oil & Col. Trds. J.*, **82**, 988 (1932).

"Coconut Oil and the Philippine Situation," J. D. Craig, *Soap*, **8**, No. 3, 25 (1932).

"Coconut Oil Industry Started in Jamaica," *Oil, Pt. Drug Reptr.*, **122**, No. 15 47 (1932).

"The Coconut Industry in the Adaman Islands," A. T. Werning, *Trop. Agric. Ceylon*, **79**, 349 (1932).

"The Coconut Industry on the Malabar Coast of India," F. R. Mason, *Malayan Agric. J.*, **24**, 476 (1936).

"The Copra Industry of the British Solomon Islands," H. T. Pagden, *Malayan Agric. J.*, **24**, 128 (1936).

"The Coconut Industry of the Philippine Islands," F. C. Cooke, Bull. No. 23, General Series, Dept. Agric. Straits Settlements and Federated Malay States, 1936.

"Coconut Oil. II. Method for Conversion into Solids," J. Banzon, *Phil. Agric.* **26**, 399 (1937). Product melts at about 55° C. and can be used for making candles.

"Some Solutions to the Problems of the Philippine Coconut Industry," V. G. Lava, *Phil. Social Sci. Review*, **11**, 1 (1939).

"Copra Deterioration During Storage and Shipment," F. C. Cooke, *Malayan Agric. J.*, **27**, 424 (1939).

"The Fatty Acids of Coconut Oil," H. Nobori, *J. Soc. Chem. Ind. (Japan)*, **43**, 199 (1940); *Chem. Absts.*, **34**, 8315. An oil was investigated of coconuts grown on Hainam Island, S. China.

"Chemical Studies on Coconut Products. III New Process for the Extraction of Coconut Oil," V. G. Lava, P. E. Torres and S. Sanviet, *Phil. J. Sci.*, **74**, 247. Part IV, **75**, 143 (1941).

Papaya Seed Oil. This oil is found in the seed of the melon-like, sizable fruit of the tree, *Carica papaya,* of the *Caricaceae,* which is now cultivated in most tropical countries.

H. W. von Loesecke and A. J. Nolte [*J. Am. Chem. Soc.*, **59**, 2565 (1937)] investigated seeds and oil from fruit grown in the southern part of Florida. The air-dried seeds contained 7.47 per cent of moisture, 25.3 per cent of oil, 27.2 per cent of proteins, 7.85 per cent of ash, and 0.09 per cent of a volatile oil to which the cress-like odor of the seeds is due. Other constituents were not determined. The characteristics of the oil extracted by petroleum ether were as follows: Sp. g. 20/20° 0.9091; $N_D^{20°}$ 1.4666; Sap. V. 189.5; Iod. No. (Hanus) 72.6; Acid V. 3.05; R.M.V. 1.05; Pol. No. 0.20; Acetyl V. 3.8; Unsap. 1.32 per cent; Sat. acids 16.97 per cent; Unsat. acids 78.63 per cent.

The oil contained the following percentages of acids: oleic 76.50, linoleic 2.13, palmitic 11.38, stearic 5.25, and arachidic acid 0.31.

Parkia Seed Oil. This oil is found in the seeds of the tree *Parkia biglandulosa* belonging to the *Minosaceae*. The seeds are reported to contain about 18 per cent of oil.

D. R. Paranjpe [*J. Indian. Chem. Soc.*, **8**, 767 (1931)] obtained the following characteristics for a sample of the oil: Sp. g. at 15° C. 0.9208; $N_D^{21°}$ 1.4705; Sap. V. 189.5; Iod. No. 80.9; R.M.V. 1.12; Pol. No. 0.25; Acid V. 5.2; Unsap. 1.11%; Hehner V. 94.7. The mixed fatty acids contained the following percentages of constituents: oleic 30.6, linoleic 39.4, palmitic 8.8, stearic 13.3, and behenic 7.9.

Peanut Oil. Peanut oil is obtained from the seeds of the legume *Arachis hypogaea,* of which there are quite a number of varieties. There are other species of peanuts, among which may be mentioned the *Arachis nambyquarae, Voandzeia subterranea, Stylosanthis* and *S. mucrowata.* The *A. nambyquarae, Hochme,* which was described in 1922, bears pods 2 to 3 inches long, which usually contain 2 very large seeds. This, like the *A. hypogaea,* is a native of Brazil, where it is cultivated by the Nambyquara Indians in Rondonia, Matto Grasso. Apparently, the peanuts and peanut oil of commerce are all from varieties of the *A. hypogaea,* which originally was carried from Brazil to Africa by slave ships; by the same means, the peanut was brought from Africa to Virginia.

The peanut (*Arachis*) is a much-branched plant somewhat resembling clover in its foliage, but with quadri-foliate leaves. After the small single blossoms have bloomed, the flower stems bend down and force the little pods into the soil, where they develop and mature. The plants of some varieties are erect and others are prostrate.

The more important peanut-producing countries are China, India, United States, Senegal, Manchuria, Nigeria, French Sudan, Gambia, Dutch East Indies, Japan, Spain and Argentina. In India, the annual production is from four to over seven billion pounds. China and Manchuria together produce about as many peanuts as India. In recent years the United States has ranked third in the production of peanuts. Next in order of rank are Senegal and Nigeria.

Although a very small podded variety has been grown for a long time, the extensive peanut industry of China had its beginning about 1889 when Archdeacon Thompson, an American missionary, took 4 quarts of Virginia peanuts to Shanghai and distributed them for planting.

Peanuts are variously known as arachis nuts, earth nuts, ground nuts, and by other names in different localities. The plants thrive best in light, sandy soils well provided with plant foods in regions where the rainfall during the growing season does not exceed 26 inches.

Five varieties of shelled peanuts which were grown during the season of 1915 in the same kind of soil at Florence, South Carolina, were examined at the U. S. Department of Agriculture with the following results:

Variety	Moisture	Oil	Crude Fiber	Protein	Ash
			Per Cent		
Virginia Runner	3.35	46.58	2.73	29.60	2.76
Virginia Bunch	3.28	45.73	2.84	29.52	3.11
Spanish	3.30	49.10	2.30	31.20	2.67
African	3.45	45.90	2.26	30.30	3.31
Valencia	3.75	49.60	2.13	33.64	2.67

It will be observed that the Spanish and Valencia varieties contain the largest quantities of oil and protein. The oil and protein content of any given variety is subject to more or less variation due to differences in soils and climatic conditions as well as to the degree of maturity and moisture content.

In the United States, peanuts are grown throughout all the southern states, but the commercial production is chiefly confined to rather limited areas. Although nine distinct varieties are grown, the three commercially important types are the large-podded Virginia Bunch and Runner, and the small-podded Spanish peanuts. The Spanish nuts weigh about 30 pounds per bushel and the Virginia about 22 pounds. The Spanish nuts have a higher proportion of kernels to shells than the Virginias. The Spanish kernels usually contain from about 47 to 50 per cent of oil and those of the Virginia types of peanut vary from about 38 to 47. A ton of Spanish nuts yield from 70 to 80 gallons of oil and 1300 to 1400 lbs. of cake, whereas a ton of shelled nuts give from 100 to 115 gallons of oil and 1100 to 1200 lbs. of cake containing 40 to 50 per cent of proteins. It should be noted that the Spanish and more recent Improved Spanish peanut are adapted to thrive and produce well under a wider range of soil and climatic conditions than any other variety; besides they mature in less time.

In recent years the annual production of peanut oil in the United States has ranged from 51 to over 150 millions of pounds. Only about one-fourth of the peanut crop prior to 1942 was used by American oil mills; the remainder not required for planting is utilized for other purposes, such as nuts roasted in the shell, salted nuts, peanut butter, and peanut candy.

For the production of oil, the Spanish and Improved Spanish varieties are grown in this country, but at times more or less Virginia peanuts are also used for this purpose. The oil is expressed both by hydraulic presses and expellers. In addition to the mills which produce only peanut oil, many cottonseed mills, at times, press peanuts. In any mill, the first operation is to separate the trash, dirt, stones, nails, etc.,

from the nuts. The cleaning is all done by machinery. The cleaned nuts are passed through the hullers or shellers, which are provided with screens and fans for the separation of the kernels from the shells. The kernels are crushed with rolls, heated in the "cooker," and pressed hot in the hydraulic press in a manner similar to that employed for cottonseed. Only one pressing is made and the press cake, which contains from 6 to 8 per cent of oil, is ground into meal. Usually a portion of the shells are ground with the cake to produce meal with the desired protein content. The idea appears to be to produce peanut meals corresponding in protein content to the various grades of cottonseed meal on the market. The press cake and meal are chiefly used as a feed for stock, for which it is particularly well adapted.

Formerly, large quantities of unshelled peanuts were crushed and pressed, which resulted in a low yield of oil, because much of it was absorbed by the shells.

In the expeller process, the shelled nuts are crushed and usually warmed to some extent in the steam-heated conveyor or "temperer," which feeds the material to the expeller. After the expeller has been in operation for an hour or two, it becomes hot, because of the friction of the crushed peanuts against the inside walls of the steel barrel. When sound shelled nuts are used, a yellow oil is obtained which, after being filtered, but without further treatment, is suitable for use as a salad or cooking oil, and has excellent keeping qualities.

Commercial hydraulic and expeller oil varies in color from pale yellow to a strong reddish yellow or even brown, depending upon the quality of the peanuts and the methods of expression. After expression, the oil is filtered, which is preferable, or allowed to stand in tanks until the foots (meal) have settled. Crude peanut oil, which is separated from the foots directly after expression, has excellent keeping qualities compared with the oil in contact with more or less foots [Baughman and Jamieson, *Chem. Absts.*, 21, 1195 (1927)]. Too much emphasis cannot be placed on the importance of keeping the oil-mill buildings and all the equipment clean and in good condition at all times. Peanut or any other oil deteriorates rapidly when brought into contact with rancid oil or fermenting foots.

Crude peanut oil is refined by the caustic soda process, bleached, if necessary, with fuller's earth (and activated carbons), and deodorized in the same manner as cottonseed oil.

Edible peanut oil is used chiefly in this country (United States) along with coconut oil after partial hydrogenation in the manufacture of vegetable margarines. Some is used as a salad and cooking oil, and at times in the manufacture of vegetable shortenings. The oil is also used to some extent for cooking sardines prior to canning in olive oil. When sold as a salad oil, it is not customary to "winter" or "demarginate" peanut oil as is the case with cottonseed oil, because the former does not readily deposit "stearin" or solidify at the temperature of the ordinary household refrigerator. Inedible grades of the oil and the soap stock from the refineries are used chiefly by the soap maker.

In addition to the peanuts specially grown for the oil, large quantities of damaged or undersized nuts which accumulate at the cleaning and shelling plants are pressed, and the oil, depending upon the quality, is either refined or sent to a soap maker. The red skins and germs separated at candy and peanut butter factories are collected by some oil mills and expressed. Roasting the nuts frequently increases the oil content of the red skins, which contain but little oil, to over 20 per cent. The oil from the germs and skins is only suitable for soap making.

Peanut shells, not ground with the press cake, are burned under the boilers or sold as bedding for stock and other minor uses. Ground shells have been used by the tin plate industry in place of wheat middlings, but were not found so satisfactory as the latter on account of their tendency to scratch the plates.

The well-defined grades of crude and refined peanut oil will be found in the "Rules" of the Interstate Cotton Seed Crushers' Association.

In order to meet the demand in Europe for peanut oil and cake, large quantities of African and Asiatic peanuts are exported to England, France, Holland and Germany, where the oil is expressed or extracted with solvents. When a very pale-colored oil is desired, it is customary to remove as much as possible of the red skins, then crush the kernels with corrugated "oil" rolls and press them cold in hydraulic presses. After the first pressing, the cakes are ground, mixed with a little water, heated somewhat, and pressed again. These cakes are ground, "cooked," and pressed hot. The cold-pressed oil, after filtration, is ready for use as a salad or cooking oil. The oil from the second pressing is generally used for edible purposes without refining, when obtained from sound nuts. The hot-pressed oil is refined and deodorized before using it for edible purposes. The soap stock obtained from refining the oil and the inedible grades is used by soapmakers. The oil or press cake is used as a cattle food, except the inedible grades, which are used as fertilizer.

Considerable quantities of peanut oil are produced in China, India and Japan, which is either used locally or exported. In China, peanut oil is much prized as a cooking oil and it is reported that China (and Manchuria) could utilize about all they can produce; but when export prices are favorable, they export this oil and use some other oil of local production in its place. The bulk of the oil produced in China is still obtained by the use of the primitive native presses, but some is expressed in the modern mills located at the larger export centers. Normally, it is estimated that about half of the Chinese and Manchurian crops is available for export as peanuts or as oil.

The following references may be of interest:

U. S. Department of Agriculture Bulletins: *Dept. Bull.* **1096** (1922), "By-Products from Crushing Peanuts," by J. B. Read; *Farmer's Bull.* **1127** (1924), "Peanut Growing for Profit," by W. R. Beattie; *Dept. Bull.* **1401** (1926), "Marketing Peanuts," 98 pp., by H. J. Clay and P. M. Williams. "Peanut Proteins," by C. O. Johns and D. B. Jones, I, *J. Biol. Chem.*, **28,** 77 (1916); II, **30,** 33 (1917); III, **36,** 492 (1918). "Digestibility of Proteins in Vitro. III Arachin," by D. B. Jones and H. C. Waterman, *J. Biol. Chem.*, **52,** 357 (1922). "Value of the Peanut as a Food Product," by D. B. Jones, *Peanut Promoter,* **5,** No. 3, 50.

"Cultivation, Preparation, and Utilization of the Ground Nut," *Bull. Imp. Inst.*, **23**, 291 to 331 (1925). "The Peanut and Its Cultivation in Western Australia," F. J. S. Wise, *J. Dept. Agric. W. Australia*, **7**, 498 (1930). "The Ground Nut," S. D. Timson, *Rhodesia Agric. J.*, **27**, 15 (1930). "China's Peanut and Soybean Industries," *Allgm. Oel Fettzeit.*, **30**, 144 (1933). "The Classification of Groundnut Varieties," T. R. Hayes, *Trop. Agric., West Indies*, **10**, 318 (1933). "Oil Formation in Groundnut with Reference to Quality," J. S. Patel and C. R. Sesharé, *Indian J. Agric.*, **5**, 165 (1935); *Chem. Absts.*, **29**, 7519. "Studies on the Peanut of West French Africa," L. Margaillan, *Bull. mat. grasses inst. colonial Marseille*, **21**, 4 (1937), and by L. Margaillan and M. H. Reyband, *ibid.*, **22**, 227, 233 (1938). These articles contain a large quantity of analytical data. "Microscopical Studies of Peanuts With Reference to Processing," J. F. Leahy, Georgia Agr. Exp. Sta. Bull. 205 (1940) gives useful information, including the cooking of crushed peanuts prior to expressing the oil. "Marketing Peanuts and Peanut Products," H. J. Clay, U. S. D. A. Misc. Pub. 416 (1941).

Analysis of Crude Peanut Oil for Neutral Glycerides. Jamieson and Baughman [*Cotton Oil Press*, **6**, No. 4, 33 (1922)] examined nine samples with the results shown in table. Sample 1 was a cold-pressed oil, while the others were hot-pressed oils. The refining loss was determined by the official method of the American Oil Chemists' Society and the Interstate Cottonseed Crushers' Association. It will be observed that these crude peanut oils contain but little non-glyceride constituents. The

	Acidity as Oleic Acid	Neutral Oil	Fatty Acids	Other Substances	Refining Loss Official Method
			Per Cent		
1	0.11	99.50	0.17	0.33	2.78
2	0.73	98.96	0.79	0.25	3.61
3	0.88	98.81	0.96	0.23	4.66
4	1.00	98.75	1.18	0.07	2.97
5	0.90	98.71	1.09	0.20	5.15
6	0.91	98.59	1.04	0.37	3.85
7	1.85	97.45	2.35	0.24	5.30
8	2.45	96.74	3.01	0.25	7.12
9	5.84	92.23	6.92	0.85	15.98

neutral glycerides (or oil) do contain small quantities of sterols, lecithin, etc., but inosite phosphates are removed by the treatment with alkali along with the carbohydrates and proteoses.

Composition of Free Fatty Acids of Peanut Oil. Jamieson and Baughman [*Cotton Oil Press*, **7**, No. 2, 35 (1923)] obtained the following results:

	Oils				
Sample	Acidity Per Cent	Iodine No. (Hanus)	Saturated Acids Per Cent	Unsaturated Acids Per Cent	Iodine No. (Hanus)
1	2.8	93.8	20.3	74.6	123.6
2	7.8	94.9	16.3	76.6	120.0
	Free Fatty Acids from Oils 1 and 2				
1		89.2	22.8	72.1	120.9
2		92.5	18.8	76.1	119.0

It will be noted from the figures given that the free fatty acids contain approximately the same proportions of saturated and unsatu-

rated acids as found in the oils. For a long time it was believed that the free fatty acids of various oils were chiefly unsaturated.

Characteristics of Peanut Oil. The analyses of authentic peanut oils shown in the table were made by Jamieson and Baughman, *Cotton Oil Press,* **6,** No. 1, 34 (1922).

Oils 8 and 9 were from Chinese nuts, while the others were from various southern states of the United States. With the exception of 7 and 14, which were cold-pressed, the oils were refined by the caustic soda method and the refined oils were used for the determination of the recorded characteristics. Averages: *Virginia type:* Iod. No. 92.0; Sat. Acids 16.1%; Unsat. Acids 79.1%; *Spanish type:* Iod. No. 93.7; Sat. Acids 20.1%; Unsat. Acids 75.2%. It will be noted that the oils from the Virginia type of nuts contain less saturated acids than those from the Spanish type of peanuts. These samples were obtained during 1920, 1921, and 1922.

Some of the characteristics of peanut oils from different sources recorded by various observers are as follows: Sp. g. at 20° C. 0.9118 to 0.9145; Sap. V. 185 to 192; Iod. No. 83 to 95; Acetyl V. 9 to 9.1; N_D at 20° C. 1.4680 to 1.4720, at 25° C. 1.4680 to 1.4707, at 40° C. 1.4260 to 1.4643; Titer 28° to 30°.

OILS EXPRESSED FROM VIRGINIA TYPE OF PEANUTS

No.	Acid Value	Refining Loss %	$N^{20°}$ D	Sp. g. 25/25° C.	Iodine No. (Hanus)	Saponification Value	Saturated Acids —Per	Unsaturated Acids Cent—	Titer (° C.)
1	2.50	4.28	1.4680	.9128	93.1	187.1	15.5	79.5	31.0
2	1.46	3.61	1.4690	.9124	89.2	186.9	15.9	79.1	30.5
3	1.76	4.66	1.4690	.9125	89.7	186.6	16.3	79.2	31.0
4	2.00	2.97	1.4690	.9123	89.8	186.8	16.5	79.0	30.8
5	1.26	3.87	1.4690	.9123	90.2	186.6	16.4	79.0	30.7
6	1.42	3.01	1.4690	.9123	89.0	187.2	15.8	79.5	30.5
7	0.02		1.4690	.9136	94.8	187.8	16.4	78.7	31.7
8	13.40	14.40	1.4685	.9142	96.8	187.2	15.3	79.5	31.0
9	0.22	2.78	1.4720	.9130	95.0	186.6	16.6	78.8	31.0

OILS EXPRESSED FROM SPANISH TYPE OF PEANUTS

10	2.64	6.27	1.4670	.9138	94.5	188.4	19.8	75.1	31.5
11	3.70	5.30	1.4700	.9137	94.3	187.6	20.4	75.0	31.6
12	1.82	3.81	1.4700	.9131	93.1	187.3	18.7	76.6	30.9
13	4.78	6.13	1.4700	.9133	92.7	187.2	20.5	75.1	32.0
14	0.12		1.4690	.9148	90.1	188.2	20.6	74.2	31.9
15	10.84	14.30	1.4690	.9142	96.2	188.4	19.7	75.8	31.6
16	1.82	3.91	1.4700	.9134	94.2	187.1	20.3	75.2	31.3
17	5.12	6.91	1.4700	.9136	94.8	187.6	20.6	74.7	31.1

Composition of Peanut Oil. Jamieson, Baughman and Brauns [*J. Am. Chem. Soc.,* **43,** 1372 (1921)] examined the oils without refining, which they expressed by means of an Anderson expeller from the White Spanish and Virginia types of peanuts. The oil from the Spanish nuts had the following characteristics: Sp. g. 25°/25° C. 0.9148; Iod. No. (Hanus) 90.1; Sap. V. 188.2; Acid V. 0.12; Acetyl V. 8.7; R.M.V. 0.27; Pol. No. 0.12; Sat. Acids 20.6%; Unsat. Acids 74.6%;

Unsap. 0.22%. Oil from Virginia peanuts: Sp. g. 25°/25° C. 0.9136; Iod. No. 94.8; Sap. V. 187.8; Acid V. 0.3; Acetyl V. 9.5; R.M.V. 0.21; Pol. No. 0.29; Sat. Acids 16.4%; Unsat. Acids 78.7%; Unsap. 0.27%.

The composition of these two oils was found to be as follows:

Glycerides of	Oil from Spanish Peanuts	Oil from Va. Peanuts
	Per Cent	
Oleic acid	52.9	60.6
Linoleic acid	24.7	21.6
Palmitic acid	8.2	6.3
Stearic acid	6.2	4.9
Arachidic acid	4.0	3.3
Lignoceric acid*	3.1	2.6
Unsap. matter	0.2	0.3

* Later investigations have shown this to be chiefly a mixture of behenic and lignoceric acids. Cf. E. Jantzen and C. Tiedcke, *J. prakt. chem.*, **127**, 277 (1930); A. C. Chibnell, S. H. Piper and E. F. Williams, *Biochem. J.*, **30**, 100 (1936).

Hypogeic acid could not be detected in either oil, although repeated attempts were made. Many other investigators have failed to find it, since its presence was first reported by Gossman and Scheven [*Ann.*, **94**, 230 (1855)]. Hilditch, and Vidyarthi [*J. Soc. Chem. Ind.*, **43**, 172T (1927)] have definitely shown that hypogeic acid does not occur in peanut oil. Also it is very improbable that it occurs in any other oil.

For details of the above investigations it will be necessary to consult the original articles.

COMPOSITION OF PEANUT OIL

Acids: Samples	Oleic	Linoleic	Palmitic	Stearic	Arachidic	Lignoceric
	Per Cent					
1	71.5	13.0	6.0	3.0	3.5	3.0
2	65.7	19.2	7.3	2.6	2.6	2.6
3	51.6	26.0	8.5	6.0	4.9	3.0
4	50.6	23.6	7.8	5.9	3.9	3.0
5	58.0	20.7	6.0	4.7	3.2	2.5

Source of oil
1. West African, Hilditch and Nidyarthi, *J. Soc. Chem. Ind.*, **46**, 172T (1927).
2. Senegalese, Armstrong and Allan, *J. Soc. Chem. Ind.*, **43**, 216T (1924)
3. Myddleton and Barry, "Fats: Natural and Synthetic," p. 107.
4. Spanish peanut (U. S. A.), Jamieson, Baughman and Brauns.
5. Virginia peanut (U. S. A.), Jamieson, Baughman and Brauns.

T. P. Hilditch, M. B. Ichaporia and H. Jasperson [*J. Soc. Chem. Ind.*, **57**, 363 (1938)] examined a peanut oil which gave an iodine number of 93.3, a saponification equivalent of 295.5 and contained 0.4 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: palmitic 8.3, stearic 3.1, arachidic 2.4, behenic 3.1, lignoceric 1.1, oleic 56.0, and linoleic 26.0.

D. Holde and N. N. Godbole [*Chem. Absts.*, **20**, 3582 (1926)] made a study of the higher-melting saturated acids of East Indian peanut oil and isolated a small quantity of hexacosanic acid ($C_{26}H_{52}O_2$), which melted at 78.5° to 79° C. It was estimated that the oil contained from 0.1 to 0.2 per cent of this acid.

Adulteration. Peanut oil is sometimes adulterated with other seed oils such as cottonseed, sesame, poppy, rape, etc. This is done only

when these oils happen to be cheaper than peanut oil. The oil, however, may contain sufficient sesame or cottonseed oil to give color tests because of the custom of pressing peanuts in sesame and cottonseed oil mills. The addition of any quantity of other seed oil will lower the percentage of arachidic and lignoceric acids. The addition of corn, cottonseed, poppy seed, sesame, sunflower seed or soybean oil will raise the iodine number, which in the case of peanut oil usually ranges from 89 to 97. When color tests for either cottonseed or sesame oils are obtained, the iodine number and the percentage of arachidic and lignoceric acids should always be determined before conclusions are drawn as to the actual adulteration of the oil.

In the case of hydrogenated peanut oil, Kreis and Roth [*J. Soc. Chem. Ind.*, **32**, 201 (1913)] have shown that methods for the determination of arachidic and lignoceric acids can be successfully applied.

Peanut oil is used at times to adulterate olive oil, and the test described under olive oil can be applied for its detection or approximate determination.

Tests. There is no special color reaction for peanut oil. Its detection and approximate determination depend upon the separation of the mixture of arachidic and lignoceric acids. It should be observed that the quantity of these acids varies in peanut oil from different varieties of peanuts. The original method described by Renard [*Compt. rend.*, **73**, 1330 (1871)] is based on the separation of the saturated acids by the lead-salt-ether method and the crystallization of the mixture of arachidic and lignoceric acids from 90 per cent (by volume) alcohol. Since then quite a number of modifications of this method have been proposed. Bellier simplified the procedure by omitting the lead-salt-ether separation, but it gave low results. Ever [*Analyst*, **37**, 487 (1912)] improved this modification so that it would give better results. Although the Ever modification has been found satisfactory by various analysts, the author's associates failed to obtain good results and recommend the Renard method as described in Chapter VI. The Thomas and Yu method [*J. Am. Chem. Soc.*, **45**, 113 (1923)] has been submitted to collaborative study, but unsatisfactory results were obtained when applied to olive oil mixtures which contained more than 15 per cent of peanut oil. This method is based upon the precipitation of the saturated acids by magnesium acetate from an alcoholic solution and the subsequent crystallization from 90 per cent alcohol of the mixture of arachidic and lignoceric acids.

The tests given elsewhere for cottonseed, sesame, and rape oils are adapted for testing the purity of peanut oil.

Additional references which may be of interest are as follows:

"Peanut Flour," *Chem. Absts.*, **12**, 508, 963, 2217, 2605, 2630 (1918).
"Feeding Live Stock with Peanut Cake," *Chem. Absts.*, **12**, 961 (1918).
"Composition of Peanuts: By-Products," G. S. Fraps, *Chem. Absts.*, **12**, 2030 (1918).
"Peanut Oil Manufacturing in Marseille," A. De Ford, *The Oil Miller*, **12**, No. 4, 21 (1920).

"Catalytic Decomposition of Arachis Oil," A. Mailhe, *Chem. Absts.*, **16**, 4077 (1922).
"Improvement of Nigerian Ground Nuts," *Bull. Imp. Inst.*, **19**, 132 (1921).
"The Peanut: Its Culture and Utilization," A. Rolet, *Mat. grasses*, **16**, 6738, 6770, 6802 (1924).
"Cultivation, Preparation, and Utilization of the Ground Nut," *Bull. Imp. Inst.*, **23**, 291 (1925).
"Ground Nut Products," *Ch. Trade J.*, **77**, 447 (1925).
"Groundnut Industry in the United States," *Oil Col. Trds. J.*, **77**, 374 (1930).
"The Utilization of Peanut Hulls as Fuel," H. Guillon. *Bull. mat. grasses inst. col. Marseille*, **16**, 104 (1932).
"Solution of the Problem of the Utilization of Peanuts Hulls as Fuel," R. Martin, *ibid.*, **16**, 109 (1932); *Chem. Absts.*, **26**, 3899.
"Analytical Constants of Peanut Butter," H. L. Wikoff, Busy, and A. M. Kaplan, *Ind. Eng. Chem.*, **26**, 291 (1934).
"Analytical Values of Argentine Peanut Oils," G. G. Estrella and J. A. Duprat, *Ind. y Quim.*, **14**, 14 (1935); *Analyst*, **61**, 553 (1936).

Pecan Nut Oil. This oil is obtained from the nuts of the tree *Hicoria pecan*, which is extensively cultivated in various parts of the United States, but chiefly in the southern states. The mature kernels contain from about 60 to 70 per cent of oil which, according to Deiler and Fraps [*Am. Chem. J.*, **43**, 90 (1910)], has the following characteristics: Sp. g. at 15°/15° C. 0.9184; Sap. V. 198; Iod. No. 106. The oil has a pleasant but characteristic odor and taste. On account of the value of the nuts for edible purposes, the oil is not prepared commercially. However, the unsalable fine nut fragments which accumulate at the shelling plants could be utilized for the production of oil. With this in view, Jamieson and Gertler [*Oil and Fat Ind.*, **6**, No. 10, 23 (1929)] examined a large sample of the oil expressed from the nut waste of Southland Pecan Company at Columbus, Ga. The oil had a very mild pleasant flavor and was suitable for use as a salad or cooking oil. The oil had the following characteristics: Sp. g. at 25° C. 0.9141; $N_D^{25°}$ 1.4692; Sap. V. 190; Iod. No. (Hanus) 100; Unsap. 0.35%; R.M.V. 0.05; Pol. No. 0.30; Acetyl V. 7.4; Sat. Acids 5.09%; Unsat. acids 89.54%. The oil contained the following percentages of fatty acids: oleic 77.8 linoleic 15.8 myristic 0.04, palmitic 3.14, stearic 1.82, and arachidic acid 0.09.

Pili Nut Oil. This oil is obtained from the kernels of the nut from the tree *Canarium ovatum (C. luzonicum)* of the *Burseraceae* group, a native of the Philippines, which is very abundant in the southern portion of Luzon. There are two varieties of this tree, one producing long and the other, short nuts. The nuts are triangular in shape and have very hard, thick-walled shells. They are inclosed in thin husks (fleshy portion), which are edible when cooked and which contain an oil. At times, this oil is extracted locally and used for cooking or as an illuminant. The kernels contain over 70 per cent of a pale yellow oil having good keeping properties. The oils from the long and short types of nuts have been examined by Brill and Agcaoili [*Phil. J. Sci.*, **A, 10,** 105 (1915)] with the following results: *Long nuts:* Sp. g. at 30° C. 0.9067; Sap. V. 192.6; Iod. No. 61.3; Acid V. 2.7. *Short nuts:* Sp. g. at 30° C. 0.9067; Sap. V. 187; Iod. No. 59.6.

A. P. West and S. Balce [*Phil. J. Sci.*, **23**, 269 (1923)] made an

extensive investigation of a sample of pili nut oil which they expressed, with the following results: Sp. g. at 30° C. 0.9069; $N_D^{30°}$ 1.4646; Sap. V. 197.4; Iod. No. (Hübl) 56; Unsap. 0.2%; Acid V. 1.92. The oil contained 57.2 per cent of oleic acid and 38.11 per cent of saturated acids, consisting of 36.4 per cent of palmitic and 1.7 per cent of stearic acids. The oil contained the following percentages of fatty acids calculated as glycerides: 59.6 of oleic, 38.25 of palmitic, and 1.76 of stearic acid. The oil was observed to have good keeping properties, and if expressed in commercial quantities, it would be a valuable addition to the list of edible oils. The fine edible nuts which are collected are used locally and exported to the United States and some other countries.

Other species of *Canarium* are *C. commune,* which is cultivated in tropical Asia; *C. polyphyllum* of New Guinea, *C. oleosum, C. rufum,* and *C. colophania.* All these species yield edible nuts which are rich in oil. The *C. commune* nuts are known as "Java Almonds" and the kernels contain from 65 to 70 per cent of oil. A. Steger and J. van Loon [*Rec. trav. chim.,* **59,** 168 (1940)] found that the nuts consisted of 15.2 per cent of kernel and 84.8 of shell. The kernels contained 68.6 per cent of oil. The expressed oil had the following characteristics: $N_D^{70°}$ 1.4497; Sap. V. 195.3; Iod. No. (Wijs) 74.0; SCN V. 54.4; R.M.V. 0.64; Pol. No. 0.43; Unsap. 0.61 per cent; Glycerol Rad. 4.4 per cent. The mixed fatty acids contained the following percentages of constituents: oleic 38.3, linoleic 21.8, linolenic 1.2, palmitic 29.0, and stearic acid 9.7.

The oil from the kernels of this species had been examined by a number of investigators and the usual range of the characteristics is as follows: Sp. g. at 40° C. 0.8953 to 0.9050; $N_D^{40°}$ 1.4590 to 1.4601; Sap. V. 193 to 195; Iod. No. 64 to 66; Unsap. 0.3 to 0.6%; Acetyl V. 8 to 16; Titer 37° to 41°.

Canari Oil from *C. oleusum:* $N_D^{20°}$ 1.4664, at 40° C. 1.4591; Sap. V. 197; Iod. No. 63; Unsap. 0.97%; Sol. Pt. 12° to 13° C.

The husks surrounding the nuts contain about 35 per cent of oil which had the following characteristics: $N_D^{20°}$ 1.4584; Sap. V. 183.5; Iod. No. 78.2; Unsap. 4.9%; Sol. Pt. 16.5° C.

The oil from the kernels of the New Guinea species—*C. polyphyllum* —was examined by M. Krause [*Der Tropenpflanzer,* **17,** 147 (1913)] with the following results: Sp. at 30° C. 0.9042; $N_D^{21°}$ 1.4750; Sap. V. 190 to 200; Iod. No. 53 to 60; M. Pt. 22° to 30° C.

Pistachio Nut Oil. This oil is obtained from the nuts (kernels) of the small tree *Pistacia vera* of the *Anacardiaceae* family which is cultivated in the countries bordering the Mediterranean, Arabia, northwestern India, and some other localities. The kernels usually contain from 45 to 50 per cent of oil, but Beythien [*Pharm. Zentr.,* **70,** 551, 571 1929)] only obtained 25.6 per cent from Levant kernels. It is stated that the cold-pressed oil is a golden yellow, whereas that extracted by solvents is dark green.

The characteristics of the oil which have been reported by various

investigators are as follows: Sp. g. at 15° C. 0.9179 to 0.9200; $N_D^{20°}$ 1.4729; Sap. V. 188 to 192; Iod. No. 85 to 98; Unsap. 1.0 to 3.1 per cent; Titer 13 to 14°.

The most extensive investigation of the oil has been that made by D. R. Dhinga and T. P. Hilditch [*J. Soc. Chem. Ind.*, **50**, 9T 1931)]. The oil, which was extracted from kernels obtained from Punjab, India, gave an iodine number of 97.8, a saponification equivalent of 287.8, an acid value of 6.7, and contained 3.1 per cent of unsaponifiable matter. The percentage composition of the mixed fatty acids from this oil is as follows: oleic 69.6, linoleic 20.0, myristic 0.6, palmitic 8.2 and stearic 1.6. It is reported that the oil is much used in India for medicinal purposes.

F. L. Vodret [*Annali Chim. Appl.*, **19**, 76 (1929); *Brit. Chem. Absts.*, **B1929**, 363] examined the kernels (and oil) of *Pistacia lentiscus* from Sardinia. The kernels of this species contain from 10 to 14 per cent of oil. The oil examined by Vodret had the following characteristics: Sp. g. at 15° C. 0.918; $N_D^{22°}$ 1.4671; Sap. V. 209; Iod. No 81.6; R.M.V. 0.96; Sol. Pt. −6° C.; Unsap. 0.96 per cent. The oil was reported to contain the following percentages of acids: palmitic 24.82, stearic 11.63; oleic 47.62, and linoleic 6.25. It will be observed that the total acids amount to only 90.3 per cent, but in view of the small quantity of unsaponifiable matter, it would, unless otherwise accounted for, be expected that the total acids would amount to 94 per cent or more.

It should be noted that the composition of this oil is different from that given for the Punjab *P. vera* oil.

Picramnia Fats (Butters). The fats are found in the seeds of various *Picramnia* species found in Central and South America. They belong to the *Simarubaceae* family, but are sometimes placed under the *Terebinthaceae*.

Arnand [*Compt. rend.*, **114**, 79 (1892)] found that the kernels from the seeds of the *P. tariri* (sow) from Guatemala contained about 67 per cent of fat, from which he obtained a previously unknown unsaturated acid $C_{18}H_{32}O_2$ melting at 50.5° C. This was named tariric acid. It gives a dibromide which melted at 32° C., and it is claimed to be an isomer of sterolic acid [*ibid.*, **134**, 473 (1902)]. Grützner [*Chem. Zeit.*, **17**, 185 (1893)] isolated this acid from *P. camboita*.

A. Steger and J. van Loon [*Rec. trav. chim.*, **52**, 593 (1933)] examined the fat from Guatemalan seeds with the following results: Sp. g. at 78°/4 C. 0.8867; $N_D^{70°}$ 1.4543; Sap. V. 193.6; Iod. No. (Wijs) 83.0; R.M.V. 0.52; Acid V. 13.4; M. Pt. 50° C.; Sat. Acids 4.6%; Unsat. acids 89.8%. The unsaturated acid fraction consisted of tariric (6.7 stearolic) acid. They stated that this acid which melted 50–51° gave, upon bromination, only one crystalline compound—6.7 dibromoleic acid melting at 33.3° C.

Grimme [*Ch. Rev. Fett Harz Ind.*, **17**, 158 (1910)] reported that the kernels from the seed of *P. carpinterae* contained 76 per cent of fat having the following characteristics: M. Pt. 50° to 52° C.; $N_D^{50°}$ 1.4624;

Sap. V. 186.2; Iod. No. (Wijs) 63.9; Unsap. 1.7%. The saponification value was given as 156.2, but without doubt it was a misprint.

Seed and fat from *P. lindeniana,* from Guatemala. The seed contained 39 per cent of fat, which had the following characteristics: Sp. g. at 50° C. 0.8880; $N_D^{50°}$ 1.4608; M. Pt. 40° to 41° C.; Iod. No. (Wijs) 56.8; Sap. V. 192.7; Acid V. 3.3; Unsap. 1.08%. The fat was reported to contain the following percentages of acids: oleic 20.9, tariric 19.9, myristic 21.0, palmitic 31.5 and stearic 2.7.

Piqui-α Fats. These fats are found in the fruit of the tree *Caryocar villosum (Caryocaraceae),* native to Brazil. The tree was introduced into Malaya about 1920. Fruits from these trees as well as the fruit and seed fats, have been examined by C. D. V. Georgi [*Malayan Agric. J.,* **17,** 166 1929)]. The percentages of the various parts of the fruits, which weigh about 300 grams, are as follows: pericarp 74, mesocarp which surrounds the one to four seeds 13, shell of seed 11.3, and kernel 1.7. The mesocarp contained 47.4 per cent of fat and 34.4 of moisture. The kernels contained 45.1 per cent of fat and 26.6 of moisture. The mesocarp fat gave the following characteristics: Sap. V. 204.9; Iod. No. (Wijs) 46.6; Acid V. 2.2; Unsap. 0.7%; M. Pt. 27 to 28°. Kernel oil: Sap. V. 202.9; Iod. No. 52; Acid V. 0.4; Unsap. 1.3%; M. Pt. 31–32°. The fats could be used for making soap or, after refining, for edible purposes.

These fats from Malayan fruits have been extensively investigated by T. P. Hilditch and J. G. Rigg [*J. Soc. Chem. Ind.,* **54,** 109T (1935)]. The mesocarp, or fruit oil, gave an iodine number of 47.8, a saponification equivalent of 281.6 and contained 0.8 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: myristic 1.8, palmitic 45.1, stearic 1.8, oleic 49.6, and linoleic acid 2.0.

The percentages of component glycerides of the original fat, after grouping the myristic acid with the palmitic acid, and similar small quantities of stearic and linoleic acids with the oleic acid, are as follows: tripalmitin 2.0, dipalmito-oleins 42, and palmito-dioleines 56.

The kernel oil gave an iodine number of 48.6, a saponification equivalent 284.0, and contained 1.7 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: myristic 1.4, palmitic 48.4, stearic 0.9, oleic 46.0, and linoleic acid 3.3. It was found that the fat did not contain over 2.5 per cent of fully saturated glycerides. There were 1.13 mols. of saturated acids per mol. of unsaturated acids in the fat. It is evident from this information that the fat conforms to the usual seed fat rule of the even distribution of the fatty acids throughout the glyceride molecules. Owing to the small quantity of fat available, further determination of its glycerides structure was not possible. The similarity of the fruit and kernel fats is noteworthy as well as unusual. Apparently, the only other known case is that of olive pulp and kernel oils.

Pongam (Hongay) Oil. This oil is obtained from the seeds of the tree *Pongamia glabra,* found in India, Malaya and elsewhere. The

oil is also known as Honge. The fruits or pods are about 3 inches long and enclose reddish beans which are about an inch long and weigh over a gram. They contain from 27 to about 39 per cent of oil, which at 15° C. has the consistency of soft butter. The oil has a bitter taste and an unpleasant odor. The characteristics are as follows: Sp. g. at 15° C. 0.937, at 40°/40° C. 0.924; $N_D^{40°}$ 1.4697 to 1.4723; Sap. V. 177 to 189; Iod. No. 83 to 94; Unsap. 2.4 to 9%; R.M.V. 1.04 to 1.10.

The composition has been investigated by R. D. Desai, J. J. Sudburrough and H. E. Watson [*J. Indian Inst. Sci.*, **6**, 93 (1923)], with the following results: myristic acid 0.23, palmitic 6.06, stearic 2.2, arachidic 0.3, lignoceric 3.22, oleic 61.3, linoleic 9.72, linolenic 0.46, and dihydroxy-stearic acid 4.4 per cent—as glycerides. The oil is used in India for the treatment of skin diseases and as an illuminant.

The seed oil of *Pongamia pinnato (Leguminosae)* growing in the Philippines has been investigated by F. A. Soliven [*Phil. Agric.*, **23**, 576 (1934) *Chem. Absts.*, **29**, 2766 (1935)]. The percentage of constituents in the kernels, which amount to 94 per cent of the seed, were as follows: moisture 12.41, oil 26.63, proteins 23.39, and carbohydrates 32.66. The ash (3.05%) was found to contain 42.11 per cent of ferric oxide. The oil gave a saponification value of 180, an iodine number of 91 to 96, and contained 2.6 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: saturated acids 23.04, oleic 11.30 and linoleic 65.65. It will be observed that these results are very different from those given above for the oil from *P. glabra.*

Rambutan Tallow. This fat is obtained from the seeds of the tree *Nephelium lappaceum,* belonging to the *Sapindaceae,* which is found in China, the Sunda Islands, Malaya, and elsewhere. The seeds weigh about 2 grams and contain from 34 to 40 per cent of fat. A sample of the fat was examined by C. D. V. Georgi [*Malay Agric. J.*, **10**, 222 (1922)] with the following results: Sp. g. 99°/15.5° C. 0.8629; $N_D^{40°}$ 1.4590; Sap. V. 193.0; Iod. No. (Wijs) 43.8; M. Pt. 40° to 42° C.; Acid V. 4.8; Titer 5.15°.

Baczenski [*J. Soc. Chem. Ind.*, **14**, 1049 (1895)] reported the following characteristics: Sap. V. 193.8; Iod. No. 39.4; M. Pt. 42° to 46° C.; Titer 57°. G. T. Morgan and E. Holmes [*J. Soc. Chem. Ind.*, **44**, 219T (1925)] state that this tallow contains *n*-eicosanic acid ($C_{20}H_{40}O_2$).

T. P. Hilditch and W. J. Stainsby [*J. Soc. Chem. Ind.*, **56**, 197T (1934)] examined the fat extracted from Malayan kernels with petroleum ether. It gave an iodine number of 42.3 and contained 0.5 per cent of unsaponifiable matter. The mixed fatty acids contained the following percentages of constituents: palmitic 2.0, stearic 13.8, arachidic 34.50, oleic 45.12 and eicosenoic (C_{20} monoethylenic)? 4.23. X-ray examination of the isolated arachidic acid showed that it was *n*-eicosanic acid, the identity of which had been similarly shown previously by Morgan and Holmes [*J. Soc. Chem. Ind.*, **44**, 219T (1925)]. Because of the absence of olein and of the fact that their permanganate oxidation

experiments indicated only the presence of 1.4 per cent of fully saturated glycerides, Hilditch and Stainsby estimated that the fat contained approximately 43 per cent of oleo-disaturated and 56 of dioleo-monosaturated glycerides. They concluded from their investigation that this product conformed closely to the general seed fat rule of "even distribution" of saturated and unsaturated acids among the glycerides composing the fat.

The rambutan fruit is much esteemed in Malaya. Propagation of the tree is discussed by J. Lambourne [*Malayan Agric. J.*, **25**, 11 (1937)].

Pulasan Fat. This fat is obtained from the seeds of the tree *Nephelium mutabile* of the *Sapindaceae*. The seeds, which weigh about 2 grams, contain about 60 per cent of a hard white fat resembling that of rambutan tallow. These fats can be used for edible purposes or the manufacture of candles and soap.

C. D. V. Georgi [*Malay Agric. J.*, **10**, 222 (1922)] reported the following characteristics: Sp. g. at 99°/15.5° C. 0.8597; $N_D^{40°}$ 1.4579; Sap. V. 199; Iod. No. (Wijs) 41.6; M. Pt. 40° to 42° C.; Acid V. 7; Titer 50.9°.

T. P. Hilditch and W. J. Stainsby [*J. Soc. Chem. Ind.*, **53**, 197T (1934)] examined the solvent-extracted fat with the following results: Iod. No. 36.6; Acid V. 1.5; Unsap. 0.5 per cent; Titer 52.8. The mixed fatty acids contained the following percentages of constituents: oleic 43.7, palmitic 3.0, stearic 31.0, and arachidic 22.3. It appears to contain a trace of a C_{20} monoethylenic acid.

As pointed out by the investigators, the fat is somewhat more saturated in character than the botanically related rambutan tallow. In the present case, the relative proportions of stearic and arachidic acid are reversed, the component acids of rambutan containing 13.8 per cent of stearic and 34.5 of arachidic acids. The derived probable proportions of glycerides in pulasan fat are as follows: mono-oleo-disaturated about 63, dioleo-mono-saturated about 36, and about 1.5 per cent of fully saturated glycerides.

Sawarri or Suari Fat. This product is obtained from the seeds of various species of *Caryocar* of the *Caryocaraceae*, both native to Brazil, Peru and probably some other South American countries. The more important species are *C. amygdaliferum, C. brasiliense, C. butyrospermum,* and *C. tomentosum,* all of which yield closely similar hard white fats. The seeds weigh about 20 grams. The kernels, which amount to about 25 per cent of the seed, contain from 60 to 70 per cent of fat. The kernels are considered excellent for eating.

The fat was examined by Lewkowitsch [*J. Soc. Chem. Ind.*, **9**, 844 (1890)] and by Bolton and Hewer [*Analyst*, **42**, 44 (1917)].

Characteristics: Sp. g. at 40°/15° C. 0.8981; $N_D^{40°}$ 1.4567; Sap. V. 19.7 to 199.5; Iod. No. 41 to 50; R.M.V. 0.65; M. Pt. 30° to 37° C.; Titer 46° to 47°.

The fat has a very pleasant flavor and is an excellent edible fat, but

its hardness makes it necessary, for some purposes, to mix or blend it with more or less oil.

Sequa Oil. This oil is found in the seeds from the fruit of the *Fevillea cordifolia,* belonging to the family of *Cucurbitaceae,* native to South America and the West Indies. The kernels contain from 57 to 62 per cent of oil, which at ordinary temperatures is a pale, cream-colored solid. It has a bitter taste and a disagreeable odor. The oil is poisonous, but might be employed for making soap. The following characteristics are given by Bolton; $N_D^{40°}$ 1.4751; Sap. V. 192.2; Iod. No. 52.1; Unsap. 0.7%; M. Pt. 34° C.; Acid V. 2.

Siene (Rattle box) Bean Oil. This oil is found in the seeds of the *Danbentonio longifolia (Leguminosae)* which grows wild on the Gulf coast of Florida and Texas. T. S. Perrin [*J. Amer. Chem. Soc.,* **59,** 1401 (1937)] found that a sample of the seeds contained the following percentages of constituents: moisture 11.7, proteins 21.2, oil 3.8, starch 27.9, fiber 17.7, nitrogen-free extract 15.2, and ash 2.8.

The ether-extracted oil characteristics were as follows: $N_D^{25°}$ 1.4730; Sap. V. 177.5; Iod. No. 97.3; Acid V. 4.5; Unsap. 3.0%; Sat. acids 13.8; Unsat. acids 78.4.

Soap Tree Oil. This oil is found in the seeds from the fruit of the tree *Sapindus trifoliatus,* belonging to the *Sapindaceae.* The oil is not produced commercially, but in Bengal the fruit is cultivated and used for detergent purposes.

The seeds contain about 34 per cent of oil (kernels 45) which was examined by D. R. Paranjpe and P. R. Aggar [*J. Indian Inst. Sci.,* **12A,** 179 (1929); *J. Soc. Chem. Ind.,* **48,** B487 (1928)] with the following results: Sp. g. at 100° C. 0.8540; $N_D^{25°}$ 1.4764; Sap. V. 194; Iod. No. 58.3; R.M.V. 1.5; Unsap. 1.2%; Sat. acids 38.5%; Unsat. acids 61.5%.

Percentages of fatty acids as glycerides: oleic 61.5, palmitic 5.6, stearic 8.5, *n*-eicosanic 21.9, and lignoceric acid 2.5.

This oil is of interest on account of the large quantity of eicosanic acid present (the identity of which appears to be established).

Sterculia (Kaloempang or Calumpang) Oils. These oils are found in the fruit of the tree *Sterculia foetida* of the *Sterculiacae,* which is widely distributed in Borneo, Java, Sumatra, Indo-China and Malaya. The fruits, which are known as "Java olives," "Beligno seeds," and "Kaloempang beans," are enclosed in long, narrow pods. The fruits consist of the following parts: Epicarp, the thin violet-covered outer skin, 2.5 to 4%; mesocarp, the soft reddish brown pulp, 16 to 19%; endocarp, the dark-colored shell enclosing the kernel, 27 to 33%, and endosperm or kernel, 48.5 to 50%. The whole fruit contains about 30 to 33 per cent of oil, the pulp usually 9 to 11, and the kernels 47 to 53 per cent of oil. The pulp oil is a soft fat which melts at about 30° C. to a clear oil; that from the kernel is a yellow liquid. The oil expressed from the whole fruit is usually liquid.

Wedemeyer [*Analyst,* **31,** 361 (1906)] examined the oil from the whole fruits with the following results: Sp. g. at 15° C. 0.926; $N_D^{40°}$ 1.4154; Sap. V. 188; Iod. No. 76.6; R.M.V. 0.8.

Bontonx and others examined the pulp and kernel oils: *Pulp oil:* Sap. V. 192.8 to 194; Iod. No. 56 to 59; Titer 43° C. *Kernel oil:* Sp. g. at 15.5° C. 0.919 to 0.926; $N_D^{40°}$ 1.4620 to 1.4645; Sap. V. 187 to 199; Iod. No. 75 to 83; Acetyl V. 18.8.

C. D. V. Georgi (*Brit. Chem. Absts.*-B, **1929,** 154) has examined the oil from fruits grown in Malaya.

A. Steger and J. van Loon [*Rec. trav. chim.,* **60,** 87 (1941)] examined the pulp oil with the following results: Iod. No. (Wijs) 76.2; SCN V. 49.1; Sap. V. 201; Sat. acids (Bertram) 40.4%.

The seeds of the tree *Sterculia appendiculata,* which is found in East Africa, contain about 55 per cent of kernels, having an oil content of about 29 per cent. C. Grimme [*Chem. Rev. Fett Harz Ind.,* **17,** 180 (1910)] examined the oil with the following results: $N_D^{20°}$ 1.4729; Sap. V. 185; Iod. No. 82; Unsap. 6.4%; Sol. Pt. −2° C.

L. Adriaens [*Mat. grasses,* **24,** 9386, 9417, 9442 (1932)] examined the oil of the seed coats and kernels of the seed of the *Sterculia bequaerti* (or *tragacantha*). The seed coats contained 44.4 per cent of oil. It gave the following characteristics: Sap. V. 207.3; Iod. No. 80.6; Unsap. 0.21 per cent; Titer 37.8°; Sat. acids (uncorr.) 37.0 per cent. The kernels contained 38.2 per cent of oil. It gave the following characteristics: Sap. V. 190.3; Iod. No. 81; Unsap. 0.43 per cent; Titer 24.6°; Sat. acids, about 10 per cent.

Sugar Apple Seed Oil. This oil is in the seed of the tree *Anona squamosa* belonging to the *Anonaceae.* The tree, which is known also as the Bottle Tree, and by other names, is indigenous to the West Indies, and is cultivated there and in many other tropical regions for its fruit. The seeds contain from 14 to 21 per cent of oil. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.9216; $N_D^{60°}$ 1.4558; Sap. V. 181 to 188.3; Iod. No. 85.6 to 88.2; R.M.V. 0.6; Pol. No. 0.2; Unsap. 0.2 per cent.

R. V. Ghaneker and P. R. Ayyer [*J. Indian Inst. Sci.,* **10A,** 28 (1927)] found that the oil from the seed of fruit grown in India contained the following percentages of acids: oleic 18.1; linoleic 55.1, palmitic 14.7, stearic 10.7 and cerotic ? 0.9.

Tangallak (Habai) Butter. This fat is obtained from the seeds of the tree *Litsea sebifera* of the *Lauraceae,* found in Annam, Indo-China, Western Java and elsewhere. The seeds, which are the size of small peas, contain about 80 per cent of kernels, having about 60 per cent of fat. The extracted fat is usually brown and has a strong aromatic odor and a disagreeable taste.

The characteristics are as follows: $N_D^{40°}$ 1.4498; Sap. V. 257.0; Iod. No. 8.5; R.M.V. 2.7; Pol. No. 10.5; Unsap. 1.5%; M. Pt. above 40° C. The fat is said to be difficult to refine, but would serve for the local manufacture of candles

Sumach Seed Oil. This oil is from the seeds of the *Rhus coriaria* of Sicily which belongs to the *Anacardiaceae.* G. A. Bravo [*Ann. chim. applicata,* **24,** 427 (1934)] examined the seeds and oil. The seeds con-

tained about 14 per cent of oil. The characteristics of the oil were as follows: Sap. V. 191.9; Iod. No. (Hübl) 97.5; Unsap. 1.63 per cent. The oil contained the following percentages of acids in terms of triglycerides: oleic 55.7, linoleic 23.5, palmitic 14.60, and stearic 2.6.

Talisay (Tropical or Indian Almond) Oil. This oil is obtained from the edible seed or kernel of the nut-like fruit of the tropical tree, *Terminalia catappa,* of the *Combretaceae.* It is a large, handsome tree which reaches a height of about 75 feet. In some of the West Indies and in South America this Asiatic introduction is planted as a shade and ornamental tree.

The oil content of the kernels varies from about 50 to about 64 per cent. C. Grimme [*Chem. Rev.,* **17,** 181 (1910)] examined kernels which contained 63.4 per cent of oil. He reported the following characteristics: $N_D^{20°}$ 1.4682; Sap. V. 185.7; Iod. No. 77; Unsap. 1.87 per cent.

A. O. Cruz and A. P. West [*Phil. J. Sci.,* **48,** 5 (1932)] found that the kernels of a sample of Philippine seeds contained 52 per cent of oil which gave an iodine number (Hanus) of 75.4, a saponification value of 193.2, an acid value of 2.3, and contained 0.54 per cent of unsaponifiable matter. The oil contained the following percentages of acids: oleic 39.09, linoleic 21.92, myristic 0.94; palmitic 27.14, stearic 3.82, and arachidic 0.72.

The oil can be used for edible purposes and for making soap.

Yellow Oleander (Tiger Apple) Seed Oil. This oil is in the kernel from the fruit (a drupe) of the tree *Thevetia nerufolia* of the *Apocynaceae.* The tree, which reaches a height of 20 feet, is a native of the American tropics, is cultivated in India, the East and West Indies. The "nuts" contain from 16 to 30% of kernel. The poisonous kernels contain usually from about 60 to 64% of oil. R. Bhattacharya and P. R. Ayyar [*J. Indian Inst. Sci.,* **10A,** 15 (1927)] reported the following characteristics: Sap. V. 194.1; Iod. No. 68 to 76; R.M.V. 0.4; Pol. No. 1.5; Unsap. 1.4%. The oil contained the following percentages of fatty acids calculated as glycerides: oleic 64.3, linoleic 6.3, palmitic 17.1, stearic 11.8 and arachidic 0.4. It is stated that the oil is not poisonous. Constituents other than the oil of the kernels have been investigated by K. I. and A. L. Chen [*J. Biol. Chem.,* **105,** 231 (1934)].

Teaseed Oil. This oil is obtained from several species of tea plants. The commercial oil is chiefly from the seed of *Thea sasangua,* which is cultivated in Assam, China, Japan and elsewhere for the production of oil. The kernels, which amount to about 70 per cent of the seed, contain up to 60 per cent of oil. The oil is used as a lubricant, as a textile oil by the silk industry, for making soap, and, after refining, for edible purposes.

The characteristics are as follows: Sp. g. at 15° C. 0.915 to 0.919; $N_D^{20°}$ 1.4691, at 40° C. 1.4619; Sap. V. 190 to 195; Iod. No. 80 to 87; R.M.V. 0.3 to 1.1; Titer 13° to 14.5° C.; Sol. Pt. −5° to −10° C.

H. N. Griffiths, T. P. Hilditch, and E. C. Jones, [*J. Soc. Chem. Ind.,* **53,** 13T (1934)] found that the mixed fatty acids from a sample of tea-

seed oil which gave an iodine number of 86.3, contained the following percentages of constituents: oleic 83.3, linoleic 7.4, myristic 0.3, palmitic 7.6, stearic 0.8, and arachidic acid 0.6 T. P. Hilditch and H. M. Thompson [*ibid.*, **56**, 43, 434T (1937)] found that the mixed fatty acid also contained 0.8 per cent of hexadecenoic acid. For information on the glyceride structure of the oil, both the original articles should be consulted.

The decorticated seed from *Thea sinensis,* which is cultivated for its leaves, depending upon its source, contains from 16 to 26 per cent of oil. Tsujimoto [*Analyst,* **33**, 424 (1908)] and Menon [*J. Soc. Chem. Ind.,* **32**, 201 (1913)] examined samples of the oil from widely different sources, but the oils were quite similar. The range of the characteristics for these oils is as follows: Sp. g. at 15° C. 0.9028 to 0.9178; $N_D^{20°}$ 1.4707; Sap. V. 190 to 192; Iod. No. 90.4 to 93; R.M.V. 0.6 to 0.7.

It will be observed that the iodine number is distinctly higher than that given by the oil from the seed of *T. sasanqua.*

The small tree *Thea japonica,* native to Japan, which is particularly abundant in the island of Idzu, produces seeds which are used locally for the production of oil; the better grades of this are used as a hair oil and for the lubrication of watches, etc. Tsujimoto (*J. Soc. Chem. Ind.*, **1908**, 27, 545) examined 12 samples with the following results: Sp. g. at 15.5° 0.9159 to 0.9166; $N_D^{20°}$ 1.4679 to 1.4691; Sap. V. 189.9 to 192.6; Iod. No. (Wijs) 80 to 81.3; R.M.V. 0.48 to 0.53; Acid V. 1.6 to 8.8.

Tests. For the detection of the teaseed oil, see the method given under olive oil. Methods previously suggested for this purpose have not been found useful.

Tsubaki Oil. This oil is found in the seeds from the tree *Camellia japonica* of the *Theaceae.* H. P. Kaufman and J. Boltes [*Fette u. Seifen,* **45**, 152 (1938)] examined the seed and the extracted oil. The kernels contained about 66.7 per cent of oil, which after extraction had the following characteristics: Sap. V. 187.2; Iod. No. 78.0; SCN V. 76.1; Acid V. 1.05; Unsap. 0.2 per cent. The oil contained the following percentages of acids: oleic 82.6, linoleic 2.1, and saturated acids 10. In Japan, it is used as a hair oil.

Ungnadia (Mexican buckeye). This oil is found in the seeds of the small tree *Ungnadia speciosa,* which grows on the mountains between western Texas and New Mexico. The seeds usually contain about 50 per cent of oil. The seeds also contain a cyanogenetic glucoside and are poisonous.

Cheel and Penfold [*J. Soc. Chem. Ind.*, **38**, 74T (1919)] obtained the following characteristics: Sp. g. at 15° C. 0.9117; Sap. V. 203; Iod. No. (Wijs) 84; Unsap. 0.6%.

Schaedler, *Pharm. Zeit.*, **34**, 340 (1889): Sp. g. at 15° C. 0.912; $N_D^{20°}$ 1.4666; Sap. V. 192; Iod. No. 82.

The oil was found to keep well.

Wrightia annamensis Seed Oil. The tree *Wrightia annamensis*

of the *Apocynaceae,* which is found in Annam, bears slender pods about 6 inches long in which are seeds about the size of oats. M. L. Margaillon [*Compt. rend.,* **192,** 373 (1931)] examined the seeds and oil. The seeds contained the following percentages of constituents: moisture 5.8, fat 36.1, protein 29.1, fiber 5.1, carbohydrate 19.6, and ash 4.3. The characteristics of the oil were as follows: Sp. g. at 25° C. 0.966; $N^{20°}$ 1.480; Sap. V. 184; Iod. No. 85; Acid V. 5.4; acetyl V. 127; unsap. 1.0 per cent. The dark red oil was soluble in alcohol. It was stated that the chief acid in the oil was probably similar to the ricinoleic acid found in castor oil.

Ximenia (Wild Olive) Seed Oil. This oil is found in the seed of the fruit from the shrub *Ximenia americana,* a member of the *Olacaceae,* found in India, South Africa, and South America. It is a prolific fruit producer even on very poor dry land. The fruits, each of which weighs about 2 grams, are drupes and in Africa they are known as lumeque nuts. The pulp and seed shells amount to from 41 to 50 per cent and the kernels from 59 to 45 of the orange red fruit. The kernels which have been examined contained from 49 to 60.6 per cent of oil and from 3.6 to 5.1 of moisture.

The kernel oil from South African fruits gave the following characteristic: Sap. V. 173.4; Iod. No. 94.9; Unsap. 0.6 per cent. For other information, see *Bull. Imp. Inst.,* **33,** 277 (1935). The range of characteristics obtained by various observers for oil from Africa and South America is as follows: Iod. No. 80.9 to 94.5; Sap. V. 155.3 to 183.1; Unsap. 0.5 to 2.9 per cent.

S. V. Puntambekar and S. Krishna [*J. Indian Chem. Soc.,* **14,** 268 (1937)] examined the oil from kernels of fruit produced in India with the following results: Sp. g. at 20° C. 0.9262; $N_D^{20°}$ 1.4710; Iod. No. (Hanus) 82.5; Sap. V. 169.2; Acid V. 2.3; Unsap. 1.7 per cent. The mixed fatty acids contained the following percentages of constituents: oleic 60.8, linoleic 6.7, ximenic (hexacosenic) 14.6, stearic 1.2, cerotic 15.2, and resin acids 1.5.

The investigators were unable to isolate the ximenic acid ($C_{26}H_{50}O_2$) in a pure condition, but found that by hydrogenation it was changed to cerotic acid. The occurrence of ximenic and cerotic acid in quantity in a fatty oil had not been previously found.

H. A. Bockenoogen [*Fette u. Seifen,* **46,** 717 (1939), *Chem. Absts.,* **34,** 3521 (1940)] reported the following characteristics: Expressed oil: Sap. V. 166.8; Iod. No. 89.8; SCN V. 67.0; Acid V. 6.5. Extracted oil: Sap. V. 167.3; Iod. No. 84.2; SCN V. 76.0; Acid V. 10.0. The extracted oil was obtained from the press cake. The mixed fatty acids from the expressed oil were reported to contain the following percentages of constituents: stearic 4, cerotic 2, oleic 54, linoleic 10, ximenic 25, and lumequeic acid 5.

Ximenic acid ($C_{26}H_{50}O_2$) has the structure: $CH_3-(CH_2)_7-CH=CH-(CH_2)_{15}COOH$ and that of lumequeic acid ($C_{30}H_{58}O_2$) is: $CH_3-(CH_2)_7-CH=CH-(CH_2)_{19}COOH$.

The oil which is expressed in southern India is used as a substitute

for ghee. There, also, the fruits, which have a pleasant taste, are used for making jam.

Zachun (Hegli) Seed Oil. This oil is found in the seeds from the fruits of trees belonging to the *Zygophyllaceae* family. The trees are native to tropical Africa. The fruits, which resemble dates and weigh 7 to 8 grams, consist of a sticky pulp and a hard, woody nut which encloses the kernel.

The *balanites aegyptiaca* is chiefly found in northern Nigeria, Uganda and the Sudan. The kernels, which amount to 9 to 10 per cent of the nuts, contain from 41 to 58 per cent of oil.

The oils examined by the Imperial Institute [*Bull. Imp. Inst.*, **6**, 365 (1908)] gave the following results: Sp. g. at 15° C. 0.919; Sap. V. 194 to 197; Iod. No. 92.5 to 98.2; Unsap. 0.6%; Acid V. 1.4 to 5; Titer 34° to 34.6°. (cf. *Bull. Imp. Inst.*, **1935**, 271).

The kernels from the fruits of *B. maughamii*, found in Portuguese East Africa, contain from 45 to 55 per cent of oil with the following characteristics: $N_D^{40°}$ 1.4640; Sap. V. 191.5; Iod. No. 100.6; Unsap. 88%; Acid V. 2.4; Sol. Pt. −1° C.

Although it is difficult to remove the sticky pulp from the nut, and also difficult to remove the kernels, the natives prepare the oil for their own use.

Another species is the *Balanites orbicularis*, which yields the so-called Kullan nuts of British Somaliland. These "nuts" weigh about 2.1 grams and contain about 64 per cent of kernel. They generally contain but one kernel. The kernels have about 37 per cent of a limpid, yellow oil, for which the following characteristics have been reported: Sp. g. at 15° C. 0.9184; $N_D^{40°}$ 1.4623; Sap. V. 192.7; Iod. No. 75.9; Unsap. 0.5%; Acid V. 0.3; Titer 38.6° [*Bull. Imp. Inst.*, **27**, 289 (1929)].

The extracted meal contained the following percentages of constituents: moisture 9.6, oil 1.4, crude protein 30.5, crude fiber 3.7, carbohydrate 50.4, and ash 4.4. It had a bitter taste and probably contains more or less saponins.

Chapter III

Semi-drying Oils

Apple Seed Oil. This oil is found in the seed of *Pyrus malus* of the *Rosaceae*. J. Pritzker and R. Jungkunz [*Z. Unters Lebensm.*, **70**, 255 (1935)] examined the oil obtained from apple seeds with the following results: $N_D^{40°}$ 1.4678; Sap. V. 187.7, Iod. No. 122.4; R.M.V. 0.2; Pol. No. 0.4; Unsap. 1.1%; Sat. acids 7.2%. The seeds contained about 18 per cent of oil.

Pear Seed Oil. The seeds of the *Pyrus communis* of the *Rosaceae* contain about 22 per cent of oil. The sample of extracted oil which was examined by J. Pritzker and R. Jungkunz [*Z. Unters Lebensm.*, **70**, 255 (1935)] had the following characteristics: $N_D^{40°}$ 1.4672; Sap. V. 189.5; Iod. No. 124.1; R.M.V. 0.3; Pol. No. 0.3; Unsap. 1.0%; Sat. acids 10.3 per cent.

This oil and that from apple seeds give the Bellier-Kreis color test [*Chem. Ztg.*, **26**, 897 (1902)] as does apricot kernel oil.

Apricot Kernel Oil. This oil is obtained by pressing the kernels from the pits, which are separated from the fruit of *Prunus armeniaca* in large quantities in the manufacture of dried apricots. The kernels constitute about 20 per cent of the pits and contain from 40 to 45 per cent of oil. When first expressed, the oil is nearly colorless, but on standing it gradually becomes yellow. All the color, however, can readily be removed by bleaching with fuller's earth on activated carbons. The oil is used for edible purposes, in toilet creams, and certain pharmaceutical preparations.

The shells, which are separated in some plants from the kernels by means of a brine solution, can be used as fuel or they may be converted into carbon in retorts and the gas used to generate steam [A. W. Allen, *Chem. Met. Eng.*, **32**, 435 (1925)].

The usual range of the characteristics is as follows: Sp. g. at 15° C. 0.915 to 0.920; $N_D^{15°}$ 1.4629 to 1.4640; Sap. V. 188 to 193; Iod. No. 100 to 108.

Jamieson and McKinney [*Oil and Soap*, **10**, 147 (1933)] examined a sample of expressed refined oil supplied by Sewall S. Brown and Company for investigation. The characteristics of the oil were as follows: Sp. g. 25/25° 0.9158; $N_D^{25°}$ 1.4700; Sap. V. 190.2; Iod. No. (Hanus) 108.7; R.M.V. 0.2; Pol. No. 0.1; Acetyl V. (Andre-Cook) 4.2; Unsap. 0.7 per cent; Sat. acids 3.57 per cent; Unsat. acids 90.56 per cent.

The oil contained the following percentages of acids: oleic 60.61, linoleic 29.95, palmitic 2.43, stearic 1.09, and lignoceric 0.05.

The press cake remaining after the expression of the oil can be ground to a meal and sold as a fertilizer which has been found well adapted for use as a lawn dressing; or the meal can be moistened with water and, after standing a few hours, distilled with steam to recover the volatile oil, which amounts to about 1.5 per cent of the meal. After distillation the residual meal is dried and sold as a fertilizer; or after determining it to be free from hydrocyanic acid formed by the hydrolysis of the amygdalin glucoside, it can be used as a livestock feed. An analysis of untreated press cake showed that it contained 6.64 per cent of nitrogen (41.5 of proteins), 2.2 per cent of phosphoric acid, and 1.14 per cent of potassium oxide.

At times, various vegetable oils are used to adulterate apricot kernel oil, but more often it is used as an adulterant of almond oil.

Examination. Determine the characteristics and compare the results with those given. If the iodine number is low, make the modified Renard test for peanut oil. In the case of an abnormally low saponification value, make the test for rape oil as described under olive oil. When the samples of oil are more or less yellow, make tests for cottonseed and sesame oil.

A modification of the well known Bieber color test for this oil has been devised by H. Mohler and H. Benz [*Z. anal. Chem.*, **94**, 184 (1933); *Analyst*, **58**, 764 (1933)] is made as follows: In a test tube mix 4 drops of the oil to be tested with 4 drops of chloroform. Add down the side of the test tube one drop of fuming nitric acid (shake), and 10 seconds later add a second drop, as before. Apricot kernel oil gives at once a blood-red color which gradually changes to a brownish red. Peach kernel oil alone gives a red color in one minute, and almond oil gives a light brown in about two minutes. A freshly made mixture of 5 per cent of apricot kernel oil and 95 per cent of almond oil gives a brilliant red color in about 5 minutes after the addition of nitric acid. After the mixture of oils has stood several weeks, it requires 15 minutes for the color to develop. When applying this test, it is important to follow carefully the directions as given in every particular. With the older Bieber procedure, not less than 20 per cent of apricot kernel oil in almond oil could be detected.

Cherry Kernel Oil. The kernels from the pits or stones from the fruit of the cherry, *Prunus cerasus,* contain from 30 to about 38 per cent of oil. The pits, which are separated in quantity at the canneries and "liqueur" factories, are cracked and the kernels are separated by means of a brine calcium or magnesium chloride solution having a density of about 1.15. The kernels, which float, are removed, washed, dried and then they are crushed and pressed cold. This is followed by a second hot pressing. The cold-pressed oil is yellow and has a mild, pleasant flavor. It is used in southern Germany and elsewhere for edible purposes. The hot-pressed oil is used chiefly in making soap.

In the United States, large quantities of the pits collect at the sour

cherry canning plants. The pits amount to 12 to 15 per cent of the fruit and consist of 28 per cent kernel and 72 per cent shell. The kernels contain from about 32 to 40 per cent of oil. The states of Wisconsin, Michigan, and New York are at present the largest producers of sour cherries. The oil is expressed and refined at Sturgeon Bay, Wisconsin. The kernels are separated from the shells by mechanical means and pressed in expellers. The oil, after refining, is used in the manufacture of certain cosmetics and as a salad oil. The press cake is used as a fertilizer.

The following characteristics are given for the European oil: Sp. g. at 15° C. 0.922 to 0.929; Sap. V. 192 to 198; Iod. No. 111 to 122; $N_D^{40°}$ 1.4697 to 1.4713; Titer 13° to 15° C.; Sol. Pt. −16° to −20°. F. Rabak [*U. S. Dept. Agric. Bull.*, **350** (1916)] examined the oil from cherry kernels grown in the United States as follows: Sp. g. at 25° C. 0.909; $N_D^{25°}$ 1.4635; Sap. V. 181; Iod. No. 92.8; R.M.V. 4.7; Acetyl V. 12.6; Unsap. 0.44%; Sol. Pt. 13° C. He found that the shells of the pits contained 8.3 per cent of oil, which gave characteristics very close to those of the kernel oil.

Jamieson and Gertler [*Oil Fat Ind.*, **7**, 371 (1930)] investigated both the crude and refined oil from the Sturgeon Bay Plant, known as the Cherry Oil Company. The characteristics were as follows: *Crude oil:* Sp. g. at 25°/25° C. 0.9176; $N_D^{25°}$ 1.4742; Iod. No. (Hanus) 118.7; Acid V. 4.39; Unsap. 0.66%. *Refined oil:* Sp. g. at 25°/25° C. 0.7183; $N_D^{25°}$ 1.4740; Iod. No. 115.3; Sap. V. 190.7; Acid V. 0.09; R.M.V. 0.3; Pol. No. 0.2; Unsap. 0.3%; Sat. Acids 7.7%; Unsat. Acids 87%.

The oil contained the following percentages of acids: oleic 46.85, linoleic 40.11, myristic 0.19, palmitic 4.04, stearic 2.79, and arachidic 0.72.

Peach Kernel Oil. This oil is obtained from the kernels of the pits or "stones" from the fruit of *Prunus persica*. The kernels contain from 32 to 35 per cent of oil. Because of the difficulty in cracking the thick, hard shells as compared with cracking the much thinner apricot pits, comparatively little peach kernel oil is now prepared. The oil has been used for the same purposes as apricot kernel oil. Much of the so-called peach kernel oil on the European market is in reality apricot kernel oil. Comparatively little study has been made of the oil and the available data are meager. The range of the characteristics which have been reported is as follows: Sp. g. at 15° C. 0.918 to 0.925; $N_D^{25°}$ C. 1.4682 to 1.4701; Sap. V. 189 to 192; Iod. No. 96 to 110; Titer 13° to 13.5°.

Plum Kernel Oil. The kernels from the pits or stones of the common plum, *Prunus domestica*, contain from about 30 to over 40 per cent of oil. Prune kernels frequently contain 40 to 42 per cent of oil. In Europe prune kernels are separated and pressed in a manner similar to that used for cherry kernels. The oil is used for edible and technical purposes, depending upon the quality. The oil has been ex-

amined by Kassner and Eckelmann [*J. Soc. Chem. Ind.*, **34**, 668 (1915)]; Utz [*ibid.*, **38**, 505A (1919)]; Alpers [*ibid.*, **38**, 729A (1919)]; Fordyce and Torrance [*Analyst*, **44**, 238 (1919)], as well as by others.

The characteristics are as follows: Sp. g. at 15° C. 0.916 to 0.921; $N_D^{40°}$ 1.4624 to 1.4647, at 25° C. 1.4640 to 1.4700; Sap. V. 188 to 196; Iod. No. 100 to 105; Titer 12° to 15° C.; Sol. Pt. −5° to −8° C.

E. Delvaux [*Fette u. Seifen*, **43**, 183 (1936); *Chem. Absts.*, **31**, (3720)] reported the characteristics of the oil examined by him as follows: Iod. No. (Kaufmann) 100.3, SCN V. 81.2; Unsap. 0.40 per cent. It contained the following percentages of acids: oleic 68.9, linoleic 21.0, and 5.9 of saturated acids.

There is no characteristic test for this oil. It will be observed that the iodine number is notably less than that usually found for European cherry kernel oil.

Brazil Nut Oil. This oil is obtained from the nuts of the tree *Bertholletia excelsa (Lecythidaceae)*, native to Brazil. It has been introduced into other tropical countries. The nuts contain about 51 per cent of shell and about 49 of kernel. The kernels contain from 65 to 70 per cent of oil. The oil, which is expressed in Brazil, depending upon its quality, is used for edible purposes or making soap. It is usually pale yellow and has a flavor like the nuts. Characteristics: Sp. g. at 15° C. 0.9170 to 0.9180; $N_D^{25°}$ 1.4643; Sap. V. 192 to 200; Iod. No. 98 to 106; Titer 29° to 32° C.; Unsap. 0.5%. C. D. V. Georgi [*Malayan Agric. J.*, **10**, 222 (1922)] examined the oil from nuts grown in Malaya with the following results: Sp. g. at 15.5° C. 0.9166; $N_D^{20°}$ 1.4711; Sap. V. 192, Iod. No. (Wijs) 101.7; Acid V. 1.2; Titer 31.4° C.; Unsap. 0.5%.

Schuette, Thomas, and Duthey [*J. Am. Chem. Soc.*, **52**, 4114 (1930)] made an extensive examination of the oil which they expressed and the residual oil solvent extracted from the press cake. The characteristics of the expressed oil were as follows: Sp. g. 25° C. 0.9150; $N_D^{20°}$ 1.4678; Iod. No. (Wijs) 99.9; Sap. V. 194; Unsap. 0.64%; R.M.V. 0; Pol. No. 0; Acetyl V. 12.3; Sat. Acids 20.29%; Unsat. Acids 73%. The oil contained the following percentages of fatty acids: oleic 51.26, linoleic 18.84, myristic 1.70, palmitic 12.92, and stearic 2.47. It will be noted that only 17.09 per cent of the 20.29 per cent of saturated acids is accounted for. For other details, the original should be consulted.

Beechnut Oil. This oil is obtained from the nuts of the European red beech tree, *Fagus sylvatica*. The nuts consist of 33 per cent of husks and 67 of kernels. The nuts contain from 15 to 20 per cent of oil and the kernels over 40 per cent. The cold-pressed oil is clear, yellow, and viscous, and has a sweet taste. The hot-pressed oil has a slightly bitter taste, which can be removed by boiling in water. The oil, which is expressed in small quantities in Europe, is used for edible purposes, soap making, and as an illuminant [*Bull. Imp. Inst.*, **19**, 519

(1921)]. Beech trees are very erratic in bearing nuts, large crops being obtained usually only at intervals of several years. At times, large quantities of oil are expressed in the Soviet Republic. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.9205 to 0.9225; $N_D^{15°}$ 1.470 to 1.4732; Sap. V. 191 to 196; Iod. No. 111 to 120; Titer 17°.

E. Delvaux [*Fette u. Seifen,* **43,** 183 (1936); *Chem. Absts.,* **31,** 3720 (1937)] stated that dried beechnuts contained 42.2 per cent of oil. The characteristics were as follows: Iod. No. (Kaufmann) 111.9; SCN V. 79.2; Hexabromides 3.37 per cent; Unsap. 0.27 per cent. The oil contained the following percentages of fatty acids: oleic 48.4, linoleic 33.2, linolenic 2.8, and saturated acids 11.5.

Cantaloupe Seed Oil. Seed from cantaloupes *(Cucumis melo L.)* grown in the Imperial Valley, California, contain about 30 per cent of oil. Baughman, Brauns, and Jamieson [*J. Am. Chem. Soc.,* **42,** 2398 (1920)] examined the oil expressed by an expeller. The cold-pressed oil has a pale yellow color and a pleasant fruity taste. The characteristics of the oil are as follows: Sp. g. 25°/25° C. 0.9210; $N_D^{20°}$ 1.4725; Iod. No. (Hanus) 125.9; Sap. V. 192.3; Acid V. 0.43; Acetyl V. 15.8; Sat. Acids 14.3%; Unsat. Acids 80.2%; and Unsap. 1.1%. The composition of this oil was determined with the following results: Glycerides of oleic acid 27.2, linoleic acid 56.6, stearic acid 4.5, palmitic acid 10.2, and myristic acid 0.3 per cent.

Cape Chestnut Seed Oil. This oil is obtained from the seed of the tree *Calodendrum capense,* a large tree growing in South Africa. The black, angular seeds, which weigh about a gram, consist of about 43 per cent of kernel and about 57 of shell. The kernels contain about 59 per cent of oil, which has a slightly bitter taste. Also, the press cake has a bitter taste.

According to the report in the *Bull. Imp. Inst.,* **20,** 6 (1922), the oil has the following characteristics: Sp. g. at 15°/15° C. 0.9219; $N_D^{40°}$ 1.4150; Iod. No. 108.7; Sap. V. 192.6; Unsap. 0.5%; R.M.V. 0.5; Pol. No. 0.2; Titer 26.8° C., Acid V. 0.4.

The meal contains the following constituents: moisture 7.3, crude protein 40, fat 7.0, crude fiber 3.9, carbohydrates 37, and ash 4.6 per cent. On account of the bitter taste and the presence of an alkaloidal substance, its use for feeding is not recommended, but it could be used for fertilizer. The oil could be used for making soap.

Cayeté Oil. This oil is obtained from the seeds of the plant *Omphalea megacarpa,* which is found in South America and Trinidad. The seed consists of an inner, yellow, oily kernel, which is covered with a white pith-like skin, this being loosely enclosed in a thin, grayish-brown, friable shell. The kernels, which amount to about 75 per cent of the seed, contain from about 52 to 67 per cent of oil. The oil is without any very pronounced taste and has a slight but not unpleasant odor and is regarded as a valuable non-irritant cathartic (Prof. Cash, *Imp. Inst. Col. Rpt.,* **88,** 473), the dose being about 4 grams.

Bolton and Hewer [*Analyst,* **42,** 35 (1917)], who examined this oil, stated that it is less viscous than castor oil, optically inactive, and only slightly soluble in alcohol. They reported the characteristics as follows: Sp. g. at 15.5° C. 0.922; $N_D^{40°}$ 1.4648; Sap. V. 192.2; Iod. No. 115.8; Unsap. 0.49%; Acid V. 0.2.

Corn Oil. Corn oil is obtained from the germ of the Indian corn or maize, the seed of the plant *Zea mays.* Some corn oil is produced in South Africa, Argentina, and Canada, but the United States has now an annual production of about 200 million pounds.

The germ is about half oil, but on the basis of the whole kernel, the oil content is from 3 to 6.5 per cent. Were it not for the fact that in the preparation of hominy, starch, glucose, and other corn products, the germ is almost completely separated from the rest of the kernel, corn oil would not have become an important commercial product.

Formerly, some corn oil of very poor quality was obtained as a by-product of the alcohol industry. During the fermentation of the corn mash, the oil rose to the surface of the solution and was removed by skimming. When the degermination of corn became general about 40 years ago, the separated germ material was at first added to stock feeds, but as the demand for vegetable oils increased, the germs began to be pressed for oil. Formerly, hydraulic presses were used, but for many years the oil has been expressed by Anderson oil expellers.

Degermination. The methods of manufacturing corn products fall into two classes. The "dry process" is used for making meal, flour, hominy, etc., while the "wet process" is employed for starch and glucose.

Dry Process. The cleaned corn, while being agitated in a suitable container, is sprayed with water or treated with steam until it has a moisture content of about 20 per cent, after which it is passed through the degerminating machine. This machine consists of a horizontal, tapering drum which revolves on a central shaft within a casing of the same shape. The surface of the drum and the inner surface of the case are covered with cone-shaped protuberances about three-fourths of an inch long. The drum is operated at about 700 rpm. The corn enters at the top and narrow end of the machine, and as it is carried forward, the hulls and germs are loosened, but the starchy portions are not ground to any extent. The germs and other fine particles largely pass through perforations, while the coarse material passes out at the further end of the machine. The separated germ material contains more or less of bran and meal, depending on the uniformity of the corn, as well as on the adjustment and operation of the degerminator. After reducing the moisture content to about 14 per cent in a drier, it is customary to pass the product through hominy reels to separate further the bran and meal from the germs. The final product, which contains from 18 to 20 per cent of oil, is then sent to the oil mill. About a half pound of oil is obtained from a bushel of corn.

Wet Process. The cleaned corn in large wooden vats is soaked from 30 to 40 hours in a large quantity of water which contains about

0.2 per cent of sulfurous acid. The acid aids in softening the corn, besides acting as a preservative and bleaching reagent. The treated corn is drained and passed through a special type of attrition mill which shreds the kernels and loosens the germs. The type of mill in general use consists of two vertical plates mounted on a horizontal shaft, geared to a motor. Some mills have one stationary plate. The shredded corn is mixed with a large quantity of water and transferred to the floating vats, which are long, narrow metal containers, broader at the top than at the bottom. The mixture is slowly agitated and kept moving at the surface toward one end of the vat where the germs, most of which float, pass over the edge. The germs, together with the starchy water, are transferred to perforated reels where they are thoroughly washed with water to remove the adhering starch. Then they are passed through the moisture expellers and conveyed to steam-heated, rotary driers where the moisture content is reduced to 5 per cent or less. The germ material separated by this process contains much less of the other parts of the corn than that obtained by the "dry process," with the result that it contains from 40 to nearly 50 per cent of oil. The average yield is about 1.25 pounds of oil per bushel of corn degermed by the wet process.

Expression of Oil. Although the oil may be expressed by hydraulic presses, it is customary in this country to use Anderson expellers. The dried germ material is passed through a set of flaking rolls which reduces it to a coarse meal. This is transferred to the steam-heated temperers from which it is delivered to the expellers. The oil, after passage through the slowly rotating screen ("oil reel") which retains the coarser part of the press foots that are gradually returned to the expellers for repressing, is filtered through paper in a filter press. The oil is usually of a golden or dark yellow and when fresh has a distinct corn meal flavor. The oil from "dry process" germs is usually of somewhat better quality than that from the "wet process" germs. The press cake is ground to meal which is used in making stock feeds.

Extraction. In recent years the oil has also been obtained by means of continuous solvent extractors.

Refining. The crude corn oil is refined by the caustic soda process, bleached with fuller's earth, and deodorized in a "vacuum" deodorizer with superheated steam, before it is used for edible purposes. During the treatment of the crude oil with caustic soda, it has been found that the addition of 2 per cent of soda ash will give a firm soap stock upon cooling which entrains less of the neutralized oil than when caustic soda alone is used. It has been observed that the oil is bleached much more during deodorization than it is by fuller's earth or activated carbon. However, it is necessary to bleach before deodorization if a light-colored oil is desired.

After refining, the oil is usually "wintered" in a manner similar to that employed with cottonseed oil. This treatment separates a small quantity of substances including wax, which, if allowed to remain,

would gradually separate and give the oil an objectionable appearance.

Sievers (*U. S. Dept. Agric. Bull.*, **1054**) made an investigation in the laboratory on the comparison of the oils obtained by expression and extraction with benzol. He found no striking differences in the characteristics of the oils obtained by either method. It was found that the expressed oils gave a lower refining loss than those extracted. No material difference was noted in the completely refined oils immediately afterwards; but on standing, some deterioration took place, particularly in the case of the extracted oils. For further details on the production, etc., of corn oil, consult *Bulletin* **904** by Sievers and *Bulletin* **1010** by Sievers and Shrader.

Rabak [*J. Ind. Eng. Chem.*, **12**, 46 (1920)] has studied the effect of the mold *Penicilium* upon the oil in corn. Under certain conditions, this mold attacks corn having an excessive content of moisture. It was found that as the spoilage of the corn progressed, its oil content decreased and at the same time the oil underwent a marked change in its character. The free fatty acids, the hydroxy acids, and the unsaponifiable matter increased at a rapid rate.

Properties and Uses. No special test has been discovered for this oil. The oil belongs to the semi-drying class and has somewhat better drying properties than cottonseed oil. When mixed with linseed oil, it has some value as a paint material, but on account of its price, corn oil is not used as an adulterant of linseed oil. Some of the oil along with linseed oil is used in grinding heavy paste paint to prevent hardening in the containers. It has been used in the manufacture of linoleum and oil-cloth. Wilborn (*Brit. Chem. Absts.*-B, **1927**, 18) prepared a "stand oil" by heating the oil at 300° C. for 10 hours in an atmosphere of carbon dioxide. With this he made a good drying enamel which upon aging did not yellow like the enamels in which linseed or tung oils were used. Corn oil, unless it is hydrogenated, gives a rather soft soap. Reichert and Trelles [*Chem. Absts.*, **15**, 3759 (1921)] hydrogenated the oil at 210° to 230° C. with a nickel catalyst and obtained a product with an iodine number of 21 which melted at 57° C. In the United States, most of the corn oil produced is refined and used for edible purposes. It is used as a salad and cooking oil as well as in the manufacture of some lard substitutes. When "unwintered" oil is stored at the refinery, sometimes it becomes slightly turbid, and on further standing a finely divided precipitate gradually settles to the bottom of the tank. This has been mistaken for stearine, but it is a wax which will be described later. Similarly, refined deodorized sunflower oil sometimes deposits wax.

Characteristics of Expressed Corn Oil. Sp. g. at 15° C. 0.921 to 0.927; Iod. No. 116 to 130; Sap. V. 188 to 193; Unsap. 1.3 to 2.0%; and titer of fatty acids 18° to 20° C.; refractive index at 15° C. 1.4765 to 1.4768, 25° C. 1.4733 to 1.4742, and at 40° C. 1.4656 to 1.4662. "Analysis of Authentic Commercial Corn Oils," by Jamieson and Baughman [*The Cotton Oil Press*, **7**, No. 12, 34 (1924)]:

CHARACTERISTICS OF CRUDE CORN OILS

Sample	Acidity as Oleic Acid	Neutral Oil Per Cent	Refining Loss	Iodine No. (Hanus)	Saponification Value
1	1.40	96.74	10.4	124.8	190.5
2	1.42	98.97	7.5	125.9	189.6
3	1.37	98.40	7.4	125.6	191.2
4	1.37	97.87	11.1	125.6	191.3
5	1.68	97.26	9.9	125.8	191.2
6.	2.02	95.89	12.2	125.3	191.5
7	1.82	95.81	15.1	124.5	192.4
8	1.37	97.45	9.9	125.7	191.2

CHARACTERISTICS OF THE OILS WHEN REFINED

Sample	Sp. G. 25°/25° C.	$N^{20°}_{D}$	Iodine No. (Hanus)	Saponification Value	Unsaponifiable Matter	Saturated Acids	Unsaturated Acids
					Per Cent		
1	0.9197	1.4746	125.8	190.3	1.49	9.5	85.4
2	0.9192	1.4746	126.4	189.5	1.60	8.8	86.4
3	0.9199	1.4746	125.7	190.2	1.23	9.8	85.4
4	0.9189	1.4746	126.7	190.8	1.10	10.0	85.2
5	0.9189	1.4746	126.7	191.3	1.03	9.4	85.9
6	0.9208	1.4750	125.2	190.8	1.20	9.2	85.7
7	0.9213	1.4750	124.9	190.9	1.20	9.3	84.6
8	0.9201	1.4750	126.7	191.2	1.12	9.2	86.2
Average	0.9198	1.4748	126.0	190.6	1.25	9.4	85.6

Source and History of Samples

1. Corn from Iowa and Illinois, degerminated by wet process.
2. Corn from Iowa, degerminated by dry process.
3. Source unknown, degerminated by wet process.
4. Corn from Central Illinois, degerminated by wet process.
5. Western corn, Illinois mill, degerminated by wet process.
6. Western corn, New Jersey mill, degerminated by wet process.
7. Source unknown, New York mill, degerminated by wet process.
8. Oil from white corn, Illinois, degerminated by wet process.

Although the sterol portion of the unsaponifiable matter of corn oil has been the subject of a number of investigations at various times, little was known regarding its composition until Anderson and Shriner [*J. Am. Chem. Soc.*, **48**, 2976 (1926)] made an extended study of the unsaponifiable matter from 10 kilos of the oil. They found that it contained three isomeric sterols ($C_{27}H_{45}OH$), which are called α, β, and γ sitosterol, a dihydrositosterol $C_{27}H_{47}OH$, and a very small quantity of the stigmasterol, $C_{30}H_{50}O$. The authors stated that it was possible to prepare only the gamma sitosterol in a pure condition. It crystallizes in colorless, plate-like prisms: M. P. 145° to 146° C.; $(\alpha)_D$ −42.43°. For details and other data, the original should be consulted.

Composition of Corn Oil. Comparatively little was known about the composition of this oil until Baughman and Jamieson [*J. Am. Chem. Soc.*, **43**, 2696 (1921)] made a quantitative investigation. As the results reported by former workers were not quantitative and they were decidedly contradictory, they will not be discussed. The oil which was expressed by an Anderson expeller from 100 pounds of "dry process" corn germs had the following characteristics: Sp. g. at 25°/25° C. 0.9185; $N^{20°}_{D}$ 1.4717; Iod. No. (Hanus) 117.2; Sap. V. 187.3; Acetyl

V. 10.0; Acid V. 2.5; Unsap. 1.72% (Iod. No. 113); Sat. Acids 11.2% and Unsat. Acids 83.3% (Iod. No. 137.2). The composition of this oil was as follows:

Acids	Original Oil Per Cent	As Glycerides Per Cent
Oleic	43.4	45.4
Linoleic	39.1	40.9
Palmitic	7.3	7.7
Stearic	3.3	3.5
Arachidic	0.4	0.4
Lignoceric	0.2	0.2
	Unsaponifiable	1.7

All the acids except lignoceric had been previously detected. Corn oil also contains very small quantities of various phosphatides, carbohydrates, coloring matter, etc., but no extensive study has been made of these constituents.

R. E. Longenecker [*J. Biol. Chem.*, **129**, 13 (1939)] examined the mixed fatty acids from a sample of corn oil and reported the following percentages of constituents: oleic 48.8, linoleic 34.0, hexadecenoic 1.6, myristic 1.7, palmitic 11.0, and stearic 2.9.

Corn Oil Wax. This wax has repeatedly been mistaken for stearine. A sample of the wax which had separated from the refined and deodorized oil was partially investigated by G. S. Jamieson with the following results: Acid V. 1.9, Acetyl V. 0.4, Iod. No. (Hanus) 42; Sap. V. 120.3; and Unsap. 36.46%. The unsaponifiable contained about 4.5 per cent of melissyl (myricyl) alcohol (M. Pt. 84° to 85° C.) and 31.9 per cent of ceryl alcohol (M. Pt. 79° C.); the acetate melted at 65° C. On account of the small quantity of the sample, it was impossible to identify the fatty acids combined with the alcohols. The wax, which was of a light brown color, after one crystallization from alcohol, chloroform, or petroleum ether, gave in each case a pure white product with a M. Pt. 80° to 81° C. Repeated recrystallization did not raise the melting point.

Shriner, Nabenhauer, and Anderson [*J. Am. Chem. Soc.*, **49**, 1290 (1927)] examined a corn oil wax which separated along with other substances during the refining of the crude oil in the form of a yellow pasty mass. The wax was separated by mixing the paste with a large quantity of ligroin and centrifuging. After recrystallizing the separated wax from hot ligroin and amyl alcohol, beautiful shining plates were obtained which melted at 81° to 82° C. From 13.5 kg. of the paste, 120 grams of the pure wax was obtained; the former represented a concentration from a very large quantity of corn oil. They found that this wax was composed of myricyl esters of *n*-tetracosanoic and an isobehenic acid. It will be observed that the wax examined by Jamieson contained chiefly esters of ceryl alcohol, but this wax was obtained upon the long standing of many thousands of pounds of highly refined deodorized corn oil.

For further information the following references may be consulted:

Univ. Ill. Agr. Exp. Sta. Bull. **257**, by M. Helen Keith, 1925, gives a complete bibliography on corn and corn products.

"Refining of Oils and the Making of Fine Salad Oils and Cooking Fats," by David Schwartz, *The Cottonseed Oil Mag.*, **41**, No. 2, 21 (1925).

"Fat Metabolism of Infants and Young Children, IV, The Digestion of Some Vegetable Fats by Children on a Fixed Diet," by L. E. Holt, A. M., Courtney and Foles, *Am. J. Dis. of Children*, **18**, 157 (1919).

"Relative Digestibility of Corn Oil, Cottonseed Oil and Lard," by E. W. Rockwood and P. B. Siviches, *J. Am. Med. Assocn.*, **71**, 1649 (1918).

"Digestibility of Some Seed Oils," by A. D. Holmes, *U. S. Dept. Agr. Bull.* **687** (1918).

"The Value of Corn Oil as a Substitute for Olive Oil and Cottonseed Oil," by B. E. Pool and L. E. Sayre, *Trans. Kan. Acad. Sci.*, **26**, 41 (1913).

"The American Industry of Corn Products," by T. B. Wagner, *J. Soc. Chem. Ind.*, **28**, 343 (1909).

"Olive Oils and Olive Oil Substitutes," by L. M. Tolman and L. S. Munson, *J. Am. Chem. Soc.*, **25**, 954 (1903).

"Production of Edible Maize Oil in the United States," *Oil Col. Trds. J.*, **75**, 1259 (1929).

"Autoxidation of Corn Oil as Related to Its Unsaponifiable Constituents," Mattill and Crawford, *Ind. Eng. Chem.*, **22**, 341 (1930).

"The Manufacture and Utilization of Products from Maize," Anon., *Oil Col. Trds. J.*, **76**, 797, 883, 1457, 1544, 1685 (1929); *ibid.*, **77**, 36 (1930).

"Corn Oil Preparation and Usefulness," G. A. More, *Oil and Soap*, **8**, 15 (1931).

"Corn Oil Production," R. Heublum, *Seifensieder Ztg.*, **61**, 638, 670 (1934).

"Solvent Extraction of Corn Oil from Distiller's Grains," C. S. Bornff and D. Miller, *Oil and Soap*, **14**, 312 (1937).

Millet Seed Oil. This oil is found in the seed of the plant, *Panicum miliaceum*, belonging to the *Graminae*. The seeds contain from about 3 to 6 per cent of oil. The characteristics of the oil which have been determined by various investigators are as follows: Sp. g. at 15° C. 0.9218 to 0.9275, at 20° 0.9206; $N_D^{20°}$ 1.4723, at 40° 1.4659; Sap. V. 181.8 to 184; Iod. No. 92 to 114; Titer 25-26° C.; Unsap. 2.5 to 5.0 per cent. Attention is called to the following references:

Francis and Freedman, Bull. No. 117 Agric. Exp. Sta. Oklahoma (1917).
Dunbar and Binnewiess, *J. Am. Chem. Soc.*, **42**, 658 (1920).
S. Ueno and N. Kuzei, *J. Soc. Chem. Ind., Japan*, **33**, 452 (1930); *Analyst*, **56**, 117 (1931).
H. Ito, *Chem. Absts.*, **29**, 627 (1935).

Oat Oil. This oil is obtained from the seeds of the oat, *Avena sativa*. Oats contain from 3 to 5 per cent of oil which, when extracted from freshly ground sound oats, is nearly neutral; otherwise the oil is characterized by considerable quantities of free fatty acids. L. A. Munro and D. C. Bimington [*Ind. Eng. Chem.*, **20**, 425 (1928)] have described an extractor specially designed for the preparation of cereal oils.

The characteristics are as follows: Sp. g. at 15° C. 0.925; $N_D^{40°}$ 1.4701; Sap. V. 185 to 192; Iod. No. (Wijs) 100 to 114; R.M.V. 0.6; Pol. No. 0.3; Unsap. 1.3 to 2.6%; Sol. Pt. varies from 5° to about 20° C.

Amberger and Hill [*Analyst*, **53**, 227 (1928)] found that the fatty acids from the oil consisted of 10 per cent of palmitic, 58.5 of oleic, 17.2 of α-linoleic, and 13.9 of β-linoleic acid.

Y. Saegi [*J. Agr. Chem. Soc., Japan*, **11**, 199 (1935); *Chem. Absts.*,

29, 5293 (1935)] found the following characteristics for oat oils: Sap. V. 193.4 and 198.8; Iod. No. 113.6 and 115.8; R.M.V. 6.82 and 12.98; Pol. No. 5.24 and 12.4; Acid V. 40.1 and 44.6; Unsap. 1.73 and 1.74 per cent. The oils were reported to contain the following percentages of acids: oleic 49 and 55.7, linoleic 15 and 19.7, palmitic 9.45 and 10.0. Evidently, these Japanese oils also contained notable quantities of acids of considerably lower molecular weight than those given.

References: Berry [*J. Agric. Sci.*, **10**, 366 (1920)], Dubovitz [*Chem. Zeit.*, **42**, 13 (1918)], Paul [*Analyst*, **46**, 238 (1921)].

Rice Oil. This oil is obtained by expression and solvent extraction from rice bran (plant *Oryza sativa*). The bran contains from about 8 to 16 per cent of oil depending upon its source. In recent years, large quantities of the oil have been obtained in Japan. There it is being used, after refining, for edible purposes. Considerable quantities of the so-called semi-refined oil were exported to the United States and elsewhere. When refined again and deodorized, it can be used for edible purposes.

RICE OILS

	Oil of Hambus var.	Oil of Ramai var.	Oil of Amer. rice
Iod. No. (Hanus)	99.5	99.3	99.9
Sapon. value	188.1	185.9	185.3
Unsaponifiable, (%) ...	3.98	4.02	4.64
Acid value	40.9	42.2	73.7
Oleic	43.7	43.3	39.2
Linoleic	26.5	26.4	35.1
Myristic	0.6	0.4	0.5
Palmitic	16.5	16.1	11.7
Stearic	1.7	2.5	1.7
Arachidic	0.6	0.4	0.5
Lignoceric	0.7	0.9	0.4

The tendency of the crude oil to develop in a very short time large quantities of free fatty acids has been shown by C. A. Browne [*J. Am. Chem. Soc.*, **25**, 948 (1903)] to be due to a very active lipase. The caustic-soda refining of the oil, soon after its extraction, retards the rapid formation of free fatty acids.

The characteristics reported by various observers for the crude oil are as follows: Sp. g. at 15° C. 0.918 to 0.928; $N_D^{40°}$ 1.4658 to 1.4670; Sap. V. 183 to 194; Iod. No. 92 to 109; SCN V. 68 to 70; R.M.V. 0.3 to 1.7; Unsap. 3 to 5 per cent.

H. P. Trevithick and R. R. Lewis [*Oil and Soap*, **13**, 232 (1936)] examined a sample of imported crude oil and reported the following results: Sp. g. at 15/15° C. .9192; Sap. V. 188.8; Iod. No. (Wijs) 103.5; SCN V. 68.8; Acid V. 101.5; Unsap. 4.89 per cent; Color 35 yellow and 60 red.

H. S. Mitchell and M. F. Lauro examined the caustic-soda refined oil with the following results: Sp. g. at 25° C. 0.9178; $N_D^{40°}$ 1.4659; Sap. V. 187.1; Iod. No. (Wijs) 106.1; SCN V. 69.7; R.M.V. 0.11; Pol. No. 0.05; Acetyl V. (Andre-Cook) 8.3; Unsap. 3.1%; Acid V. 0.1; Titer 26.9°; Flash Pt. 585° F.; Fire Pt. 680° F.

Jamieson [*Oil Fat Ind.*, **3**, 256 (1926)] examined an oil extracted by ether from bran of American rice, A. A. Cruz, A. P. West [*Phil. J. Sci.*, **47**, 48 (1932)] the ether-extracted oil from the *Hambus* variety of rice, and A. O. Cruz, A. P. West, and V. B. Arogon (*ibid.*, **48**, 5) the ether-extracted oil from the *Ramai* variety of rice. The more important characteristics and percentages of acids in the oils are given in the table on page 182.

Attention is called to the following references: E. C. Potter [*Chem. Met. Eng.*, **40**, 365 (1933)] discusses rice as a raw material for process industries; Sei-ichi Ueno [*J. Soc. Chem. Ind., Japan*, **40**, 200 (1937); *Chem. Absts.*, **31**, 611 (1937)] deals with the oil and its utilization; D. Marota and A. Calo [*Ann. chim. applicata*, **22**, 763 (1932)] discuss the extraction and composition of organic phosphorus compounds from rice polishings and various oil-seed hulls; A. P. West and A. O. Cruz [*Phil. J. Sci.*, **52**, 1-78 (1933)] deal with rice mill products, the preservation of rice bran, and its nutritive value. "Rice Bran as a Raw Material for Oil," T. Hidaka, *J. Soc. Chem. Ind., Japan*, **42**, 219-220 (1939); *Analyst*, **64**, 750 (1939). "Industrial Uses of Rice Bran Oil," *J. Soc. Chem. Ind.*, **58**, 1014 (1939). "Special Methods For Refining Oils," R. G. Dresser, *Oil and Soap*, **17**, 124 (1940), applies to rice bran oil.

Rye Oil. Rye contains about 2 per cent of oil. The oil from the bran, embryo, flour and seed has been partially investigated, with the following results [See C. D. Ball, *Cereal Chem.*, **3**, 19 (1926)]:

Investigator	Stellnag 1890	Spaeth 1894	Alpers 1908	Alpers 1908
Source	Bran	Flour	Seed	Embryo
Sp. g. at 15° C.		0.8769	0.9334	0.9322
N_D° ?		1.4765		1.4774
Sap. V.	175.	172.8	196	174.3
Iodine No.		118.5	81.8	127.7
R. M. V.		0.88		0.33
Unsap. (%)	7.64			

J. W. Croxford [*Analyst*, **55**, 735 (1930)] examined 4 oils extracted by ether from rye, rye flour, etc., with the following results:

Samples	Sp. g. 15°/15° C.	Acid Value	Iodine No.	Saponification Value	Unsaponifiable Per Cent
A	0.9374	27.8	118.3	178.7	11.2
B	0.9412	10.7	129.9	173.4	9.05
Ryvita		20.0	110.7	187.0	8.9
Rye Flour	0.9283	24.0	126.8	186.0	8.2

There was little or no vitamin in these oils. For other information and data, the original should be consulted.

A. W. Stout and H. A. Schuette [*J. Am. Chem. Soc.*, **54**, 3298 (1932)] examined the separated rye germs and found an oil content of 11 per cent. The oil gave the following characteristics: Sp. g. at 20/20° C. 0.9229; $N_D^{20°}$ 1.4779; Sap. V. 176.8; Iod. No. (Wijs) 139.9;

SCN V. 85.0; R.M.V. 0.05; Pol. No. 0.3; Acid V. 5.8; Unsap. 7.28%; Acetyl V. 20.2; Sat. Acids 10.12%; Unsat. acids 77.46%.

The oil contained the following percentages of acids as glycerides: oleic 31.92; linoleic 44.15; linolenic 4.99, myristic 2.33, palmitic 8.11, and stearic 0.18.

The pigments of rye germ oil are discussed by H. A. Schuette and R. C. Palmer, [*Oil and Soap,* **14,** 295 (1937)]. S. W. Gloyer and H. A. Schuette [*J. Am. Chem. Soc.,* **61,** 1901 (1939)] have investigated the sterols. In addition to the α, β and γ sitosterols, they isolated a new isomer of stigmasterol and α sitosterol which they named α_3 sitosterol ($C_{29}H_{48}O$).

Wheat Oil. This oil is obtained from the seeds of the cultivated wheat (*Triticum* species), of which there are many varieties. The whole seeds contain about 2 per cent of oil; the bran 5 to 6, and the germs 12 to 18 per cent.

Contrary to statements in the literature, wheat oil when properly prepared has good keeping qualities. Samples in full containers kept in the dark for 3 years showed but a very slight increase in free fatty acids.

The range of the characteristics found by various observers is as follows: Sp. g. at 15° C. 0.929, at 25° 0.9248 to 9268; $N_D^{20°}$ 1.4762 to 1.4851; Sap. V. 180 to 189; Iod. No. 115 to 126; Unsap. 3.5 to 4.7%; R.M.V. 0.2 to 0.5; Pol. No. 0.2 to 0.4; Sat. acids 13.3 to 16.00%; Hexabromides, tr. to 2.3.

Jamieson and W. F. Baughman [*Oil and Soap,* **8,** 136 (1932)] examined the ether-extracted oil and obtained the following results: Sp. g. at 25° C. 0.9268; $N_D^{25°}$ 1.4762; Sap. V. 186.5; Iod. No. (Hanus) 125.6; SCN V. 79.7; Acetyl V. (Andre-Cook) 9.9; Unsap. 4.7%; Sat. acids 13.3%; Unsat. acids 75.3%; Hexabromides, a trace; Iod. No. Unsat. acids 160.7. The unsaponifiable contained 73.5 per cent of sterols. The oil contained the following percentage of acids: oleic 26.6, linoleic 39.1, linolenic 9.6?; palmitic 12.15, stearic 0.84; and lignoceric 0.3. Although every effort possible was made to obtain accurate results, it is believed that the percentage of linolenic acid found is probably somewhat too high.

B. Sullivan and C. H. Bailey [*J. Am. Chem. Soc.,* **58,** 383 (1936)] extracted the oil (using alcohol, then ether) from germs separated from Marquis spring wheat. Some of the characteristics reported are as follows: Sap. V. 184, Iod. No. (R. & K.) 125.0; SCN 84.7; Unsap. 4.0%; Sat. acids 16.0%; Hexabromides 2.28.

The percentages of unsaturated constituents in the mixed fatty acids were as follows: oleic 28.14, linoleic 52.31 and linolenic 3.55.

These authors (*ibid.,* 390) investigated the unsaponifiable fraction of the oil and found that it contained 70 per cent of sterols, of which 30.7 per cent was in the form of esters.

The phytosterols of wheat endosperm have been extensively investigated by R. J. Anderson, Shriner and Burr, [*J. Am. Chem. Soc.,* **48,**

2987 (1926)]. The phosphatides are discussed by Channon and Foster [*Biochem. J.*, **28**, 853 (1934)] and the crystalline alcohols from the unsaponifiable fraction of rice and wheat oils by A. R. Todd, F. Bergel, H. Waldman, and T. S. Work [*ibid.*, **31**, 2247 (1937)].

For some years, wheat oil has been produced commercially and sold largely for medicinal purposes. It contains a notable quantity of the fat-soluble vitamin E [W. P. Kennedy, *Physiol. Rev.*, **6**, 485 (1926). A. R. Todd, F. Bergel and T. S. Work, *Biochem. J.*, **31**, 2257 (1937)]. Also see A. R. Todd, F. Bergel and T. S. Work, [*Biochem. J.*, **31**, 2257 (1937)] on the isolation of beta-tocopherol from the oil.

Cotton, Cottonseed and Cottonseed Oil

Cottonseed oil is obtained from the seeds of different varieties of the several species of the plant *Gossypium* belonging to the natural order of *Malvaceae*. The wild species are found in the tropical regions of both hemispheres, where they grow in the form of small trees. From some of these species, hundreds of cultivated varieties have been developed, differing more or less from each other in the plant characters as well as in the length, strength and fineness of the cotton fiber or lint they produce. Outside of the tropics, cotton is grown as an annual crop. In strictly tropical regions, it is usually cultivated as a perennial crop, but because of the gradual reduction both in yield and quality of the staple, it is customary to replant every 3 to 7 years, depending upon local conditions.

A broad grouping into five general classes according to uses and commercial value has been made by A. Agelasto, C. B. Doyle, G. S. Meloy, and O. C. Stine ("The Cotton Situation," U. S. Dept. Agriculture Yearbook, **1921**, pp. 323 to 406), and is as follows:

(1) Sea Island Cotton *(Gossypium barbadense)*, a native of tropical America. It has yellow flowers with purple spots, bolls mostly 3 locked, black seeds, fuzzy only at ends, and very long silky fiber. It is the most valuable of the wild cottons, surpassing all other types in length, strength, and fineness. Prior to the coming of the boll weevil, the average yearly crop in the United States was about 90,000 bales. In 1916, the production was 116,000 bales, but by 1920 the production was less than 2000. More extensive planting of this cotton has been made again in recent years and yields up to 4,941 bales have been obtained. Depending upon the location, etc., the staple varies in length from $1\frac{1}{2}$ to 2 inches.

(2) Egyptian Cotton *(Gossypium barbadense)* is similar to Sea Island cotton in the appearance of the plants and has a fine silky strong fiber ranging from $1\frac{1}{16}$ to $1\frac{3}{4}$ inches in length and is second in value only to Sea Island. The bulk of the crop is produced in Egypt, but considerable quantities are grown in the irrigated valleys of Arizona and California.

(3) Upland Long Staple Cotton *(Gossypium hirsutum)*, which is grown chiefly in the United States, occupies a commercial position

between the Egyptian and the upland short staple varieties. The plants resemble those of the short staple type, having unspotted white flowers, bolls of 4 or 5 locks, and seeds usually well covered with white, brown, or green fuzz in addition to the staple. The staple or fiber ranges in length from 1⅛ to 1¾ inches. Most of this crop is grown in the delta lands of the Mississippi, in the Pecos and Red River Valleys of Texas, in Oklahoma, Arkansas, California, and South Carolina. The annual production is about 1.5 million bales.

(4) Upland Short Staple Cotton *(Gossypium hirsutum)* constitutes about 92 per cent of the United States cotton crop and about 50 per cent of the world crop. "American Middling," the standard short staple grade, is the basis of price quotations for all short staple cottons. The staple varies in length from five-eighths to one inch, with some varieties exceeding an inch when grown under the most favorable conditions. Hundreds of varieties are cultivated in the American Cotton Belt, differing in habits of growth, size of bolls, earliness of opening, abundance, length and uniformity of staple. American upland varieties have been introduced into Russian Turkestan and Transcaucasia and now constitute the major portion of the crop in these regions. They are also being grown in China, Korea, Asia Minor, India, and Brazil.

(5) Asiatic cottons include *Gossypium herbaceum* and several related botanical species, *G. indicum, G. neglectum,* and *G. arboreum.* The staple is short, often only three-eighths to three-quarters of an inch, but strong and rather tough. Asiatic cottons are cultivated in Asia Minor, China, India, Indo-China, and Japan, but in several districts these are giving place to the American upland type.

Cotton bolls of cultivated cottons usually contain 4 or 5 locks of fiber and from 40 to 45 seeds. Depending upon the variety, 100 seeds weigh anywhere from 4 to about 19 grams. The large seed varieties yield more fiber per boll, but the proportion of fiber to seed is less than in the small seed varieties.

The value of the seed, on account of its utilization for oil and cake, as is well known, has become an important economic factor in the production of the cotton crop. The annual world production of cottonseed oil is about 4.3 billion pounds.

Much information will be found in H. B. Brown's book entitled "Cotton: History, Species, Varieties, Morphology, Breeding, Culture, Diseases, Marketing and Uses" (McGraw-Hill Publishing Co., New York, 1927). Also attention is called to "Cotton Growing Countries: Present and Potential," by the International Institute of Agriculture at Rome, which was published in 1926 by P. S. King and Son, Ltd., London.

Cotton Growing and the Importance of One-Variety Communities. Dr. O. F. Cook (*U. S. Dept. Agric. Bull.,* **1111,** entitled "One Variety Cotton Communities"), in reference to the cultivation of cotton in the United States, has clearly shown the importance of growing but one variety in a given community or district, and this applies equally to every cotton producing country. It is also important

that the variety planted should be the one best adapted to the local conditions of the district in question as regards climate, soil, rainfall, local insect pests and local plant diseases which may attack the cotton plants. From an economic standpoint, it is a fundamental requirement (which in the United States, as well as in some other countries, is not yet recognized or practiced to anything like the extent that it should be) that but one variety of seed should be grown in a given community. Only by doing this, can the seed of superior, worthwhile varieties be kept pure for succeeding plantings. Incidentally, in connection with the cultivation of a pure variety of cotton which yields a superior uniform quality of lint, the seed produced are also of superior quality, and this should be of no little interest to the manufacturers of cottonseed products. For information on the one-variety communities that have been established in the United States prior to 1922, largely through the efforts of the Department of Agriculture, the bulletin to which reference has been made should be consulted. This, as well as other departmental bulletins and other publications on cotton, etc., will be found in the libraries of agricultural colleges, experiment stations, and those of many cities.

It is interesting to note that the one-variety communities in California have the protection of a special act of the state legislature which established pure seed districts for the Acala variety of cotton and made it unlawful to interfere with its production by planting other varieties within the boundaries of the specified districts. By 1940, there were about 1600 single cotton variety communities established in the United States and in which about three million acres of land were planted to cotton.

Mixed variety production, due to crossing of varieties in neighboring fields and mixing of seed at the public gins, results in smaller yields per acre and rapid deterioration of the lint and seed from every standpoint; consequently the importance of the establishment of the one-variety communities to the farmer, textile and cottonseed products manufacturer cannot be over-emphasized. The farmers themselves and even many leaders of agricultural progress are not sufficiently aware of the practical importance of good varieties of cotton, nor the precautions of isolation, separate ginning and continued selection that are needed to maintain the purity and uniformity of their cotton crop from year to year. Furthermore, the successful establishment of the one-variety community depends, in the absence of legislative acts, to no small extent upon the complete organization of the community. Furthermore, it must be emphasized that organization for community production in no way lessens the responsibility of the individual cotton farmer in the careful management of his farm.

North America

The United States. The "Cotton Belt" applies to the area of specialized cotton production in the South extending from the Atlantic coast through North Carolina, South Carolina, Georgia, Florida, Ala-

bama, Mississippi, Arkansas, western Tennessee, northern Louisiana, and into Texas and Oklahoma. Both soil and climate are very important factors in the determination of areas suitable for cotton production. The most productive soils in normal seasons are the dark-colored clay lands, particularly those rich in lime, such as the black prairies of Alabama, Mississippi and Texas, and the red, brown and black well-drained river bottom land and second bottoms such as are found in Mississippi, Tennessee, and Arkansas. The sandy loams of the Coastal Plain and the red subsoil Piedmont lands, when fertilized, also give high yields of cotton.

This Cotton Belt has an average summer temperature of 77° F. along the northern boundary, with a growing season of about 200 days. This temperature and growing season appear to be the limit beyond which commercial production becomes unprofitable.

The important producing areas outside of the so-called cotton belt are the warmer irrigated valleys of Arizona, New Mexico and California (sometimes called the western division of the Cotton Belt).

The area planted to cotton varies from season to season. For some years it varied from 39 to 46.9 million acres, but since 1934, the acreage has ranged from 24.25 up to 33.62 millions. During this period, seed production varied from 4.28 to 5.51 million tons, with the exception of 1937 when it was 8.42. From 75 to 83 per cent of these seed were processed for oil and cake. The oil production each season varied from 1.2 to 1.68 billion pounds. It may be of some interest to note that from 5,058,744 tons of seed, 1,603,352,111 lbs. of oil, 2,280,894 tons of cake and meal, 1,084,644 bales of linters, 1,367,325 tons of hulls and 73,363 bales of hull fiber were obtained.

Attention is called to the following references:

"Cotton Varieties in Georgia" (variation of oil content of seed and resistance to disease besides much other information), L. E. Rast, *Ga. State Coll. Agric. Bull.* **121**, 1917.

"Cotton Ginning" (a very important contribution), G. S. Meloy, *U. S. Dept. Agric. Farmer's Bull.* **1465**, 1925.

"Sea Island and Meade Cotton in Southeastern States," O. F. Cook and C. B. Doyle, *U. S. Dept. Agric. Circ.* **414**, 1927.

"Cotton Harvesting Machines," *Oil Miller and Cotton Ginner*, **31**, No. 2 (1927).

"Mechanical Harvesting in Northern Texas," D. L. Jones and D. Scoats, *ibid.*, **33**, No. 3, 31 (1929).

"The Chemical Composition of the Cotton Plant," G. S. Fraps, *Texas Agric. Exp. Sta. Bull.* **247**, 1919.

"Present Contributions to the Chemistry of the Cotton Plant," C. A. Browne, *Oil and Fat Ind.*, **2**, 87 (1925).

"Regulations Regarding Cotton Pests and Diseases in British Colonies and India," *Bull. Imp. Inst.*, **20**, 192 (1922).

"The Constituents of the Benzine Extract of American Cotton," R. G. Fargher and M. E. Probert, *J. Textile Inst.*, **14**, 49T (1923).

"Cotton Wax," *Oil Col. Trades J.*, **76**, 187 (1929).

"Relation of Cotton Wilt, Root Rot and Fusarium Wilt to Acidity and Alkalinity of the Soil," J. J. Traubenhaus, W. N. Ezekiel and D. T. Killough, *Texas Agric. Exp. Sta. Bull.* **389**, 1928.

"Lint Percentage and Lint Index and Methods of Determination," G. S. Meloy, *U. S. Dept. Agric. Bull.* **644**, 1918.

"Lint Frequency in Cotton with Method of Determination," E. A. Hodson, *Ark. Coll. Agric. Bull.* **168,** 1920.

"Cotton Improvement under Weevil Conditions," O. F. Cook, *U. S. Dept. Agric. Bull.* **501,** 1924.

"Community Production of Acala Cotton in the Coahilla Valley of California," H. G. McKeaver, *U. S. Dept. Agric. Bull.* **1467,** 1927.

"The Correlation between the Soil Salinity and Flowering Date of Cotton" (with bibliography), J A. Harris, *J. Agric. Research,* **38,** 109 (1929). Cf. *ibid.,* **37,** 213 (1928).

U. S. Cotton Standards Act. Service and Regulatory Announcements No. 115.

"Farm Study of the Cotton Plant," J. W. Hubbard, *U.S.D.A. Farmers Bull.* 1661 (1931).

"Common Problems of Growers and Seed Crushers," E. B. Whitaker, *Cotton Oil Press,* **16,** No. 2, 49 (1932).

"The Mechanical Harvesting of Cotton," H. P. Smith, *et al.,* Bull. 452, Texas Agric. Exp. Station, College Station, Texas, 1932.

"Cotton in Tropical Africa," P. E. A. Janssens, in French, 402 pages, A. R. Bansart, Brussels, 1932.

"Common Errors in Cotton Production," O. F. Cook, *U.S.D.A. Farmers' Bull.* 1686 (1932).

"The Effect of Latitude, Length of Growing Season, and Place of Origin of Seed on the Yield of Cotton Varieties," G. A. Hale, *J. Agric. Res.,* **46,** 731 (1933).

"All About Cotton," A. H. Garside, 411 pp., F. A. Stokes Co., New York, 1935.

"Colonization in the Argentine Chaco," *Foreign Crops and Markets (U. S. Dept. Agric.),* **32,** 793 (1936) ; includes a discussion of the Argentine cotton belt.

"Cotton Standardization in One Variety Communities Essential," C. B. Doyle, *Cotton and Cotton Oil Press,* **38,** No. 13, 28 (1937).

"Cotton Industry in San Joaquin Valley," O. Adams, *Cotton and Cotton Oil Press,* **38,** No. 45, 3 (1937).

"Summary of Papers Presented at the Eighteenth Cotton Congress Held in Egypt in 1938," *Monthly Bull. Agric. Sci. and Pract.,* **29,** 475-486T (1938).

"Trends and Possibilities of Cotton Production in China," F. J. Rossiter, *Foreign Agric. (U. S. Dept. Agric.),* **2,** 119 (1938). All phases of industry are discussed.

"The Origin of Lint and Fuzz Hairs of Cotton," A. G. Lang, *J. Agric. Res.,* **56,** 507 (1938).

"Cotton in Peru," J. Legros, *Monthly Bull. Agric. Sci. and Pract.,* **29,** 263T (1938).

"Agriculture in China," F. J. Rossiter, *Foreign Agric.,* **3,** 431 (1939) ; contains much information on cotton industry in China.

"Production of Cotton in Latin America," C. H. Barber, *Foreign Agric.,* **3,** 375 (1939).

Mexico. The principal cotton-growing states are Chihuahua, Coahuila, Durango, and Lower California. There are several native varieties of cotton descended from indigenous species. Two varieties (Acala and Durango) have been introduced into the United States. ("Acala Cotton: A Superior Upland Variety from Southern Mexico," O. F. Cook and C. B. Doyle, *U. S. Dept. Agric. Circ.,* **2,** 1927.) One plantation in Lower California has over 100,000 acres upon which Acala cotton is grown.

The yield of cotton in Mexico is subject to wide variation because in some localities the crop is sometimes destroyed by floods, but with these exceptions the annual yield varies from 260 to 395 thousand bales of 478 pounds. The seed amounts to from 151 to 192 thousand tons. Mexico produces considerable quantities of oil and cake. One of the oil mills which is located at Gomez Palacio in the State of Durango has 39 hydraulic presses.

Central America. Only very small quantities of cotton are produced

in Central American countries; in some of these, much more could be grown.

West Indies. For many years, cotton has been produced on various islands of this group. Sea Island cotton is the principal variety planted. The annual crop is over 10,000 bales of lint. There are a few oil mills on the more important producing islands.

South America

Argentina. In the northern part of Argentina there are extensive areas of fertile land where the temperature and rainfall are well suited for the cultivation of cotton. The chief limiting factors in this region are the shortage of labor and the production of more profitable crops. This cotton belt is situated in the provinces of Corientes, Santiago del Estero, La Rioja, Catamarca, as well as in parts of Entre Reos, Santa Fé, Salta, Tucuman, and the territories of Chaco, Formosa, and Missiones [*Cottonseed Oil Mag.,* **51,** No. 2, 24 (1925)]. Of these regions Chaco is by far the most important. In recent years, it has produced from 70 to over 90 per cent of the cotton crop.

The Argentine cotton belt probably contains 50 million acres of land suitable for the production of this crop, but in view of the labor supply and other factors, the prospects are that not over 2.5 million acres will be planted to cotton within the next decade.

In recent years, the production of cotton has ranged from 232,000 to 369,000 bales of 478 pounds, and cottonseed from 116 to 185 thousands of tons.

Brazil. Cotton is grown, for the most part, in northeastern Brazil and in the four southern states. The long-staple perennial tree cotton is grown chiefly in the northeastern states, but some is produced in Bahia and Minas Geraes. In the four southern states, American upland types of cotton are grown as an annual crop. Prior to 1930, these states produced less than 20 per cent of the total crop, but by 1939 it amounted to about 65 per cent. At that time Sao Paulo produced over half of Brazil's cotton crop of 1,989,000 (478-lb.) bales.

Since 1933, all cotton sold must be graded in accordance with the official classification. In connection with the Government's cotton improvement program, it is interesting to note that some years ago regulations were made prohibiting the planting of any variety other than the one found best adapted to a given region.

The production of cottonseed now amounts to well over a million tons per year. Part of the seed is crushed by the 50 or more oil mills (many of which are of small capacity) and the remainder, except that required for planting, is exported. There are also a number of cottonseed-oil refineries in Brazil.

Peru. Since 1924, about 300,000 acres have been planted to cotton in Peru. Practically the entire crop comes from the irrigated valleys of the coastal desert. The most important producing districts lie between Supe, to the mouth of Callao, and Pisco. In recent years, crops have varied from 325 to 396 thousands of (478-lb.) bales of

cotton, of which about 85 per cent have been exported, the remainder being used by the domestic textile mills. About 100,000 metric tons of the seed are crushed for oil and cake in 25 mills. Oil not required for local consumption is exported to Bolivia, Chile, and Central America. The chief producing centers are Lima, Huacho, Paita, Sullana, Ganete, Pisco, Ica and Camana. Also, there are a number of oil refineries, four being located at Lima.

The cotton industry of Peru is discussed by Rosenfeld and Jones in *Economic Geography*, **3**, 507-523 (1927).

For those interested in varieties, attention is called to the wilt-resisting Tanguis, which has for some time been the most important cotton grown in Peru; it is grown successfully on practically all types of Peruvian soils.

Other Countries. Chile, Colombia, Ecuador, Guianas, Paraguay and Uruguay produce small quantities of cotton. Venezuela usually produces from 30 to 40 thousand bales of lint a year. There cottonseed oil is produced and refined for local use.

Asia

India. For a period of about 3000 years, India ranked first in the production of cotton, but it now ranks second. The yield averages less than 100 lbs. of lint to the acre. The staple is very short, much of it being only about one-half inch long. Cotton is grown in nearly all parts of the country, but Central India is the most important producing region. Between 20 and 24 million acres are planted and the yield varies from 2 to about 4.5 million (500 lbs.) bales of lint, the seed amounting from 1 to about 1.3 million tons. Although increasing quantities of the oil are being expressed in India, large quantities of seed are exported, chiefly to England.

The recent rapid expansion in the cultivation of peanuts is extending to the cotton lands of the central provinces. In some cases peanuts are grown in rotation with cotton, but in others peanuts are replacing the cotton crop. Much information on cotton production (varieties, soils, cultivation, etc.) in India will be found in *Monthly Bull. Agric. Sci. and Practice*, **27**, 405T (1936) under the title, "The Indian Cotton Situation, 1929-35."

Russia: U. S. S. R. The bulk of the cotton produced is grown in the central Asiatic territories of Turkestan, Bokhara, Kheva and Transcaucasia. In these regions, American upland varieties are largely cultivated. Also, some long-staple Egyptian cotton is now being produced. About 5 million acres of land are planted to cotton. Two million or more bales of lint and about two million tons of seed are obtained during favorable seasons.

China. Since very early times China has grown cotton. It is interesting to note that the Chinese were probably the first to utilize cottonseed in the production of oil and cake. Centuries ago, they crushed and pressed the seed in their primitive presses. The oil was used in their hand lamps and for making soap. The cake was used chiefly in

those early days as fertilizer. In addition to the short-staple native cottons, a number of American upland varieties, which were introduced some years ago, are being extensively grown. Production in recent years has been estimated to range from 3.2 to over 3.8 millions of (478-lb.) bales and seed from 1.6 to over 2.2 million tons. Nearly all the cotton crop produced is used in China, but some lint, seed, oil and cake are exported. For those who wish other information about this industry, attention is called to "Agriculture in China" by F. J. Rossiter, *Foreign Agric. (U. S. D. A.),* **3,** 431 (1939).

Japan. Cotton is grown on a small scale, chiefly in the island of Kinchiu and neighboring islands. The production amounts to about one million pounds of lint, whereas the large Japanese spinning industry requires the importation of over a billion pounds of lint per year from East India, America, Korea and China.

Chosen (Korea) produces about 66 million pounds of lint on about half a million acres of land (*International Cotton Bulletin,* **1924,** No. 8, Manchester, England). The annual production of cottonseed in recent years has ranged from 66 to 102 thousand tons.

Africa

For centuries, native cottons have been grown in various parts of Africa and the lint used locally by the natives. In recent years, various types of American cottons have been introduced. Experiment stations have been established in quite a number of the colonies not only for the purpose of determining the varieties best adapted to the locality but also to assist and encourage the growing of cotton. The progress during the last decade in the development of African agriculture along various lines through the experiment stations and other agencies is noteworthy. In many sections, lack of transportation facilities still constitutes one of the chief handicaps to the rapid expansion of the agricultural industries, and in particular that of cotton. However, railroads are being extended and roads built that are suitable for motor transport of agricultural and other products. In order to get an adequate idea of the recent developments to which attention has been called, it will be necessary to consult the reports appearing in the various African agricultural journals, those published by the colonial offices or institutes of different European countries, and the Imperial Institute of London.

Egypt. The cotton-growing area of Egypt, which at the present time is the most important producing country of Africa, consists of a narrow belt 550 miles in length extending along the Nile and the fan-shaped delta region, containing in all about 4 million acres. About 2 million acres are planted to cotton, all of which is grown under irrigation on account of the scanty rainfall. The principal varieties grown are known as Ashmouni, Sakellarides, and Afifi. The yield of lint ranges from about 1.7 to 1.9 million (478-lb.) bales and the seed from 7 to 9 hundred thousand tons. The larger part of the lint is exported to England and the United States. England also buys considerable

quantities of seed, oil and cake from Egypt. The average figures prepared by the Egyptian Government which show the distribution of the seed are as follows: For export 68, crushing 20, and 10 to 12 per cent for planting. From the analyses seen, the seed contains from 23 to 24.5 per cent of oil (moisture—7 to 8.5 per cent), which is much above the average for seed from other countries.

There are a number of oil mills, but only one presses decorticated seed. This one is equipped with 46 hydraulic presses and 6 oil expellers. Most of the other mills are very small.

The Anglo-Egyptian Sudan. This country, located in east central Africa, contains an immense area adapted for the cultivation of cotton, in regard to both climate and soils. In time, it may well become one of the world's major producing regions. Egyptian and certain American varieties of cotton are cultivated, partly under irrigation and partly as a "rain crop." Over 240,000 acres are planted to this crop and the yield is about 4.4 million pounds of lint. As much as 14,000 bales of the long-staple cotton has been exported to the United States within a single year, presumably for the manufacture of automobile tire fabrics.

In view of the favorable conditions under which cotton may be produced in this area, marked expansion of acreage may be expected.

Nigeria. Cotton is a common crop in Nigeria, except in the coastal region, which varies from 50 to 150 miles in width. Native cottons have been produced by the natives for centuries. These short-staple cottons are still grown, as well as the long-staple varieties of American origin. Neither the acreage nor the yield is known, but the exports amount to over 15 million pounds of lint and the local consumption is estimated as between 20 and 40 million pounds.

Uganda Protectorate. Formerly, Egyptian varieties of cotton were grown in this Protectorate, but now the long-staple American "Allen" and "Sunflower" types constitute the crop, which amounts from 70 to 75 million pounds of lint and 90,000 tons of seed.

Other African Countries. Those having 50,000 acres or more planted to cotton are Belgian Congo, Senegal, French Sudan, South Rhodesia and the Union of South Africa. Some cotton is being grown in most, if not all, of the African countries. In recent years, three cottonseed oil mills have been established in the Belgian Congo.

Australia

The prospective cotton-growing areas of Australia are Queensland, the Northern Territory, northern New South Wales, the irrigated districts of northwest and South Australia and Victoria. It appears that Queensland offers the best prospects for the cultivation of cotton. The soil and climatic conditions are most favorable in a belt 1300 by 200 miles that extends from the southern border to Cape York. At different times, cotton has been grown in many parts of this extensive belt. Sea Island, Brazilian, Egyptian, and upland varieties have at one time or another been planted, with the obvious result that in many localities the varieties have become hopelessly mixed; besides, the practice of

growing annual and perennial cottons has further complicated matters. Cotton growing from its beginning in Australia up to 1923 is ably discussed by W. H. Johnson, *Bull. Imp. Inst.*, **21**, 596 (1923).

During the past 10 years renewed interest has been taken in the cultivation of cotton. During the 1940-41 season, 12,000 bales of cotton and 6,000 tons of seed were obtained. As is now well known, the future success of this undertaking will in no small way depend upon the firm establishment of one-variety communities with a suitable variety adapted to the local conditions, along with provisions for maintaining the purity and quality of the seed supply.

Europe

Some cotton is grown in Bulgaria, Greece, Italy, Romania and Yugoslavia. Of these, Greece appears to be the largest producer.

Cottonseed

Storage. When seed is delivered to the mills in quantities greater than the daily capacity of the equipment, it is customary to store it either in seed houses or silos for future use. Although problems connected with seed storage still remain, much progress has been made toward their solution. Seed storage on the part of many cotton and other seed oil millers still receives far too little consideration. Space does not permit of a detailed discussion of seed storage or structural features of the modern seed houses and silos, but some of the more important considerations will be mentioned and references will be given for those interested in getting additional information.

Seed should be stored in suitably ventilated steel or concrete structures, so situated and built that neither rain nor seepage water can enter them. Also, adequate facilities must be provided for unloading seed at the mills so as to protect them from rain and dirt. Most modern mills have rectangular seed houses, but some store seed successfully in concrete tanks or silos. In any case, the seed are elevated to near the top of the inside of the storage structure by screw conveyers and distributed below as desired. Other conveyers in the open galleries below the floor level withdraw the seed as required for milling. Precautions are to be taken in filling seed houses or tanks, so that no sparks from motors, etc., are given off; otherwise destructive explosions and fires may result from the ignition of the fine lint and dust in the air. Only non-sparking types of electric motors should be installed in oil mills and all other plants having organic or other dust. In addition, all machinery should be effectively grounded to prevent static discharges. The neglect of these and other precautions still takes a large annual toll of life and property.

The storage of wet seed usually results in heating, and not infrequently in spontaneous combustion. Seed that contains more than 10 or 11 per cent of moisture should be sufficiently dried before going into storage. When excessive quantities of foreign matter are present,

the seed should be cleaned, then dried if necessary and stored. Seed that has undergone much field damage, even when the moisture content is 10 per cent or less, should be watched while in storage by observing the temperature of the inner parts of the piles.

Damaged Seed. This source of loss, which is preventable in many instances by proper care before and after ginning, is an economic loss because the oil from damaged seed is of lower value. It has a higher refining loss than that from sound seed. Also the cake from damaged seed is of poor quality and is often not suitable for feeding purposes. The storage of such seed results in further deterioration and is subject to heating.

Attention is called to the following references:

"The Cottonseed Products Industry with Special Reference to Storing and Marketing of Seed," W. E. Ayers, *Cotton Oil Press,* **3,** 34 (1919).

"Wet Hulls Cause of Spontaneous Combustion," a note in the *Cotton Oil Press,* **2,** No. 9, 30 (1919).

"Chemical Changes in Cottonseed During Heat and Storage," J. Malowan, *Cotton Oil Press,* **5,** No. 4, 40 (1921).

"Drying and Storage of Cotton Seed," G. B. Alfad, *Cotton Oil Press,* **5,** No. 5, 40 (1921).

"Why Should Seed be Cleaned Before Going to Seed House?" H. J. J. Thiesson, *Cottonseed Oil Mag.,* **39,** 11 (1923).

"Economic Waste of Dirty Cottonseed," Anon., *Cotton Oil Press,* **10,** No. 5, 25 (1926).

"How Cottonseed Deteriorates Through Moisture," J. Malowan, *Oil and Fat Ind.,* **4,** 127 (1927).

"How Should a Cotton Seed Storage House be Built?" H. O. Fulson, *Oil Miller and Cotton Ginner,* **31,** No. 4, 17 (1927).

"Storage System for Seed and Hulls Affords Many Economies (Concrete tanks)," *Oil and Fat Ind.,* **4,** 45 (1927).

"The Proper Handling of Seed to Prevent it from Heating," T. J. McNulty, *Cottonseed Oil Mag.,* **45,** No. 9, 30 (1927).

"Scientific Moisture Control for Cottonseed Oil Mills," J. E. Roberts, *Cottonseed Oil Mag.,* **46,** No. 7, 17 (1926).

"Cleaning Cotton Seed," C. B. Richardson, *Cotton Oil Press,* **11,** No. 11, 32 (1927).

"Steel Buildings for Cotton Seed Storage in Oil Mills," O. Adams, *Oil Miller and Cotton Ginner,* **34,** No. 5, 13 (1929).

"Change of Moisture Content of Cottonseed Products with Respect to Atmospheric Conditions," E. Freyer, *Oil and Soap,* **10,** 166 (1933).

"Additional Data on the Relation of Moisture Content to Increase of Free Fatty Acid Content of Cottonseed in Storage," E. Freyer, *Oil and Soap,* **11,** 162 (1934).

"Improved Methods of Handling and Storing Cottonseed," R. Y. MacIntyre, *Cotton and Cotton Oil Press,* **38,** No. 25, 3 (1937).

Description. Depending upon the variety, cottonseeds are covered with short fibers or are bald. Sea Island and Egyptian cottons are the chief varieties with bald seeds, but the fuzzy-seeded varieties frequently produce some bald seed.

Cottonseeds having a moisture content from 6 to 12 per cent contain 3 to 4 per cent of ash, 16 to 26 per cent of proteins, 24 to 31 per cent of carbohydrates, 14 to 25 percent of oil and 14 to 21 per cent of crude fiber. The seeds contain little or no starch. American cake and meal contain the following percentages of constituents when made from decorticated seed: Moisture 7 to 9, oil 6.5 to 7, proteins 32 to 42, carbohydrates 28 to 33, crude fiber 10 to 15, and ash 4.8 to 6.

A typical analysis of commercial cottonseed hulls is as follows: Moisture 8 to 9, ash 2.6, proteins 3.5, carbohydrates 38.0, crude fiber 46, and oil 1 per cent.

The hulls vary from about 40 to 55 per cent and the kernels or meats from about 44 to 61 per cent of the seed. The hulls contain from 0.3 to 1 per cent of oil and the kernels from 28 to 40 per cent. Chemists and oil millers should consult "Correlating the Variables in Cotton Seed," by G. S. Meloy, *Chemical Markets,* **23,** 448 (1928).

The oil and protein content of the seed vary with the variety of cotton, locality, soil, seasonal and climatic conditions. As a rule seed from the long-staple cottons have the higher oil content. Sievers [*Oil and Fat Ind.,* **1,** 56 (1924)] found the oil content of seed grown at American experiment stations to vary from 18.6 to 27.8 per cent. The average oil content of the entire American crop is about 19.5 per cent, whereas that of the entire Indian crop is about 18.5. Where Egyptian and Sea Island cottons are the chief crops, the oil content will average from about 22 to 24 per cent.

Outside of the irrigated semi-arid regions, the moisture content of cottonseed is subject to wide variations even during the same season; consequently, for comparative purposes, the oil and protein percentages should be calculated on the moisture-free basis, and this fact so stated.

Creswell and Bidwell (*U. S. Dept. Agric. Bull.,* **948,** 1921) collected the data from over 44,000 analyses of cottonseed that were made for oil mills in the United States. This study showed that between 1916 and 1919 the average production of oil per ton of seed was 306 pounds, The production ranged from 284 pounds in Texas and Oklahoma to 322 for, Mississippi; all other producing states averaged about 300 pounds. The average oil production varied in different years, and ranged from 290 pounds in 1918-1919 to 314 pounds in 1916-1917 season, which indicates seasonal effects. Also, these authors call attention to the fact that the proportions of oil and meal obtained vary widely in different localities. This variation is due to differences in climate, soil, season, fertilizer, and the variety of cotton grown.

Attention is called to the following references:

"The Composition of Cottonseed Meal and Cotton Seed," G. S. Fraps, *Texas Agric. Exp. Sta. Bull.* **189,** 1916.

"Quantitative Determination of Lint and Cotton Seed," T. L. Rettger, *J. Oil and Fat Ind.,* **3,** 135 (1926).

"Cotton Seed (Analyses and Yields of Products)," T. C. Law, *Cotton Oil Press,* **2,** No. 4, 41 (1918).

"Barrow-Agee Annual Seed Report," *Cotton Oil Press,* **3,** No. 8, 38 (1919). Subsequent annual seed reports by Law and Barrow-Agee Laboratories, covering monthly and yearly averages will be found in later volumes of the *Cotton Oil Press.*

"Cotton Seed," M. T. Harrington, *Texas Agric. Exp. Sta. Bull.* **374,** 1928, is a comparative study of the seed from 73 varieties of cotton.

"Rainfall and Oil Content (of cotton seed)," Barrow and Agee, *Cotton Oil Press,* **2,** No 8, 44 (1919).

"Grading Cottonseed by Net Kernel and Fatty Acid Content," G. S. Meloy, *Oil and Fat. Ind.,* **4,** 307 (1927).

"Standard Grading of Cottonseed," G. S. Meloy, *Cotton Oil Press,* **13,** No. 2, 43-8 (1929).

"Description of Basis Cotton Seed and Formulas for Determining Value Index in Relation to Basis Seed Quotations," G. S. Meloy, *Oil and Fat Ind.*, **7**, 135 (1930).

"New Cottonseed Sampler," *Cotton Oil Press*, **14**, No. 3, 30 (1930).

"Chemistry of the Cottonseed," *Cotton Oil Press*, **15**, No. 8, 33 (1931).

"Cottonseed . . . New Uses and Markets," A. L. Ward, *Cotton and Cotton Oil Press*, **37**, No. 43, 3 (1936).

"Chemistry in the Development of the Cottonseed Industry," C. B. Cluff, *Oil and Soap*, **14**, 234 (1937).

"Pot Cook Cellulose Yield." Comm. Report, *Oil and Soap*, **17**, 243 (1940). The method is for the determination of cellulose content of lint and hull fiber.

Cottonseed Proteins. The protein content of the whole seed varies from about 16 to 28 per cent, the more common range being from 19 to 24 per cent. The discussion of the various investigations made on the isolation and composition of the proteins, as well as the digestibility studies made with animals and *in vitro*, are beyond the scope of this work, but for those interested in these subjects the following references are given:

T. B. Osborne and G. G. Voorhees, *J. Am. Chem. Soc.*, **16**, 778 (1894).

E. Abderhalden and O. Rostoski, *Z. physiol. Chem.*, **44**, 265 (1905).

W. G. Friedman, *J. Biol. Chem.*, **51**, 19 (1922).

T. S. Hamilton, W. B. Nevens and H. S. Grindley, *J. Biol. Chem.*, **48**, 248 (1921).

D. B. Jones and F. Csonka, *ibid.*, **54**, 673 (1925).

"The Comparative Nutritive Value of Proteins of Linseed and Cotton Seed," R. M. Betke and others, *J. Agric. Research*, **36**, 855 (1928).

"The Quality of Proteins" is ably discussed by D. B. Jones in the *Cotton Oil Press*, **7**, No. 10, 34 (1924).

References to digestibility studies of cottonseed and isolated proteins:

T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, **29**, 289 (1917)

H. C. Waterman and C. O. Johns, *ibid.*, **50**, 9 (1921).

Waterman and D. B. Jones, *ibid.*, p. 285.

Jones and Waterman, *ibid.*, **52**, 357 (1922), and **56**, 501 (1923).

Jones and Waterman state that the globulin fraction of cottonseed proteins is practically 100 per cent digestible, but when one per cent of gossypol is present the digestibility is 85 per cent, and this figure is close to that (83) found for the protein digested in the form of cottonseed meal and flour. The combination of the gossypol and protein formed in the manufacture of cake is fortunately indigestible, thereby protecting animals that are fed with cake or meal from the toxic action of the gossypol.

Gossypol. The toxic phenolic substance present in raw cottonseed was first isolated by Marchlewski [*J. prakt. Chem.*, **60**, 84 (1899)] and named gossypol. E. W. Schwartze and C. L. Alsberg [*J. Agric. Research*, **25**, 285 (1923)] examined 39 samples of seed, representing 12 varieties of cotton, from the more important producing sections of the United States. They found the kernels contained from about 0.4 to 1.2 per cent and they concluded that the gossypol content appeared to depend upon factors other than that of variety. A variation of 200 per cent was found in different samples of seed of one variety from

the same plantation, but from crops of different seasons. However, there appeared to be a direct relationship between the gossypol and oil content: the higher the oil content, the larger the proportion of gossypol. This study indicated that seed from the Southwest tended to be low in gossypol, those from the Southeast somewhat higher, and those from the Pacific coast regions, the highest.

Before discussing the more recent investigations of gossypol, mention should be made of that by F. E. Carruth [*J. Am. Chem. Soc.*, **40**, 647 (1918)], in which he found that gossypol was a phenolic compound and to which he assigned the formulas $C_{30}H_{30}O_9$ or $C_{30}H_{28}O_9$. When crystallized from acetic acid, it contained one molecule of loosely bound acetic acid which could be removed by dissolving it in ether, adding water and then removing the ether by evaporation. He also prepared the dianilide of gossypol.

E. P. Clark [*J. Biol. Chem.*, **75**, 725 (1927)] devised a method for obtaining pure gossypol, and determined the formula to be $C_{30}H_{30}O_8$. He obtained it in the form of a bright, canary yellow, crystalline powder. It is soluble in ether and acetone, but only sparingly soluble in the other organic solvents. It is insoluble in water but dissolves readily in dilute ammonium hydroxide, sodium carbonate and the fixed alkalies; but when an excess of the latter is used, it is slowly decomposed. It has long been known that when dissolved in concentrated sulfuric acid, gossypol gives a deep scarlet color. Clark found that different preparations of gossypol, equally pure, showed a range of melting points from 205° to 214° C. The so-called acetate from various preparations melted at 189° C. and the dianilide at 302° to 303° C. He [*J. Biol. Chem.*, **76**, 229 (1928)] also showed that the gossypol in cottonseed meal designated by Carruth (*loc. cit.*) as *d*-gossypol was not an oxidation or hydrolytic product, but that in the process of manufacture of the meal, the gossypol combined with the free amino acid groups of the cottonseed proteins and that it could be recovered unchanged in nature from this combination. In the study of the structure of gossypol, which as yet has not been entirely elucidated, Clark has prepared a number of derivatives including those from various oxidation products from gossypol, for which the following references should be consulted: *J. Biol. Chem.*, **77**, 81 (1928); **78**, 150; *J. Am. Chem. Soc.*, **51**, 1475 and 1479 (1929).

The results of more recent extensive investigations of R. Adams and co-workers on the structure of gossypol are described in *J. Am. Chem. Soc.*, **59**, 1723, 1729, 1731, 1736 (1937), and many installments in volume 60.

The extraction of gossypol with various ethers has been investigated by J. O. Halverson and F. H. Smith [*Ind. Eng. Chem. (Anal. Ed.)*, **9**, 516 (1937)]. Variations in the gossypol and oil content of cottonseed are discussed by W. D. Gallup, *Oil and Soap*, **13**, 191 (1936). For the determination of gossypol in crude cottonseed oil, see Halverson and Smith, *Ind. Eng. Chem. (Anal. Ed.)*, **13**, 46 (1940).

E. P. Clark, E. M. Nelson and D. B. Jones [*Oil and Fat Ind.*, **6**, No. 7, 15 (1929)] have shown that gossypol, although very toxic as it occurs in raw cottonseed, is not so in cottonseed cake or meal since it combines with protein in such a manner that it is rendered harmless. If any free gossypol is present, the quantity is much too small to cause any harmful effects upon animals fed a normal quantity of either the cake or meal. The ill effects that sometimes occur when these products are fed in too large quantities have been ascertained to be due to the proteins, which in themselves are not adequate to maintain complete growth. Consequently, this deficiency of cottonseed meal must be supplied by the addition of other products. As is well known, animals fed with properly supplemented rations of cottonseed meal grow normally and maintain indefinitely a vigorous healthy condition.

Cottonseed Products. Those not engaged in the manufacture of these products sometimes desire to know the quantity that can be obtained from a ton of the seed. The quantity of the products obtainable varies according to the composition of the seed and the method of manufacture. The following three examples give the pounds of products per ton (2000 lbs.) of seed and represent American manufacture.

	1	2	3
Oil	320	290	263
Cake	1000	969	960
Hulls	465	508	640
Linters	95	102	50

The difference between the weight of the products and 2000 pounds is the manufacturing loss, which consists chiefly of moisture, as the weights given are based on a ton of cleaned cottonseed from upland varieties of cotton.

According to the Barrow-Agee Seed Report [*Cotton Oil Press*, **5**, No. 8, 18 (1922)] the 13-year averages of the results for the analyses of seed from Arkansas, Kentucky, Louisiana, Mississippi, Tennessee, and Texas were as follows: Ammonia 3.55, oil 19.36, and moisture 11.47 per cent. For the same period of time the average yield of products per ton of seed was 593 pounds of hulls and linters, 952 pounds of 7 per cent cake, and 41.6 U. S. gallons of oil.

Oil Mills and Equipment. It is beyond the scope of this volume to discuss the location, building and equipment of cottonseed or other oil mills. There are engineering firms that make a specialty of giving complete service, when desired, in the building and equipment of oil mills and refineries. Much information on equipment will be found in the manufacturers' catalogs. One of the first things to be decided is whether hydraulic presses or Anderson expellers are to be used and also, whether whole or decorticated seed is to be pressed. After these questions are decided, the selection of the necessary equipment can be made. However, special attention should be given to coordination of the equipment in order to avoid having various units too small or

too large in relation to the others. Many mills suffer from one or more of these defects.

Considerable information will be found in the following references:

"Expeller Milling Methods," H. P. Keaney, *Oil Miller and Cotton Ginner*, **32**, No. 6, 21 (1928).

"How to Equip a Cottonseed Oil Mill for Most Efficient Service," *Cottonseed Oil Mag.*, **40**, No. 3, 13 (1924).

"Application of Hydraulic Pressure in Oil Mills," J. Davidson, *Cotton Oil Press*, **10**, No. 4, 31 (1926).

"Ramifications of the Oil Industry," T. Auchens, *Oil and Fat Ind.*, **5**, 302 (1928).

"Visions of Ideal Oil Mill," W. L. Skees, *Cotton Oil Press*, **12**, No. 2, 71 (1928).

"Pointing the way to Profits," W. L. Skees, *ibid.*, No. 6, 29 (1928), discusses mill construction, equipment and operation.

"The Diesel Engine in Cottonseed Oil Mills," O. Adams, *Oil Miller and Cotton Ginner*, **33**, No. 4, 11; No. 5, 11 (1928).

"Oil Mill Management," *Cottonseed Oil Mag.*, **57**, No. 5, 11 (1929).

"Central Power Systems," H. F. MacMillin, *Oil Miller and Cotton Ginner*, **33**, No. 4, 20; No. 6, 22 (1928).

"Cottonseed Products Manufacturing" (Mills, equipment and manufacturing discussed), J. P. Greenwood, numerous installments, beginning in *Cotton Oil Press*, **11**, No. 9, 35 (1928), Vols. 12 and 13.

"Construction and Operation of Modern Ginning Systems," *Oil Miller and Cotton Ginner*, installments beginning **29**, No. 3, 22 (1926), to Vol. 31, No. 3.

"Waste of Fuel in Power Plants," E. E. Greening and C. J. Gaskell, *Cotton Oil Press*, **12**, No. 61, 31 (1928).

"Utilization of Waste from Cotton Gins," C. L. Fly, J. Harper, and O. M. Smith, *Cotton Oil Press*, **13**, No. 5, 39 (1929).

"Mechanical Processing of Cottonseed," W. R. Woolrich and E. L. Carpenter, 154 pages, Eng. Exp. Sta. Univ. Tennessee, Knoxville, 1935.

"Mechanical Processing of Vegetable Oils," W. W. Moss, *Trans. Am. Soc. Mech. Engrs. Pros.*, **59**, 715 (1937).

"Solvent Extraction of Cottonseed," S. S. Iljin, Abst. in *Oil Col. Trades J.*, **94**, 179 (1938) discusses extraction of oil and manufacture of flour from meal in the U.S.S.R.

"An Investigation of Invisible Expeller Losses in Expeller Operations," R. H. Pichard, *Oil and Soap*, **15**, 259 (1938).

"Cottonseed Processing Links Agriculture and Industry," J. Leahy, *Southern Power and Industry*, **57**, No. 10, 37 (1939).

"Modern Oil Milling," L. H. Downs, *Oil Col. Trades J.*, **95**, 715 (1939).

"A chronology of Cottonseed Technology," L. Bass and H. S. Alcott, *Chem. Met. Eng. News*, **18**, 139 (1940).

Manufacture of Oil and Cake. Seeds either too wet or too dry do not mill properly. Blowing humid air through the seed is considered the best procedure for increasing the moisture content, which should probably be between 8 and 11 per cent so that they can be efficiently decorticated.

Regardless of the methods of manufacture that are to be used, the first step is to clean the seed thoroughly. To remove trash, the seeds are passed first through revolving screens which retain the larger pieces, then over magnets to separate nails, etc., and finally over shaking screens and through cyclone cleaners to remove the sand and dust. The cleaned seeds (freed as completely as possible from bald seeds, which dull the saws) are fed into the delinters, which consist of a series of fine circular saws set close together on a rapidly revolving shaft. At the back of each delinter a long cylindrical brush runs so close to the

saws that it catches the cut fibers or linters and passes them to a reel at the back of the brush. The linters collect on the reel into a compact felt that looks like cotton batting. The linters, after being baled, are sold upon the basis of their quality to manufacturers of guncotton, films, artificial silk, mattresses, paper, etc. Some firms in the United States purchase linters of certain grades and prepare the cellulose, which they sell in a form ready for nitration, acetylation, etc. ["Relationship of Linters to Chemical Industries," S. E. Seaman, *Cotton Oil Press,* **13,** No. 5, 34 (1929)]. Depending upon the market price, the "cut" of linters from the seed of upland types of cotton varies from 75 to about 150 pounds per ton of seed ["Delinting and Care of Linters," C. S. McKinley, *Oil Miller and Cotton Ginner,* **36,** No. 6, 18 (1930)].

When whole seeds are to be pressed, the next step is to crush, heat and press in hydraulic presses; or in the case of expeller mills, the seeds are crushed in a disc grinder and dried in rotary hot air or grain driers so as first to reduce the moisture content to about one per cent, before pressing in the newer types of expellers.

When decorticated seeds ("meats") are to be pressed, the seeds, after delinting, are passed through "hullers" set to crack the larger seeds, and delivered onto shaking screens, through which the separated kernels or meats fall. The unbroken seeds and hulls are passed through other hullers set so as to crack the smaller seeds, and then onto shaker screens. If necessary, a third passage through the hullers is made. After the removal of the separated meats, the hulls are sent to the beaters and then to the shaker screens. This treatment leaves the hulls almost free from oil-bearing material ["Separation and Preparation of Cottonseed Meats from Hullers to Attrition Mill," J. P. Dickinson, *Oil Miller,* **16,** No. 2, 19 (1922)].

The hulls are used for bedding and feed for stock, and sometimes as fuel; but increasing quantities, after the removal of the hull fiber by machines designed for this purpose, are ground to make hull bran which is now used in many mills for reducing the protein content of the meal to the desired percentage. The older practice is to have sufficient hulls with the meats to give the desired protein content in the meal. The hull fiber is baled and sold to those manufacturing cellulose derivatives and paper [O. Kress, *Cotton Oil Press,* **3,** No. 12, 33 (1930)]. Reference: "Fuel Value of Cottonseed Hulls," *Cotton Oil Press,* **10,** No. 9, 20 (1927).

Expeller Mills. These plants should have the expeller made for handling cottonseed or decorticated seed. Some crude mills crush and press the delinted seed, whereas others press decorticated seed or "meats." The separated meats are ground to a coarse meal, dried by a rotary grain dryer or other suitable device and transferred to the steam-heated temperer, where just sufficient water is added to give a satisfactory cake when the meal is pressed. The water is added by a device which distributes it evenly throughout the meal, which is agitated in the temperer. From the temperer, the meal is fed by a feeding device into the expeller. Experience has shown that for good

extraction of oil with the new type of expeller, it is important to dry the meats (or seed) previously until the moisture content is reduced to 2 per cent or less.

As soon as the oil is expressed it is filtered by means of a filter press and transferred to the storage tanks. The misleading term "cold-pressed" cottonseed oil is still used to designate the oil expressed by expellers from the time when the whole, unheated seeds were pressed in the early type of expeller; after these had operated a short time, both the oil and cake were discharged hot because of the friction of the seed in the barrel of the expeller. This product should be called "expeller oil" to differentiate it from hot-pressed hydraulic oil, for the information of the refiner, as expeller oil requires somewhat different treatment in the refining with caustic soda.

Hydraulic Mills. In the United States, these mills press only decorticated seed, but in European and some other countries, many mills still press undecorticated seed. Both cage and steel box frame presses are used, but in this country few cage presses are in operation.

The separated meats are usually passed through oil seed rolls and delivered for convenience above the press room over the "cooker." "Cooking" of the meal is one of the most important operations in the expression of oil by the hot process. Much experience and judgment are required in the cooking in order to get a maximum yield of oil of the best possible grade. The meal should be "cooked" from 215° to 220° F. for the best results.

Although the temperature and time for cooking can be regulated, moisture is the elusive thing which accounts for most of the difficulties encountered. The variation in the character and moisture content of different lots of seed complicates cooking, and consequently no fixed rules can be used that will give the same results with all classes of cottonseed. For the best results, it is very important that the meal should be cooked uniformly throughout the batch and that the moisture content should be approximately between 8 and 10 per cent.

Attention is called to J. Davidson's instructive article on cooking with superheated steam, in the *Oil Miller and Cotton Ginner,* **32,** No. 6, 15 (1928). This method, which is being used in several mills, appears to offer several advantages over older methods. A smaller quantity of steam is used, the press cake is of higher color, and the oil gives a smaller refining loss than that obtained from the same seed, using the customary method for cooking the meats. For details of equipment and procedure the original article must be studied. A similar article is in *Cotton Oil Press,* **12,** No. 7, 18 (1928).

Attention is called to the following references:

"Cooking Meal in a Modern Mill," J. W. Stephens, *Cottonseed Oil Mag.,* **38,** No. 6, 39 (1922).

"Process for Humidifying Cotton Seed Meats," F. B. Wells, U. S. Patent 1,707,949.

"Proper Cooking of Meal," S. J. Ellis, *Cotton Oil Press,* **4,** No. 9, 57 (1921).

"Symposium on Cooking Meal," *Oil Miller,* **21,** No. 2, 11 (1925).

"A Chemist's View on Cooking Meal," T. B. Caldwell, *Oil Miller,* **21,** No. 3, 11 (1925).

"Report of Committee on Crude Mill Operations," *Oil and Fat Ind.,* **5,** 134 (1928); *ibid.,* **6,** No. 7, 20.

"The Press Room: Its Equipment and Operation," J. H. Fulford, *Oil Miller and Cotton Ginner,* **36,** No. 6, 33-36 (1930).

"Results of Recent Experiments in Oil Milling," M. K. Thornton, *Oil Miller and Cotton Ginner,* **36,** No. 6, 15 (1930).

"Problems in Processing of Cottonseed Meats," W. R. Woolrich and E. L. Carpenter, *Chem. Met. Eng.,* **40,** 291 (1933).

"What Happens to Cottonseed Meats When They are Rolled and Cooked," R. G. Reeves and J. O Beasley, *Cotton and Cotton Oil Press,* **38,** No. 49, 3 (1937).

"Pressure Cooking Contributes Increased Cottonseed Processing Profits," R. B. Taylor, *Chem. Met. Eng.,* **44,** 478 (1937).

"The Pressure Cooking of Cottonseed Meats and Its Application to the Expeller," R. H. Pickard, *Oil and Soap,* **15,** 261 (1938).

"Higher Cotton Oil Yield," *Ind. Chemist,* **44,** 142 (1939) discusses tests made at Eng. Exp. Sta. Univ. of Tenn.

"Cottonseed Pressure Cooking Research," R. W. Morton, *Mechanical Eng.,* **62,** 731 (1940), *C. Abs.,* **34,** 8315 (1940). It discusses work on the development of a continuous pressure cooker for use with expellers.

"Processing Oil Seeds and Nuts. II. New Methods and Equipment." J. F. Leahy, *Southern Power and Industry,* **59,** No. 3, 63. *Chem. Abs.,* **35,** 3113 (1941). Discusses a new cooker-expeller and gives flow sheets of oil mill operations.

"Solvent Extraction of Cottonseed Oil. Effect of Cooking on Yield." H. S. Alcott, *Ind. Eng. Chem.,* **33,** 611 (1941). Most of article deals with soybean extraction methods.

"Solvent Extraction of Cottonseed Oil," H. S. Alcott, *Cotton and Cotton Oil Press,* **43,** No. 7, 24 (1942).

"Recovery of Oil from Whole Cotton Plant," E. L. Powell and F. K. Cameron, *Ind. Eng. Chem.,* **34,** 358 (1942). Describes a solvent extraction procedure.

(The press commonly used in America is known as the steel box frame hydraulic press. It consists of a series of horizontal steel plates, approximately 14 inches wide and 34 long, set one above the other, about 5 inches apart when the press is wide open. These perforated or channeled plates are provided with close-fitting steel sides or frames, so that the whole machine is really a series of boxes without ends, piled one upon the other, the lowest resting on the hydraulic piston. Above the top frame a heavy iron plate is fastened to the hydraulic piston cylinder by 4 heavy vertical steel columns, which serve as guides for the sliding frames or boxes.)

Pressing. When the meal is cooked, a measured quantity is dropped upon a strip of press cloth placed in the open cake former—a press with a steel block containing in its upper surface a shallow depression the size of a single press box. It is so constructed that after the meal has been placed upon the press cloth, and the two ends turned up over the charge, pressure can be applied and the cake, now covered with cloth except on its two long sides, can be subjected to a preliminary squeezing to make it compact. Pressure is applied to the charge in the cake former for an instant and then released. A steel spatula the width of the cake is slid beneath the cake, which is removed in its cloth from the cake former and placed in the lowest frame or box of the press. One after the other of the frames are thus charged until the press is filled. The compressed air is then turned on gradually and the piston or ram forces the frames upward, each against the one above it. The

oil squeezed through the cloths flows over the sides of the press into the gallery around the bottom frame and out through the trough into the settling tank. So perfectly has every detail for the charging and operation of these presses been planned that they are often filled, pressed, and discharged in half an hour. The pressure used varies from 3000 to about 4000 pounds per square inch. Cottonseed oil is used in the hydraulic cylinder of the press. The compressed air is supplied to the oil in the press either directly from specially designed compressors, or from the pressure accumulator tank system.

After the removal of the cakes from the presses, they are wheeled in trucks to the stripper, which removes the press cloths. The soft ends of each cake are cut off by the trimmer and returned for repressing. The trimmed cakes are sent to the storehouse or to the cake breakers. (Some broken cake, assorted into several different sizes, is prepared for feeding on cattle ranges.) After breaking, the cake is ground into meal. The protein content of the cake or meal has been, and still is, regulated to some extent by controlling the quantity of hulls that are allowed to remain with the meats. It has become more customary to reduce the protein content, when desired, by the addition of a suitable quantity of hull bran.

Meal, that is not suitable for feeding stock, for one reason or another, is used as a fertilizer on farms or on lawns, gardens, etc.

Cottonseed meal contains approximately the following percentages of constituents: Nitrogen 6.5, potash (K_2O) 1.5, and phosphoric acid (P_2O_5) 2.5.

Attention is called to the following instructive references:

"Why Composition of Meal Varies," T. C. Law, *Cotton Oil Press,* **9**, No. 10, 21 (1926).

"Protein in Seven Per Cent Cottonseed Meal," *ibid.*, **1**, No. 10, 39 (1918).

"Cottonseed Meal as a Human Food," J. E. Halligan, *ibid.*, **4**, No. 1, 33 (1920).

"Meal and Hulls for Feeding," J. E. Halligan, *ibid.*, **3**, No. 8, 30; No. 9, 29 (1919).

"The Use of Cottonseed Meal to Increase the Percentage of Fat in Milk," A. C. McCandlish, *J. Dairy Science,* **4**, 310 (1921).

"Cotton as a Food Crop," D. Wesson, *Oil and Fat Ind.*, **3**, 121 (1926).

"The Allison Cottonseed Flour as Human Food," G. A. Baumgarten, *Cottonseed Oil Mag.*, **40**, No. 10, 28 (1924).

"Cottonseed Meal for Horses and Mules," G. S. Fraps, *Cotton Oil Press,* **8**, No. 7, 21 (1924).

"New Things in Nutrition," F. B. Morrison, *ibid.*, No. 2, 39.

"Effect of Cottonseed (Meal) Feeding on Butter Fat," J. F Geisler, *Oil and Fat Ind.*, **3**, 115 (1926).

"Present Status and Results of Cottonseed Meal Feeding Investigations," R. S. Curtis, *Cotton Oil Press,* **9**, No. 10, 25 (1926).

"Cottonseed Meal, the Cheapest Source of Protein," A. M. Soule, *Ga. Coll. Agric. Bull.* **325**; *Cotton Oil Press,* **10**, Nos. 10 and 11 (1927).

"What 'Standard' Means in Dollars and Cents," L. Johnson, *ibid.*, **8**, No. 7, 41 (1924). The working mill standards referred to are obtained by dividing the percentage of the oil in the press cake by that of the ammonia.

"Proper Preparation of Crude Vegetable Oils," J. P. Harris and B. N. Click, *Cotton Oil Press,* **11**, No. 5, 33 (1927).

"Cottonseed Meal Studies (Feeding Exps.)," C. H. Hunt, *Ohio Agric. Exp. Sta. Bimonthly Bull.* 158 (1932).

"The Control of Meal Grinding through Cake Analysis," J. L. Mayfield. *Oil and Soap,* **10**, 171 (1933).

"Interpretations of Oil Mill Products Analyses," A. K. Schwartz and E. Freyer, *Oil and Soap*, **11**, 138 (1934).
"Hydrolytic Treatment of Cottonseed Hulls," W. H. Baldwin and J. A. LeClerc, *Oil and Soap*, **16**, 178 (1939).

When cage hydraulic presses are used, the cage is moved to the charging and discharging equipment. No press cloth is employed, but a plate is placed between each two cakes. The charged cage is then returned to the press where the oil is expressed.

Storage of Crude Oil. Failure to separate press foots (meal) as quickly as possible from the crude oil and to store it in clean tanks still results in a large yearly monetary loss, due to the deterioration of the oil, which results in increased refining losses, although attention has been repeatedly called to these facts. References are as follows:

"Deterioration of Crude Oil," R. E. Montgomery, *Cotton Oil Press*, **3**, No. 1, 17 (1919).
"The Damaging Effect of Meal Settlings in Crude Oil," E. R. Barrow, *ibid.*, **11**, No. 7, 21 (1927); also see *Oil and Fat Ind.*, **4**, 383 and 387 (1927).
"A Chemist's Views on Grading Cottonseed and Storage of Crude Oil," G. W. Agee, *Oil Miller and Cotton Ginner*, **30**, No. 5, 18 (1927).
"A Study of the Possible Catylytic Effect of Some Metals and Alloys on the Changes in Crude Cottonseed Oil during Storage," F. S. Robertson and J. G. Campbell, *Oil and Soap*, **12**, 234 (1935).
"Quality Changes in the Industrial Storage of Crude and Refined Cottonseed Oil," R. R. King, *Oil and Soap*, **18**, 16 (1941).

As already mentioned, the usual practice is to allow the crude oil to run from the presses into settling tanks; when the tank is filled, the oil is allowed to stand until the press foots have settled. At this stage, the clarified oil should be drawn off without delay into a clean storage tank. An increasing number of mills are filtering the crude oil directly after it is expressed. Some add filter aids, but others do not. Apparently, in the case of expeller crude oil, no difficulties have been encountered in filtering it through filter presses without the addition of any "aid." Whether or not hydraulic pressed oil requires a filter aid, as has been claimed, remains to be determined. At present, it appears customary to use filter aids with this oil. The filtration of crude oil with filter aids is discussed by Harris and Glick in the *Cotton Oil Press*, **12**, No. 4, 39, and No. 6, 37 (1928), and F. L. Horine in *Oil and Fat Ind.*, **4**, 55 and 250 (1927). Harris and Glick state that when crude oil is warmed to 32° to 38° C. and agitated with 0.5 to 1 per cent of activated char then filtered, the refining loss is less than that of the unfiltered oil. With this treatment no bleaching was observed, but the refined oil upon bleaching in most cases gave a lighter-colored oil than that from unfiltered oil. References are as follows:

"The Process of Filtering Crude Cottonseed Oil," H. O. Fulson, *Oil Miller and Cotton Ginner*, **36**, No. 2, 17 (1930).
"Filtration of Crude Cottonseed Oil," R. H. Fash, *Oil Miller and Cotton Ginner*, **36**, No. 5, 20 (1930).

Crude Cottonseed Oil. Depending upon the method of manufacture and the quality, crude oil varies much in color. It may be red, amber, or nearly black. It has repeatedly been stated that the color of

the crude oil was chiefly due to gossypol, but the commercial product contains little gossypol. The color of the crude oil is due chiefly to resins and plant pigments. As a rule, oil pressed from damaged seed contains a larger quantity of resins than oil from sound seed. The grades of both crude and refined oil that are recognized in the United States are described in the current Book of Rules published by the National Cotton Seed Products Association. This book can be purchased from the Secretary, Santa Fe Building, Dallas, Texas.

Refining. To produce an edible oil, the "crudes" are refined by the caustic soda process, bleached, and deodorized. Before a refining is made, the chemist draws a sample, determines the quantity of free fatty acids, and with this information he proceeds to make several laboratory refining tests to determine what concentration of sodium hydroxide in water will give the best results. (*See* methods for testing crude oil.) The quantity of alkali used depends upon the amount of the free fatty acids in the oil. Then a sufficient quantity of caustic soda solution of the proper concentration is prepared for the large-scale refining. A weighed quantity of crude oil (10,000 to 120,000 lbs.) is transferred to the refining kettle—a tall, cylindrical (or rectangular) steel tank with conical bottom, provided with steam heating coils that extend part way up the sides, and a mechanical agitator.

The oil, if necessary, is warmed to about 30° C. (85° F.), the agitator started, and the correct amount of caustic soda solution gradually added from a lye tank above the kettle. After it has been agitated from 10 to 30 minutes, depending upon the character of the oil, the mixture is heated by the steam coils until the temperature is 43° C. (110° F.) to 49° C. (120° F.). At this stage the "break" occurs —the separation of the soap stock (refining foots) from the oil in the form of spongy masses or clots. The refiner dips a small sample from the kettle, from time to time, and examines it to determine when the "break" has taken place and the soap stock is in the proper condition for settling. At this point, the steam is shut off from the heating coils and the agitator is stopped. The nature and rate of agitation of the crude oil and caustic soda should be such that there is no violent beating or turmoil; otherwise undue emulsion of the oil will occur and it will be lost by entrainment in the soap stock. The speed of the agitator should be reduced somewhat just before and after the "break" takes place. The oil is allowed to stand until the soap stock has settled and become firm. The oil is carefully withdrawn with a swivel pipe or by gravity from the soap stock into a tank. If necessary, the oil is washed with warm water to remove the last of the soap, then dried. This oil is known as "summer yellow oil."

The composition of a typical soap stock is as follows: Moisture 45.6, neutral oil 18.7, fatty acids from soap 24, ash as sodium oxide 3.3, and non-fatty substances about 8 per cent. R. K. Brodie [*Oil and Fat Ind.*, **4**, 181 and 190 (1927)] collected from independent sources thousands of analyses of crude oil which included the percentage of free fatty acids as oleic acid, the refining loss, and the color of the refined

oil. They are grouped in the following table according to the free fatty acids in steps of 1 per cent (0.5 to 1.5), together with the average refining loss and coloring reading on Lovibond's color scale:

No. of Samples	Free Fatty Acids Per Cent	Refining Loss	Color 35 Yellow + Red
3,623	1	7.25	6.4
2,662	2	9.34	8.0
1,747	3	10.95	8.8
1,196	4	13.00	10.0
818	5	15.06	11.1
595	6	17.21	12.2
402	7	19.96	14.1

The soap stock is removed from the tank and sold, or it is heated in vats with water and a slight excess of sulfuric acid. The fatty acids and entrained oil which rise to the surface is collected, and is known as "acidulated soap stock."

When the price of oil is sufficiently high the soap stock is dissolved in water and centrifuged. The recovery of oil is difficult and a yield of 65 per cent of that present is considered good practice. The separated oil is returned to the refining kettle along with crude oil and the diluted soap stock from the separators is converted into the so-called acidulated soapstock. Reference: "Centrifugal Recovery of Cottonseed Oil from Soap Stock," E. E. Ayres, *Cotton Oil Press,* **4**, No. 3, 80 (1920).

Increasing use is being made of the continuous refining process. The thoroughly mixed crude oil and the caustic soda solution are brought together continuously (in the proper proportion) into the high-speed mixer chamber. From there, the mixture passes into a tubular heater where it is rapidly heated (45 to 55° C.) and then it flows into a super-centrifuge which separates the oil from the soap stock. For a given lot of crude oil, the refining loss is reported to be usually about one-third less than that of the batch-refining process.

Distilled Fatty Acids and Pitch. At the large refineries, the soap stock or acidulated soap stock is not sold, but is treated as follows: It is possible to saponify the neutral oil retained by the soap stock by heating the mixture with an excess of caustic soda, but the more customary procedure is to prepare acidulated soapstock. To this and an equal weight of water, 1.5 to 2 per cent of a Twitchell reagent (patented products made by sulfonating a mixture of oleic acid and aromatic hydrocarbons) is added. This mixture is agitated and heated by steam from perforated coils at the bottom of the vat, until the neutral oil is hydrolized or "split" as completely as possible (about 94 to 96 per cent). Then sufficient sulfuric acid is added to break the emulsion. When the fatty acids have separated, they are drawn off, washed free from mineral acid, and dried. The fatty acids are distilled in a specially designed "vacuum" still by the aid of superheated steam.

It is important that the fatty acids be as free as possible from neutral oil and thoroughly dried before distillation. Also, it should be observed that the distillation requires both experience and care, not only

to obtain satisfactory results, but to avoid the possibility of a serious accident, such, for example, as may result from the complete stoppage of the condenser with solidified acid. The distilled acids consist chiefly of oleic, linoleic, and palmitic acids, along with smaller quantities of stearic acid.

A still with a capacity of 15,000 pounds, is fed with fatty acids until from 50 to 70 thousand pounds have been added, before distilling down to tar or pitch. Whether this residue is soft or hard when cold depends on how far the distillation has been carried. After distillation is completed, the pitch is withdrawn while in the molten condition. The quantity of the still residue or pitch usually amounts to about 12 per cent of the weight of the original fatty acids. It consists of a mixture of lactones, hydroxy acids, unsaturated acids and hydrocarbons, polymerized products, and some neutral oil.

Frequently, the acids are redistilled in order to obtain a lighter-colored product. Toward the end of the first and second distillations, when the dark-colored decomposition products begin to come over, they should be collected separately from the major portion of the distillate. The distilled acids are cooled and pressed to separate, as much as possible, the liquid unsaturated acids. The liquid fraction can be further cooled and the saturated acids which separate can be recovered by filtration and pressing. At some plants, the distilled acids, as obtained, are sold to soapmakers or other firms dealing with fatty acids. The pitch is used chiefly in the manufacture of paint, insulating and roofing materials. For further information, the following references may be consulted.

"Heat Balance of a Distillation Plant for the Recovery of Fatty Acids from Cottonseed Foots (Soap stock)," Julius Alsberg, *Ind. Eng. Chem.*, **12**, 490 (1920).

"Operation of Fatty Acid Distillation Plants," O. H. Wuester, *Chem. Met. Eng.*, **25**, 651 (1921). This article discusses equipment, operation, yields, and costs.

"The Manufacture and Grading of Distilled Fatty Acids," J. W. Bodman, *Cotton Oil Press*, **5**, No. 3, 35 (1921). An illustrated instructive article dealing chiefly with equipment and its operation, including the preparation of the fatty acids for distillation and the uses of the resulting products. No grades are described.

"Oleines and Stearines," *Chem. Trade J.*, **83**, 289 (1928). This discusses the preparation of commercial grades of distilled fatty acids, and stearine pitch.

"Composition of Stearin Pitch and Reactions Occurring in the Condensation of Fatty Acids," H. Dubovitz, *Chem. Zeit.*, **47**, 616 (1923). *J. Soc. Chem. Ind.*, **42**, 896-A (1923)—38 lines; *Chem. Absts.*, **17**, 3424 (1923).

"Use of Fatty Acids of Cottonseed Oil in Manufacture of Cup Greases," *Chemicals*, **25**, No. 20, 9 (1926).

"Fatty Acid Recovery and Purification," Anon., *Soap*, **8**, No. 6, 65 (1932).

"Continuous Distillation of Fatty Acids," L. M. Tolman and S. Goranflo, *Oil and Soap*, **12**, 26 (1935).

"Heat Requirements for Fatty Acid Distillation," V. Mills and R. C. Daniels, *Ind. Eng. Chem.*, **26**, 248 (1934); equipment and operation are also discussed.

Bleaching of Alkali-refined Oil. The oil, freed as completely as possible from soap stock, is transferred to the bleaching kettle or tank, which is provided with an agitator and heating coils. The agitator is started and the oil is heated to 110° C. (220° F.) and held at this temperature until the moisture is removed. Depending upon the character

of the oil, from two to six per cent of fuller's earth is added. Also, it is not uncommon to add from 0.5 to 1 per cent of activated carbon or char. After agitating the mixture for 15 minutes or longer, it is filtered by means of filter presses, and the oil is transferred to a deodorizer or to storage tanks if it is to be held any length of time, and is deodorized just before it is to be delivered.

Depending upon its character, fuller's earth adsorbs from about 24 to 35 per cent of its weight of oil, whereas activated chars usually adsorb 50 to 60 per cent. The loss due to adsorption of the earth in bleaching usually ranges from 0.2 to 0.5 per cent of the oil treated.

Attention is called to the following references:

"Influence of Physical Characteristics of Fuller's Earth on Its Bleaching Power," A. W. Putland, *Cotton Oil Press*, **6**, No. 7, 34 (1922).

"The Oil Saturation Value of Bleaching Earths and Carbons," H. S. Bailey and J. H. Allen, *ibid.*, **7**, No. 8, 36 (1923).

"Adsorption and Catalysis in Fuller's Earth," E. K. Rideal and W. Thomas, *J. Chem. Soc.*, **121**, 2119 (1922).

"Some Notes on the Action of Fuller's Earth on Vegetable Oils," D. Wesson, *Cotton Oil Press*, **7**, No. 6, 28 (1923).

"Bleaching Studies on Cottonseed Oil," F. C. Vilbrandt and H. J. Bankston, *J. Oil and Fat Ind.*, **1**, 71 (1924).

"Explanation of How Fuller's Earth Bleaches Oils," J. D. Haseman and R. C. Wallace, *Cotton Oil Press*, **7**, No. 11, 37 (1924).

"Bleaching Action of Fuller's Earth on Oils," B. Newmann and S. Koler, *Z. angew. Chem.*, **40**, 337 (1927); *Brit. Chem. Absts.*—B, **1927**, 493.

"The Determination of Small Amounts of Free Sulphur in Bleaching Earth," J. L. Schille and K. L. Alexander, *Oil and Soap*, **19**, 87 (1942).

"Determining Bleaching Loss Coefficients" (a laboratory test for oil retention of bleaching earths and carbons), A. S. Richardson, J. T. R. Andrews, and R. G. Folzenbogen, *Oil and Fat Ind.*, **6**, No. 9, 19 (1929).

"Preparation of Fuller's Earth," W. C. Phalen, *Chem. Met. Eng.*, **21**, 469 (1919).

"Bleaching of Oils and Fats," *Chem. Trade J.*, **68**, 767 (1921). This article discusses the use of silicate earths, including Frankonite, Silitonite, and Tonsil.

"Commercial Preparation and Use of Fuller's Earth," L. E. Mallory, *Chem. Met. Eng.*, **26**, 1074 (1922).

"The Bleaching of Edible Oils with Earths," E. Bergner, *Seifensieder Ztg.*, **50**, 551 and 563 (1923). An instructive contribution.

"Bleaching Oils and Fats with Benzoyl Peroxide," A. Bolis, *Chem. Absts.*, **17**, 3105 (1923).

"Bleaching of Oils and Fats, A Colloid Chemical Problem," H. T. Twisselmann, *Seifensieder Ztg.*, **51**, 351 (1924); *Chem. Absts.*, **19**, 1061 (1924). States that capillarity, surface tension, and coagulation temperature of colored substances are of importance and author claims that bleaching action is due to earth being electrically charged.

"Is the Bleaching Action of Fuller's Earth Due to Oxidation?" C. W. Benedict, *Oil and Fat Ind.*, **2**, 62 (1925).

"Application of Absorption Carbons to Crude Vegetable Oils," J. P. Harris, *Oil and Fat Ind.*, **4**, 329 (1927). This article, in addition to the treatment of other oils, describes two large scale experiments with cotton seed oil which was agitated for a half hour at 28° C. with a quarter per cent each of char and diatomaceous earth and after filtering the oils were found to give reduction in the refining loss of 1.8 per cent with a prime oil over that of the untreated oil.

"Oxidation Products of Fatty Oils (Oils from Bleaching Earth)" *Seifensieder Ztg.*, **55**, 100 (1928). The auto-oxidation of semi-drying oils in fuller's earth leads to extended polymerization of the fatty acids at double loads, but with little formation of hydroxy acids. On further oxidation some lower fatty acids and hydrocarbon-like substances are split off.

"Determination of Adsorption Power in the Discoloration of Oils with Bleaching Earths," A. Wiberg, *Z. angew. Chem.*, **41**, 1338 (1928); *Chem. Absts.*, **33**, 2312 (1929). The method and apparatus are described by which the equilibrium point is reached in 15 minutes. The method was tested with cacao butter and soy bean oil.

"Bleaching Earths," L. Kaulsky, *Chem. Absts.*, **23**, 3054 (1929). A very long abstract.

"Theory and Practice of Bleaching Fatty Acids," H. Odeen and H. D. Slosson, *Oil and Soap*, **12**, 211 (1935).

"Chemistry of Bleaching Earths," *Oil Col. Trades J.*, **90**, 1509 (1936).

"Extraction of Spent Bleaching Earths," H. Siek, *Oil and Soap*, **14**, 314 (1937).

"Activated Carbon in Oil and Fat Purification," E. A. Sigworth, *Soap*, **13**, No. 8, 24 (1937).

"The Influence of Bleaching Absorbents on the Stability of Edible Oils," J. W. Hassler and R. A. Hagbery, *Oil and Soap*, **15**, 115 (1938).

Deodorization. There are as many types of deodorizers as there are manufacturers, but the general principle of all of them is to distill the odoriferous impurities from the oil under diminished pressure with the aid of superheated steam. The higher the vacuum that can be obtained, the more readily and efficiently can the oil be deodorized. The importance of keeping the entire equipment tight and the vacuum pump in good working order is self-evident.

The deodorizer consists of a jacketed or a single-shell vessel or tank in which is installed a closed heating coil of suitable size. The tank is connected with the condenser through which the vapors are drawn. Through the coil, a special high-flash mineral oil, heated to the proper temperature by a furnace made for this purpose, is circulated, and when the cottonseed or other oil is heated to about 200° C., the superheated steam is turned into the perforated coil at the bottom of the deodorizer. By means of this indirect heating the charge of oil can be heated in about an hour. In the older systems, the deodorizers were connected with a coil which extended into a furnace, and through this the vegetable oil was circulated to and from the deodorizer by a pump until the main body of the oil was raised to the temperature at which it could be deodorized. Other types of deodorizers heat the oil by enclosed high-pressure steam coils. Depending upon the character of the oil, the temperature employed (usually from 200° to 225° C.), and the efficiency of the equipment, the time required for deodorization is variable; it may require only 3 to 6 hours, or very much longer. When the process is completed the vacuum is maintained on the oil until it is cooled to a temperature at which it will not be injured upon exposure to the air. In some plants after deodorization, the oil is withdrawn to a cooling tank so that another charge can be treated without undue delay. The deodorizers in use take charges from 5000 to 30,000 pounds of oil and the larger refineries have a battery of two or more units. When the process is properly conducted, the oil will be noticeably bleached and have practically no flavor. Loss due to volatile constituents in the deodorization of cottonseed oil ranges from 0.12 to 0.35 per cent, according to B. Thurman [*Ind. Eng. Chem.*, **15**, 395 (1923)], who has made a special study of this subject. He found that the loss in the case of corn and soybean oils ranged from 0.35 to 0.75 per cent and

that the average loss for coconut oil was 0.4 per cent. The distillate from the deodorizer, aside from water, consists very largely of fatty acids and neutral oil.

During recent years, continuous deodorizers have come into use to some extent both in this country and Europe. In the United States, the alkali-refined bleached oil is first heated by pumping it through a heat exchanger into the evacuated top section of the deodorization tower, where it is rapidly deaerated. From there the oil is passed through an external heater, into the top of the deodorizer column; it then flows downward in very thin streams through the bubble trays at the same time that low-pressure superheated steam rises counter-current to the oil, carrying off its odoriferous volatile constituents. The deodorized oil which collects at the bottom of the deodorizer is pumped into a heat exchanger through which the oil to be deodorized is also flowing, and after passage through another cooler, it goes into the storage tank. The deodorization of the oil by this method is completed within a few minutes.

For additional information on deodorization, the following references may be of interest:

"Theory and Practice of Steam Deodorization: A Review," D. Wesson, *Oil and Fat Ind.*, 3, 361 (1926).

"The Theory of the Practice of Steam Deodorization of Saponifiable Oils." W. Brash, *J. Soc. Chem. Ind.*, 45, 73T (1926).

"Application of the Counter Current Principle to the Steam Deodorization of Saponifiable Oils," W. Brash, *ibid.*, 331T.

"Modern Deodorizing Methods," J. P. Harris and A. B. McKechnie, *Cotton Oil Press*, 11, No. 8, 27 (1927); *Oil and Fat Ind.*, 4, 371 (1927). A very instructive article.

"A Method for Refining and Deodorizing Oils. V. Conquest," *Oil and Soap*, 9, 114 (1932).

"Edible Oil Deodorizing Equipment and Methods," A. P. Lee and W. G. King, Jr., *Oil and Soap*, 14, 263 (1937); lists 21 references.

"Continuous Deodorization of Edible Oils," D. K. Dean and E. H. Chapin, *Oil and Soap*, 15, 200 (1938).

"Continuous Deodorization," D. K. Dean and E. H. Chapin, *Oil and Soap*, 17, 217 (1940).

"Steam Deodorization of Edible Fats and Oils: Theory and Practice," A. E. Bailey, *Ind. Eng. Chem.*, 33, 404 (1941).

"Grading of Crude Vegetable Oils by Means of Refining Tests. A Review and Evaluation of the Method," A. E. Bailey, R. O. Fenge and W. G. Bickford, *Oil and Soap*, 19, 97 (1942).

The following references cover more or less the entire subject of refining:

"Refining Practice and Theory," R. H. Fash, *Cotton Oil Press*, 4, No. 11, 45 (1921).

"Practical Hints for Oil Refiners," J. P. Harris, *ibid.*, 4, No. 7, 27 (1922).

"Outline of the Forces Entering Process of Refining Cotton Oil," H. E. White, *Cotton Seed Oil Mag.*, 38, No. 7, 29 (1922).

"Inventory and Production Control in Oil Refineries," A. P. Lee, *Oil and Fat Ind.*, 4, 205 (1927).

"What Is a Refined Oil?" H. Aspegren, *Cotton Oil Press*, 11, No. 7, 31 (1927).

"Refining of Fatty Oils," H. M. Langton, *Ind. Chem.*, 3, 483 (1927). The last paragraph, but one, briefly mentions various neutralization methods that have been proposed, including vacuum refining, and gives the patent numbers.

"Refining and Making of Fine Salad and Cooking Oils," D. Schwartz, *Cotton Seed Oil Mag.*, **55**, No. 8, 21 (1927).

"Edible Oil Refining: A Continuous Distillation System," *Chem. Trade J.*, **83**, 436 (1928). A process used for several years in one or more refineries in England and Germany, apparently with success, but not applicable to the direct treatment of crude cotton seed oil.

"Solvent Extraction and Refining of Vegetable Oils for Vegetable Purposes in India," *Oil Col. Trades J.*, **74**, 1495 (1928).

"Fatty Acid Recovery and Purification," *Soap*, **8**, No. 6, 65 (1932), discusses continuous processes for oil refining.

"A New Continuous Process for the Refining of Vegetable Oil," E. M. James, *Oil and Soap*, **11**, 137 (1934).

"Gossypol Content and Refining Loss on Crude Cottonseed Oil," H. D. Royce and M. C. Kibler, *Oil and Soap*, **11**, 116 (1934).

"Does It Pay to Produce Low Refining Loss Crude Oil?" G. W. Agee, *Cotton and Cotton Oil Press*, **37**, No. 45, 5 (1936).

"Chinese Cotton Oil," P. E. Ronzone, *Oil and Soap*, **13**, 165 (1936); discusses refining.

"Effect on Refining Results of Mixing Expeller and Hydraulic (Pressed) Cottonseed Oil," G. W. Owen, *Oil and Soap*, **14**, 149 (1937).

"Refining of Vegetable Oils," *Oil and Col. Trdes. J.*, **92**, 1720 (1937).

"Filtration through Glass Cloth," *Chem. Trde. J.*, **103**, 436 (1938).

"The Winterizing of Cottonseed Oil," A. P. Lee, *Oil and Soap*, **16**, 148 (1939); a brief summary of old and new methods and equipment.

"Net Loss in Crude Cottonseed Oil Refining," W. J. Reese, *Oil and Soap*, **16**, 61 (1939).

"American Oil Chemists' Society Tentative Specifications for North American Refined Cottonseed Oil," *Oil and Soap*, **16**, 141 (1939).

"The Determination of Soap in Refined Oil," H. A. Boekenoogen, *Oil and Soap*, **18**, 8 (1941).

"A New Method of Refining Oils With Non-Saponifying Alkalies—The Clayton Process," M. Mattikow, *Oil and Soap*, **19**, 83, (1942).

One or more small unit "vacuum" refining methods are used to some extent in a number of continental European countries. They are based on the removal of the water by distillation under a high vacuum, after the treatment of the crude oil with caustic soda solution. This treatment gives a practically dry soap stock, thereby minimizing the quantity of entrained neutral oil, because of the destruction of the emulsion. On account of the small size of the units and the color of the refined oil, these processes have not met with favor in America, where very light-colored oil is in great demand.

The Fluorescence of Some Refined Oils. It should be observed that fluorescence, which becomes noticeable only after a cottonseed oil is refined, is not always due to contamination by mineral oil [P. W. Tompkins, *Cotton Oil Press*, **5**, No. 2, 123 (1921)]. The presence of a few tenths of a per cent, or even less, of a mineral oil usually imparts this characteristic to vegetable oils. J. H. Anderson [*Cotton Oil Press*, **6**, No. 10, 33 (1923)] stated that mineral oil bloom can be removed from the oil by carbon. The addition of a half per cent or more of mineral oil can readily be detected by the increase in the quantity of unsaponifiable matter over that of cottonseed oil. Not infrequently, the oil from China and India has a fluorescence that is not due to the presence of mineral oil. The same is true of oil from seeds that have been badly overheated while in storage as well as the oil from "meats" that have been scorched during the cooking process [J. F. Drake, *Oil Miller*, **16**, No. 2, 27 (1922)].

L. E. Fisher [*Cotton Oil Press,* **5,** No. 12, 36 (1922)] states that the oil from the seed of a given Chinese district is often fluorescent one year and not the next, and he believes that this difference is due to climatic conditions during growth or harvesting, particularly as the same kind of fertilizer was used each year. The oil extracted from these seeds in the laboratory had the same fluorescence as that from the oil mill, showing that it was not due to mineral oil or overcooking of seed.

"Wintered" Refined Oil. The process known as "wintering," for the preparation of salad oil, consists of chilling the refined oil and holding it at the proper temperature so that the higher-melting glycerides will separate by crystallization in such a form as will permit of their removal from the oleine or liquid glycerides by means of the filter press in the "chill" room. The solid portion, or stearine, that is separated from the oil is used in the manufacture of lard substitutes. When the liquid portion of "wintered oil" has been properly prepared, it will remain clear and bright after being cooled to 0° C. for 5 hours.

The quantity of stearine separated in wintering cottonseed oil depends somewhat upon the source of the seed from which the oil was obtained. Oil from India generally yields less stearine than those from America and Egypt. In the United States the stearine separated usually varies from 12 to 25 per cent of the oil, 16 to 18 being common. Often the yield of stearine from a given oil varies considerably at different plants, because of variation in the conditions in the chill room. The stearine generally has a melting point of 40° to 44° C., but sometimes it is lower or higher. It consists chiefly of various mixed glycerides of palmitic acid with a portion of the stearic, oleic, and linoleic acids present in the oil. The comparatively wide range in the quantity of stearine separated at one refinery from oils of different sources indicates that the proportions of the various glycerides differ somewhat, those yielding the larger quantities of stearine having the larger percentage of the higher-melting glycerides, and *vice versa.*

An instructive article entitled "Commercial Equipment for Winter Yellow Oil Production," by J. H. Anderson, will be found in the *Cotton Oil Press,* **6,** No. 2, 32 (1923).

Hydrogenation. The industrial hydrogenation, or hardening, of cottonseed or other oil is based on bringing hydrogen into contact with the heated oil in the presence usually of 0.1 to 0.5 per cent or sometimes more of a nickel catalyst. For details of the various hydrogenation processes, the preparation of hydrogen and nickel catalysts, etc., the works of C. Ellis and E. B. Maxted should be consulted in addition to the references given.

It is quite customary to use a "supported" catalyst. The support in common use is diatomaceous earth. It is added (10 to 20 per cent) to the nickel sulfate solution, which is agitated, and the nickel is precipitated with a solution of sodium carbonate. The precipitate is filtered, thoroughly washed, dried, and reduced in a special furnace with hydrogen at as low a temperature as possible (300° to 500° C.). The finished catalyst should contain from 20 to 30 per cent nickel. Directly

after reduction, the catalyst is protected from the air by immersion in the same kind of oil that is to be hardened. When nickel formate is to be used, this is reduced in oil heated to 225° to 250°, with or without a support, by hydrogen. When desired this catalyst can be filtered and as it remains covered with a film of oil, air does not quickly affect its activity.

Depending upon the method, the hydrogenation is conducted under a pressure of hydrogen from 1 to 12 atmospheres and the temperature used ranges from 120° to 210° C., 160° to 180° being the most common.

With any process, it is important to use dry hydrogen in as pure condition as possible. It is also important to have the oil free from moisture and other non-oil constituents which interfere with the process or reduce the activity of the catalyst. In this country, it is customary to use electrolytic hydrogen, but that from water gas is used in some other countries where electricity is not sufficiently cheap to warrant its use from the electrolysis of water. Thirty-four cubic feet of hydrogen gas are required for each per cent of iodine number reduced per ton of oil. Hydrogenation equipment is installed in single or multiple units (batteries). It consists of a closed tank provided with a closed steam heating coil, but in some cases a double-jacketed vessel is used which requires no internal heating coil. As the hydrogenating action is strongly exothermic, it is frequently necessary to shut off the steam and sometimes to circulate cold water through the coils or jacket or reduce the flow of hydrogen in order to prevent the temperature from getting too high, particularly in the case of edible oils. Some hydrogenators are provided with high-speed agitators of various types (the so-called agitator system). In these, the hydrogen is admitted at the bottom of the tank and they are operated under a gaseous pressure of a few pounds.

Another type in which the hydrogen enters through a pipe in the top of the tank above the surface of the oil is operated under a pressure from 8 to 12 atmospheres. During hydrogenation, the oil and catalyst, after being heated to the proper temperature, are continuously pumped from the bottom through a pipe and delivered by a spray nozzle into the hydrogen that occupies the upper third of the tank. This circulatory system is used to a considerable extent in Europe, whereas the use of the agitator system, mentioned previously, is more common in America.

After hydrogenation, the oil is cooled to a temperature at which it will not be injured upon exposure to the air after filtration. At some plants, the treated oil is cooled in the hydrogenator by passing cold water through the heating coils; at others, the oil is removed to special cooling equipment of various types. After suitable cooling, the catalyst is removed by means of a filter press. In the case of edible products, it is customary to deodorize them after hydrogenation. K. H. Vakil [*J. Soc. Chem. Ind.*, **42**, 788 (1923)] suggests the removal of the hydrogenation flavor by passing carbon dioxide or nitrogen for an hour through the oil heated to 145° to 150° C.

During hydrogenation, the color of the oil is noticeably bleached.

In addition to these batch processes, mention should be made of the continuous method of Bolton and Lush [*J. Soc. Chem. Ind.*, **46**, 444T (1927)], which is in use at several plants in Europe. The batch processes use a catalyst in powder form, but in this case a dense nickel catalyst (in the form of wire, turnings, or wool) packed in a nickel or monel metal cage is employed. The cage is removable, and when necessary, the catalyst is rinsed with gasoline and regenerated either by anodic oxidation in a dilute sodium carbonate solution or by immersion in a dilute sodium hypochlorite solution. After washing and drying, it is activated on the surface by reducing the film of oxide with hydrogen at 250° C. With this process, the degree of hydrogenation of the oil can be readily controlled simply by increasing or diminishing the flow of oil to obtain the desired results. The oil is admitted at the top of the hydrogenator and comes in contact with the catalyst, where it meets the hydrogen passing upward; that which passes through the oil is collected and recirculated through the hydrogenator. The treated oil collects at the bottom of the vessel and is continuously withdrawn through a "seal" trap. During hydrogenation, the oil is heated for only 10 or 15 minutes.

During the hydrogenation of cottonseed or other oils, the refractive index is reduced, but the saponification value, free fatty acids, and unsaponifiable matter are not noticeably changed. Phytosterols hydrogenate much less readily than the cholesterol found in animal fats and oils. Use is commonly made of the refractometer in observing the progress of hydrogenation of oils, as this test can be made very quickly.

When completely hydrogenated, cottonseed oil melts at 62° to 63° C. If hydrogenation is conducted to completion under pressure, the weight of the oil is increased about 0.7 per cent. Highly hydrogenated oil can be used for making soap, as an oil bath, or in place of palm oil by the tinplate industry [Collins and Clark, *Ind. Eng. Chem.*, **12**, 149 (1922)]. Hilditch and Moore [*J. Soc. Chem. Ind.*, **42**, 15T (1923)] hydrogenated the oil at 180° C., using a nickel catalyst on kieselguhr; some of the results obtained are given in the following table:

Sample	Melting Point ° C.	Iodine Number	Composition of Mixed Fatty Acids		
			Saturated	Oleic	Linoleic
			Per Cent		
Original	Liquid	109.0	24.7	23.8	51.5
No. 1	30	86.2	27.0	46.0	27.0
No. 2	35	76.6	30.0	53.0	17.0
No. 3	39	65.9	30.0	66.0	4.0
No. 4	42	58.1	35.0	65.0	0.0
No. 5	46	49.1	43.0	57.0	0.0

It should be noted that the figures in column 5 for samples 1 to 3 show that large quantities of the iso-oleic and other oleic acids are formed, but gradually some of this is reduced to stearic acid, as indicated in samples 4 and 5.

For further information on the melting points of the hardened oil

see K. A. Williams, *J. Soc. Chem. Ind.*, **46**, 44T (1927); "Melting Point Determinations of Lard Substitutes," T. C. Whitner and H. S. Bailey, *Cotton Oil Press*, **5**, No. 10, 31 (1922).

The shortenings in the United States made from cottonseed oil melt from 35° to 43° C. and have an iodine number from 60 to 75, saturated acids 27 to 33, iso-oleic acid 7 to 18, and linoleic acid 5 to 12 per cent. The lower the content of linoleic acid, the better keeping qualities the product will have.

For those not familiar with the manufacture of vegetable shortenings it may be added that the melted, deodorized, hydrogenated product is run onto large refrigerated rolls, where it solidifies in a thin coating which is continuously removed by a scraper and conveyed to the packing room. By this method, a uniform product of excellent appearance is obtained.

Attention is called to Platt and Flemings' article, "The Action of Shortening in the Light of the Newer Theories of Surface," *Ind. Eng. Chem.*, **15**, 390 (1923). Space is not available for an adequate discussion of this study. They give a list of substances in the order of their shortening power as follows: lard, lard compound, cottonseed oil, butter, coconut oil, Vaseline and petroleum oils.

Shortenings may also be made from corn, peanut, sesame, and soybean oils, providing that first they have been properly refined.

Hydrogenation Reactions. The action of hydrogen in the presence of a catalyst, on the unsaturated acids, free or in the form of esters (glycerides, etc.), is selective; the more unsaturated are reduced to a considerable extent before the less unsaturated acids begin to react. Linolenic, linoleic, and oleic acids can be converted into stearic acid. In partial hydrogenation, such as when cottonseed oil is made into a shortening, some stearic acid is formed along with considerable quantities of the so-called iso-oleic and other oleic acids from the reduction of the linoleic acid. The iso-oleic acid is a mixture of elaidic acid, the solid geometrical isomeride of ordinary oleic acid (9-10), and another solid acid which is probably the 11-12 oleic acid. As Armstrong and Hilditch have stated, the oleic center of unsaturation is in part changed to the stereo isomer form, and further that elaidic acid passes over in part to the ordinary liquid oleic acid. It has been found that less iso-oleic acid is formed when the temperature of the oil during hydrogenation is kept low. It is obvious that the composition of a partially hardened oil can be regulated to some extent by controlling the conditions of hydrogenation. In the case of vegetable shortenings, it is important not to harden the product above the desired melting point, but at the same time to reduce the linoleic acid to a minimum.

Those interested in hydrogenation should consult the following references:

"Edibility of Hardened Oils," K. B. Lehman, *Chem. Zeit.*, **38**, 798 (1914).
"Chemical Composition of Hydrogenated Cotton Seed Oils," Moore, Richter and Van Arsdel, *Ind. Eng. Chem.*, **9**, 451 (1917).
"Hydrogenation of Oils," H. L. Barnitz, *Chem. Trade J.*, **46**, 593 (1920).

"Digestibility of Some Hydrogenated Oils," A. D. Holmes and H. J. Deuel, *Am. J. Physiol.*, **54**, 479 (1921).

"The Manufacture of Pure Hydrogen and the Catalytic Hydrogenation of Oils," D. B. Maxted, *J. Soc. Chem. Ind.*, **40**, 169T (1921).

"The Physiological Value of Hydrogenated Oils," Drummond, *Chem. Age* (London), **5**, 330 (1921).

"On the Catalytic Hydrogenation of Cottonseed Oil," Kahlenberg and Ritter, *J. Phys. Chem.*, **25**, 89 (1921).

"Selective Hydrogenation," T. P. Hilditch and Moore, *J. Soc. Chem. Ind.*, **42**, 15T (1923).

"Catalytic Hydrogenation with Nickel," R. Thomas, *J. Soc. Chem. Ind.*, **42**, 21T (1923).

"Catalytic Actions at Solid Surfaces XI, The Action of Alumina and Certain Other Oxides in Promoting the Activity of Nickel Catalyst," E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.*, **103A**, 586 (1923). Small amounts of alumina, ferric, magnesium oxides or silica, added to the nickel catalyst increase its activity in hydrogenation.

"Kinetics of Hydrogenation," E. J. Lush, *J. Soc. Chem. Ind.*, **43**, 53T, and **44**, 129T (1924).

"Hardened Oils," J. Davidsohn, *Z. Öl. u. Fett Ind.*, **43**, 717 (1923); *Chem. Absts.*, **18**, 914 (1924). A general review of changes in characteristics, color reactions, etc., brought about by the hydrogenation of oils.

"Nickel Hydride and the Mechanism in the Hydrogenation with Nickel Catalysts," W. Schlank and T. Wuchselfe'der, *Ber.*, **56**, 2230 (1923).

"Recognition of Hydrogenated Oils," K. A. Williams and E. R. Bolton, *Analyst*, **49**, 460 (1924).

"Electrolytic Oxygen and Hydrogen; Features of Knowles' Patent," *Chem. Trade J.*, **73**, 704 (1924).

"Cata'ysis at Solid Surfaces," Armstrong and Hilditch, *J. Soc. Chem., Ind.*, **44**, 701 (1925).

"Hydrogen for Hydrogenation of Oils," A. E. Knowles, *J. Soc. Chem. Ind.*, **45**, 121 and 137 (1926).

"Catalytic Hydrogenation. I. Vegetable Oils and Waxes," E. J. Lush, *Ind. Chem.*, **3**, 197 (1927). Part II, *ibid.*, 249—A Continuous Process for the Hydrogenation of Oils.

"Hydrogenation of Fatty Acids and Mixtures of Fatty Acids with Neutral Oils," R. G. Pelly, *J. Soc. Chem. Ind.*, **46**, 449T (1927).

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"Hardened Fat Manufacture," T. Andrews, *Chem. Trade J.*, **84**, 303 and 351 (1929). Discusses oil impurities as catalytic poisons, effect of organic phosphorus and sulfur as catalyst poisons, and the difficulty in treating rape oil.

"Nickel Carbonyl in Fat Hardening," W. Normann, *Chem. Umschau*, **39**, 126 (1932).

"Some Observations on the Hydrogenation of Fats. I. The Influence of Catalyst Concentration on the Selective Hydrogenation of Cottonseed Oil," D. R. Dhingra, T. P. Hilditch, and A. J. Rhead, *J. Soc. Chem. Ind.*, **51**, 195T (1932). "II. The Course of Hydrogenation of Cottonseed Oil," Hilditch and Rhead, *ibid.*, 198T. "III. Note on the Relative Amounts of Solid and Liquid Oleic Acids Present at Different Stages of Hydrogenation of Olives and Cottonseed Oils," Hilditch and E. C. Jones, *ibid.*, 202T.

"High-Pressure Hydrogenation of Fatty Oils," Y. Tanaka and R. Kobayashi, *Chem. Absts.*, **27**, 3097, 4704 (1933).

"Deposition and Utilization of Hydrogenated Iso-oleic Acid in the Animal Body," A. D Barbour, *J. Biol. Chem.*, **101**, 63 (1933).

"Silica Black as a Nickel Carrier in Oil Hydrogenation," L. R. Williams and C. A. Jacobson, *Ind. Eng. Chem.*, **26**, 800 (1934).

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"Course of Hydrogenation in Mixtures of Mixed Glycerides," W. J. Bushell and T. P. Hilditch, *J. Chem. Soc.*, **1937**, 1767.

"Continuous Hydrogenation in the Oil Hardening Industry," L. H. Manderstam, *Oil and Soap*, **16**, 166 (1939). Illustrated.

"A Continuous Catalyzer Reducing Furnace," H. Siek, *Oil and Soap*, **16**, 24 (1939).
"Catalysts for Hydrogenation," M. H. Gwynn, *Oil and Soap*, **16**, 25 (1939).
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"Formation of Iso (Oleic) Acids during Fat Hardening," K. H. Bauer and W. Herzog, *Fette u. Seifen*, **46**, 203 (1939).
"The Relative Effect of Inhibitors on Adsorption and on Catalytic Activity," E. B. Maxted and H. C. Evans, *J. Chem. Soc.*, **1938**, 1228 and **1939**, 1750.
"The Development of the Technical Application of Hydrogenation," E. F. Armstrong and K. A. Williams, *J. Soc. Chem. Ind.*, **59**, 3 (1940).

The following table gives some melting points of partially and completely hydrogenated oils:

HYDROGENATED OILS

Oil	Iodine Number	Melting Point ° C.
Castor	4.8	68
Coconut	1.0	44.5
Cotton	69.7	38.5
Peanut	47.4	51
Sesame	54.8	47.8

COMPLETELY HYDROGENATED *

Almond	72
Castor	80
Linseed	68
Olive	70
Poppy	70
Sesame	63.5

* "Catalysis in Organic Chemistry," Sabatier-Reed, p. 969.

Characteristics and Composition of Cottonseed Oil. Crude cottonseed oil has a specific gravity at 15.5° C. from 0.916 to 0.930, a saponification value from 192 to 200, iodine numbers from 100 to 115, and unsaponifiable matter from 0.6 to 2 per cent.

The usual range of the characteristics of the refined oil is as follows: Sp. g. at 15° C. 0.915 to 0.926, at 25° C. 0.9168 to 0.9181; $N_D^{20°}$ 1.4668 to 1.4720, at 40° C. 1.4643 to 1.4679; Sap. V. 191 to 198; Iod. No. 103 to 115; SCN V. 61 to 65; Titer 32° to 38° C.; Unsap. 0.7 to 1.5%; Sat. Acids 21 to 25%; Unsat. Acids 69 to 74%. *Cottonseed stearine:* Sap. V. 190 to 196; Iod. No. 90 to 103; M. Pt. 42° to 52° C.

For the determination of the specific heat of cottonseed (Sp. ht. 0.503) and other oils see D. Wesson and H. P. Gaylord, *Cotton Oil Press*, **2**, No. 6, 40 (1918), and H. P. Trevithick (lubricating oils, etc.), *ibid.*, **3**, No. 1, 40 (1919).

Data for many characteristics of 3 crude and 5 refined cottonseed oils will be found in the report of the Oil Characteristics Committee of the American Oil Chemists' Society in *Oil and Soap*, **16**, 141 (1939).

The smoking temperature of the refined oil varies from about 223° to 233° C.; of partially hydrogenated products (shortenings) from 217° to 233° C.; of lard from 175° to 195° C. As the percentage of free fatty acids increases in a given fat or oil, the smoking point is lowered. The best temperature for "deep frying" of food is from about 180° to 190° C.

The acetyl value was determined for several samples of crude oil with the following results:

Sample	Acid Value	Acetyl Value
a	2.5	10.76
b	3.4	14.1
c	5.3	12.7
d	7.3	34.4
e	21.6	14.2

From sample d several grams of di-palmitin were separated, and this accounts for the high acetyl value. These results indicate that there is no relation between the free fatty acids and the quantity of di-glyceride that may be present.

The variations and averages of the results from the examination of 41 commercial samples of crude oil by Jamieson and Baughman [*The Cotton Oil Press*, **4**, No. 3, 85, and No. 6, 48 (1920)], which were collected during the 1919-1920 season from mills in nine southern states and represented the then current production of hot-pressed oil, are given in the table. The characteristics were determined on portions of the samples which had been refined by the official method.

In order to get some data on the influence of geographic source of seed on the oil, H. J. Morrison and L. W. Bosart [*J. Oil and Fat Ind.*, **3**, 130 (1926)] examined 822 tank cars of crude oil from the 1925 crop of seed. The oil came from Alabama, Arkansas, Georgia, Louisiana, Mississippi, Oklahoma, Tennessee, and Texas. The results indicated a higher refractive index, a higher iodine number, a lower titer and a smaller proportion of stearine when the oils were "wintered," the

	Acidity as Oleic Acid	Refining Loss	Titer °C.	Refractive Index at 20° C.	Density at 25°/25° C.	Iodine No. (Hanus)	Saponification Value	Saturated Acids	Unsaturated Acids
	Per Cent							Per Cent	
Average	1.9	8.7	34.4	1.4695	0.9173	107.4	194.7	23.3	71.5
High	3.0	10.8	35.0	1.4700	0.9174	109.0	195.7	24.2	72.3
Usual Variations									
Low	0.9	5.3	33.8	1.4695	0.9171	106.0	193.9	22.9	70.6
High	9.2	29.2	35.6	1.4720	0.9181	111.2	195.7	25.3	73.9
Extremes									
Low	0.6	3.6	32.2	1.4768	0.9168	103.0	193.9	20.9	69.7

farther north the seed was grown. As found by Jamieson and Baughman (*loc. cit.*), the characteristics of the oils from widely different sections of the cotton belt did not vary much, nor did the proportion of the saturated acids. Although, as well known, the yield of stearine varies greatly, the writer believes that this is chiefly caused by differences in the quantities of the higher-melting glycerides present.

Refined oil from Egyptian seed usually gives iodine numbers from 106 to 109, and that from Indian seed from 112 to 116.

Weight of Refined Oil. One United States gallon at 20° C. weighs about 7.6 pounds.

The constituents of the crude oil have been investigated by Jamieson and Baughman [*Oil and Fat Ind.*, **3**, 347 (1926)] and the qualitative composition is indicated in the following table:

CRUDE COTTONSEED OIL

Glycerides of	Minor Constituents	
Oleic acid	Raffinose	Phytosterols
Linoleic acid	Pentosans	Phytosteroline
Myristic acid	Resins	Inosite Phosphates
Palmitic acid	Proteoses	Xanthophyll
Stearic acid	Peptones	Chlorophyll
Arachidic acid	Phospholipins	
	Mucilaginous substances	
	Free fatty acids; same as in glycerides	

E. S. Wallis and P. N. Chakravorty [*J. Organic Chem.*, **2**, 335 (1937)] found that the sterol fraction of the unsaponifiable matter from cottonseed oil consisted chiefly of β-sitosterol. No evidence was obtained even of traces of α_1, α_2 or γ sitosterols, but about 0.9 per cent of the saturated stigmasterol (m. pt. 135.5° to 137° C.) was isolated from the sterol fraction. S. Bernstein and E. S. Wallis (*ibid.*, 341) showed that β-sitosterol and stigmasterol are identical.

Refined oil contains, besides the glycerides of the acids given above, a small percentage of phospholipins (lecithin, etc.), phytosterols, and pigments giving color to the product. During the refining, the other constituents are removed by the action of the water or caustic soda. For "settlings" not meal *see* "Crude Oil Analysis."

The possible glycerides of cottonseed oil are discussed by D. Wesson in the *Cotton Oil Press*, **3**, No. 7, 34, and No. 8, 42; in the hydrogenated oil, No. 12, **44** (1919), G. S. Jamieson [*Oil and Fat Ind.*, **3**, 153 (1926)] showed that the oil contained a small proportion of palmitin.

Jamieson and Baughman [*J. Am. Chem. Soc.*, **42**, 1197 (1920)] examined a sample of oil which they expressed from a bushel of Sea Island cotton seed. The oil contained 23.0 per cent of saturated acids and 72.5 of unsaturated acids, which gave an iodine number (Hanus) of 142.2 and a saponification value of 199.4. The oil was found to contain the following percentages of acids: Oleic 33.15, linoleic 39.35, myristic 0.3, palmitic 19.1, stearic 1.9, and arachidic 0.6 per cent.

The oil from Upland cotton seed grown in Mississippi in 1926 was expressed hot and examined by these investigators [*Oil and Fat Ind.*, **4**, 131 (1927)]. The crude oil had a density at 25° C. of 0.9230, refractive index at 20° C. of 1.4745, acid value of 2.9, saponification value 199.3, and an iodine number (Hanus) 106.8. The oil, which was refined by the caustic soda method, gave the following characteristics: Sp. g. at 25° C. 0.9174; $N_D^{20°}$ 1.4725; Sap. V. 195; Iod. No. 108.2; Unsap. 0.9%; Sat. Acids 23.3%; Unsat. Acids 72.0%; Iod. No. of

Unsat. Acids 144.4. The refined oil was found to contain the following percentages of acids: Oleic 29.2, linoleic 42.8, myristic 0.5, palmitic 20.9, stearic 1.8, and arachidic 0.1 per cent.

T. P. Hilditch and H. Jasperson [*J. Soc. Chem. Ind.*, **57**, 84 (1938)] found that the mixed fatty acids from a sample of cottonseed oil contained the following percentages of constituents: myristic 2.1, palmitic 21.7, stearic 2.9, oleic 32.1, linoleic 40.3, tetradecenoic 0.5, and hexadecenoic 0.4. These investigators have shown also that soybean and some other oils contain small quantities of these lower molecular weight unsaturated acids. The figure given above for stearic acid includes several tenths of a per cent of arachidic acid.

T. P. Hilditch and E. C. Jones [*J. Soc. Chem. Ind.*, **53**, 13 (1934)] found that the cottonseed oil which they investigated consisted of nearly 60 per cent of glycerides containing one palmityl and two unsaturated acid radicals, about 24 per cent of completely unsaturated glycerides, and about 15 per cent of dipalmito-olein or dipalmitolinolein. It is probable that the unsaturated glycerides contain no triolein and little if any trilinolein, in view of the fact that the component acids contained about 30 per cent of oleic acid and 45 of linoleic acid.

More recently, T. P. Hilditch and L. Maddison [*J. Soc. Chem. Ind.*, **59**, 162 (1940)] made a further investigation of the composition of cottonseed oil. The mixed fatty acids contained the following percentages of constituents: myristic 1.4, palmitic 23.4, stearic 1.1, arachidic 1.3, tetradecenoic 0.1, hexadecenoic 2.0, oleic 22.9, and linoleic 47.8. From their investigation, it was concluded that the sample of oil contained the following percentages of glycerides: about 58 of chiefly palmito di-unsaturated, about 28 of tri-unsaturated, 13 of mono unsaturated-disaturated glycerides, and about 0.1 of palmitin. This paper includes a description of their low-temperature technique.

Analysis of Crude Oil. The samples are examined for loss upon heating (moisture and other volatile matter), meal, and other insoluble impurities, free fatty acids, and refining loss by the "caustic soda" (sodium hydroxide) method. Directions will be found for these tests under "Methods of Analysis."

In connection with "meal" (sometimes called press foots), attention is called to the fact that thoroughly settled or even filtered crude oil is not infrequently shipped from a mill to the refinery, and when delivered the oil appears to contain a large quantity of meal. In such cases, the precipitate is simply a portion of the non-oil constituents that have separated from the previously clear oil. Although this precipitate is usually very bulky, it weighs but little. This separation is caused primarily by the small quantity of moisture in the oil and is favored by the temperature changes of the oil during transit. These settlings contain no protein and but small quantities of related but simpler substances known as proteoses and peptones (*see* table giving qualitative composition of the crude oil). These settlings contain but little nitrogen

compared with the meal, and most of that is due to phosphatides. However, in the past, they have often been mistaken for meal or press foots, resulting in unwarranted complaints to the crude oil mill. Reports on the constituents of the settlings (not meal) by Jamieson and Baughman will be found in the *Cotton Oil Press,* **6,** No. 4, 33 (1922); **7,** No. 2, 35; No. 5, 29 (1923); *J. Oil and Fat Ind.,* **1,** 31 (1924); **2,** 101 (1925); **3,** 153 (1926).

American Grades of Crude and Refined Oil. Definite specifications have been in use for the purchase and sale of both crude and refined cottonseed oil in the United States for many years, and they include all grades of these products. Crude oil is graded on its acidity, refining loss, and flavor; refined oil on its color, odor, and flavor. As the specifications for the grades of crude and refined oil are subject to modification from time to time, those interested should consult the current "Book of Rules" of the National Cottonseed Products Association (formerly known as the Interstate Cottonseed Crushers' Association). The crude oil, according to its quality, is at the present time graded into Prime, Crude, Basis Prime Crude, Off Crude, Reddish Off Crude, Low Grade, Cold Pressed, and Extracted Oil. The refined oil is graded as Choice Summer Yellow, Prime Summer Yellow, Prime Winter Yellow, Good Off Summer Yellow, Off Summer Yellow, Reddish Off Summer Yellow, Bleachable Prime Summer Yellow, Prime Summer White, and Prime Winter White Oil.

"Summer" oils are so named to distinguish them from those in which the higher-melting glycerides have been separated (wintered oil).

Prime crude cottonseed oil, as now specified, must be pressed from sound decorticated seed (U. S. A.), must be sweet in flavor and odor, must be free from water and settlings, and must produce, when refined, as required by the official rules, Prime Summer Yellow Oil.

Uses of Cottonseed Oil. The refined oil is used in the manufacture of lard substitutes of various kinds (lard compound and vegetable shortening), and oleomargarin; it is used as a cooking oil, and when "wintered," as a salad oil. In the manufacture of lard substitutes, some or all of the oil is hardened by hydrogenation so that the finished product will have the desired degree of hardness. The cottonseed stearine separated in the production of wintered (salad) oil is used chiefly in making lard substitutes.

In the United States, the approximate percentages of cottonseed oil used for various purposes are as follows: 72 for shortenings, 11 for cooking and salad oils, 7 for margarine, and 10 for soap. Ten years ago, only two per cent of the oil was used in the manufacture of margarine.

Wm. Clayton ["Margarine," *Oil and Fats Record,* **3,** 58 (1921)] found that the initial decomposition temperature of cottonseed oil and similar substances was as follows: cottonseed oil 205°, Crisco 200°, corn oil 200°, olive oil 165°, lard compound 195°, and leaf lard 190° C. After using these products for deep frying, the decomposition temperature becomes lower.

Any oil unsuitable for refining and the soap stock obtained by refining the crude oil are used in making soap and soap powders. At some plants, the fatty acids are separated from the soap stock, fractionally distilled with the aid of superheated steam under a high vacuum, and the light-colored fractions used in making soap.

Examination of Refined Cottonseed Oil. Methods for the determination of color and free fatty acids, as well as the "cold test," will be found under "Methods of Analysis." The oil should be tasted to be sure that the flavor is good and the odor should be noted when the container is first opened. Oil or the hydrogenated product (vegetable shortening) intended for use in making crackers is usually submitted to the Kreis test for indications of incipient rancidity, but in such cases, on account of the delicacy of the test, it is most essential that both the buyer and purchaser get together and agree upon the interpretations of these tests of the products in question, in order to avoid serious difficulties.

The most characteristic color test for this oil is the Halphen test, and its particular use is to detect cottonseed oil in mixture with other oils. This test is given by the seed oils of various other plants of the *Malvaceae, Bombacaceae* and *Tiliaceae,* but at the present time, kapok (seed) oil is the only one produced on a commercial scale. Cottonseed oil that has been heated for a long time above 250° C. in metal vessels, or that which has been blown with air, usually does not give the Halphen test, and the same is usually true of oil that has been hydrogenated.

Kreis and Roth [*Analyst,* **38,** 160 (1913)] claim that the hydrogenated oil can be identified by the Bellier test, which is made by shaking 5 cc. of the melted sample with 5 cc. of nitric acid (sp. g. 1.4) and 5 cc. of a cold saturated benzene solution of resorcinol, a pink or violet color being given.

Cottonseed oil can also be recognized by the high melting and solidification (titer) points of the fatty acids and by the high percentage of its saturated acids (21 to 25) in contrast to the other commercial edible oils such as olive, soybean, sesame, corn, etc. Peanut oil contains up to about 20 per cent of saturated acids, but often somewhat less.

References to the Halphen and modified Halphen Tests: "Use of Pyridine in Place of Amyl Alcohol in the Reagent," Gastaldi, *Chem. Zeit.,* **2,** 758 (1912); *J. Soc. Chem. Ind.,* **31,** 934 (1912); R. A. Kuever, *J. Am. Pharm. Assoc.,* **10,** 594 (1921); J. Pieraerts, *Mat. grasses,* **18,** 7640 (1926).

Croton Oil. This oil is obtained from the seeds of *Croton tiglium,* belonging to the *Euphorbiaceae.* It is cultivated in various tropical regions of Southern Asia, China and elsewhere. The decorticated seeds usually contain over 50 per cent of oil. The commercial product varies in color and is yellow, orange or brown. It usually has an unpleasant odor and an acrid burning taste. It will blister the skin. It is used medicinally as a purgative, the dose being 0.05 cc. It is also used sometimes in the manufacture of soap.

The usual range of the characteristics are as follows: Sp. g. at 15° C. 0.937 to 0.960; $N_D^{40°}$ 1.4700 to 1.4730; Sap. V. 200 to 215; Iod. No. 102 to 108; R.M.V. 12 to 13.6; Pol. No. 1 to 1.3; Unsap. 0.6%; Titer about 19° C. The oil is dextrorotatory in polarized light. Lewkowitsch [*Analyst,* **24,** 319 (1899)] found that the "true" acetyl values for two samples of the oil were 19.82 and 32.66.

Comte [*J. pharm. chim.,* **14,** 38 (1916)] has proposed the following test for croton oil: Heat sample with twice its volume of absolute alcohol and pour a little onto a concentrated solution of alkali. A brilliant brownish-red or violet ring (according to age of oil) indicates the presence of croton oil. The writer has not tried this test.

Curcas Oil. Curcas oil, which is also known as physic nut oil, is obtained from the seeds of the *Jatropha curcas,* which is cultivated in Central America, the Portuguese colonies and in the Cape Verde and Comoro Islands. The seeds weigh about 0.5 gram each and contain about 60 per cent of kernel. The kernels contain about 50 per cent of oil. The oil varies from pale yellow to a yellowish-brown color, depending upon its quality. It has a faint unpleasant odor and powerful purgative properties, 10 drops having a greater effect than a tablespoon of castor oil. In contrast to castor oil, it is only slightly soluble in alcohol and has a much lower viscosity. The toxic properties have been investigated by J. Felke [*J. Soc. Chem. Ind.,* **33,** 651 (1914)].

A. O. Cruz and A. P. West [*Phil. J. Sci.,* **61,** 437 (1936), *Chem. Abs.,* **31,** 4518 (1937)] examined the oil from Philippine curcas seed with the following results: Sp. g. at 30/30° C. 0.9820; $N_D^{30°}$ 1.4665; Sap. V. 192.4; Iod. No. (Hanus) 94.8; Unsap. 0.45%; Sat. acids 16.82%; Unsat. acids 78.0%. The percentages of fatty acids as triglycerides were as follows: oleic 61.86, linoleic 18.65, myristic 0.45, palmitic 11.84, stearic 5.07, and arachidic 0.26%.

L. Adriaens [*Mat. grasses,* **28,** 10786, 10813 (1936) *Chem. Abs.,* **30,** 5440] examined seeds and oils from four localities in the Belgian Congo. The oils gave iodine numbers from 96.6 to 106.9 and the saturated acids ranged from 13.3 to 19.1%. Other oil characteristics and much data for the seeds are also given.

Characteristics: Sp. g. at 15° C. 0.9190 to 0.9219; $N_D^{15°}$ 1.4675 to 1.4730 at 40° 1.4618 to 1.4637; Sap. V. 188 to 193; Iod. No. 93 to 107; Acetyl V. 6.2 to 9.8; R.M.V. 0.2 to 1.0; Pol. No. 0.4 to 0.9; Unsap. 0.4 to 1.1%; Sat. acids 13.3 to 19.1%; Unsat. acids 78 to 87%; Titer of fatty acids 27.5° to 29° C.

The chief use of the oil is in making soap. Small quantities are used for medicinal purposes.

Charlock Oil. This is obtained from the seed of *Brassica arvensis.* H. S. Baily and L. B. Burnett [*Ind. Eng. Chem.,* **8,** 429 (1916)] examined the oil obtained from charlock seed separated from wheat screenings from northwestern United States with the following results:

	Expressed Oil	Ether Extract	Petroleum Ether Extract
Sp. g. 15°/15° C.	0.9221	0.9272	0.9228
$N_D^{25°}$	1.4734	1.4739	1.4729
Sap. V.	182.9	183.1	181.0
Iod. No. (Hanus)	121.1	119.8	119.3
Insol. Acids and Unsap.	95.3	95.4	94.2
Mean Mol. Wt. of Insol. Acids	339.1	338.1	334.8

The seed contained 29.6 per cent of oil and 4.1 per cent of moisture.

Chinese Colza Oil. Chinese colza oil is obtained from the seeds of *Brassica campestris chinoleifera, Vichover.* The seeds contain from 39 to about 45 per cent of oil. The expressed oil is golden yellow. Viehover, Clevenger, and Ewing [*J. Agric. Research,* **20,** 117 (1920)] made an extensive study of the plant and seed. They report the following characteristics: Sp. g. at 25° C. 0.9097; Sap. V. 173.8; Iod. No. (Hanus) 100.3; $N_D^{25°}$ 1.4695; Sol. Acids 0.07%; Insol. Acids and Unsap. 96.1%.

The volatile oil was found to be crotonyl isothiocyanate, which is also obtained from ordinary rape seed. The mustard volatile oil is allyl isothiocyanate.

The oil can be used for edible and technical purposes in the same manner as rape oil. Also the press cake can be fed to stock, but it is not suitable for use as "mustard."

Mustard Seed Oils. *Sinapis alba,* the white mustard, is cultivated for its seed in Europe and elsewhere. The seeds contain from 24 to 27 per cent of oil. The oil is expressed and the press cake is ground and used as a condiment. The oil has the following characteristics: Sp. g. at 15° C. 0.9125 to 0.9160; Sap. V. 171 to 177; Iod. No. 94 to 106; $N_D^{15.5°}$ 1.4750, at 20° C. 1.4704; Titer 9° to 10° C. The composition has been investigated by Hilditch, Riley and Vidyarthi [*J. Soc. Chem. Ind.,* **46,** 457T (1927)] with the following results: Palmitic 2.0, lignoceric 1.0, arachidic 1.0, stearic tr., oleic 28, linoleic 19.5, and erucic 52.5 per cent. No rapic acid was present. The oil is used as a lubricant and as a burning oil.

Brassica nigra, the black mustard, is grown in India, Europe and elsewhere. The seeds contain from 27 to 33 per cent of oil. The oil, which usually is of a brownish-yellow color, has a mild taste and is a by-product of the volatile mustard oil industry. In India, the oil is employed chiefly for edible purposes, but in Europe the oil is used in making soft soap. It is also used as a lubricant.

The oil has the following characteristics: Sp. g. at 15° C. 0.917 to 0.922; Sap. V. 176 to 184; Iod. No. 114 to 124; $N_D^{20°}$ 1.4720 to 1.4733; Titer 6° to 8°.

Hilditch, Riley and Vidyarthi [*J. Soc. Chem. Ind.,* **46,** 457T (1927)] found a sample of the oil to have the following composition: Palmitic 2.0, lignoceric 2.0, oleic 24.5, linoleic 19.5, linolenic 2.0, and erucic 50.5 per cent.

Sudborough and V. M. Mascarenbas [*J. Ind. Inst. Sci.,* **9A,** 25-70

(1926)] investigated the Indian rai oil (from *B. nigra*) from Mysore. Characteristics: Sp. g. at 15.5° C. 0.9178; $N_D^{20°}$ 1.4736; Sapon. V. 179.8; Acetyl V. 17.1; Unsap. 1.18%; Acid V. 0.95. Composition: Myristic 0.5, stearic 0.0, behenic 3.8, lignoceric 1.1, oleic 32.3, linoleic 18.1, linolenic 2.7, and erucic 41.5 per cent.

The plant *B. juncea,* which is closely allied to *B. nigra,* is cultivated for its seed. The oil from the seed is used largely for edible purposes in India. Crossley and Le Sueur [*J. Soc. Chem. Ind.,* **17,** 992 (1898)] examined the oil with the following results: Sp. g. at 15.5° C. 0.9206; Sap. V. 180; Iod. No. 108.3; R.M.V. 0.89.

The large seeded variety, *B. besseriana,* is extensively grown in Europe for the preparation of mustard.

Jamba Oil. This oil, which is somewhat similar to rape oil, is obtained from the seeds of the plant *Eruca sativa.* It has the following characteristics: Sp. g. at 15.5° C. 0.915 to 0.917; Sap. V. 172 to 175; Iod. No. 95 to 104; Unsap. 0.4 to 1.0%; Titer 11° to 16°.

The composition has been investigated by Sudborough and Mirchandini [*J. Indian Inst. Sci.,* **9A,** 25–70 (1926)]. They state that the jamba seeds, which are chiefly produced in north India (Punjab, Sind), contain from 26 to 31 per cent of oil. The expressed oil has the following characteristics: Sp. g. at 15.0° C. 0.9171; $N_D^{20°}$ 1.4750; Sap. V. 171; Iod. No. 96.3; Unsap. 0.7%; Acetyl V. 22.0. The composition was as follows: Stearic 4.2, behenic 4.5, lignoceric 1.2, oleic 28.7, linoleic 12.4, linolenic 2.1, erucic 46.3 per cent.

H. P. Kaufmann and H. Fiedler [*Fette u. Seifen,* **45,** 299 (1938)] examined a sample of the oil from seed grown in Germany and reported the following percentages of constituents: Oleic 5.4, linoleic 28.6, linolenic 0.9, erucic 58.5, and saturated acids 6.7.

This oil differs from rape oil in that it does not appear to be possible to make a satisfactory "blown oil." The oil has a characteristic odor and taste which render its detection easy. At times, this oil is exported from Kurrachee to Europe. For use as a burning oil, it is superior to ravison, but not equal to high-grade rape oil.

Radish Seed Oil. Radish seeds contain from 45 to about 50 per cent of oil which closely resembles rape oil. Grimme examined the oils from 4 distinctly different varieties. The oils had the following characteristics: Sp. g. at 15.5° C. 0.9165 to 0.9178; Sap. V. 179.6 to 181.6; Iod. No. 90.8 to 103.5; $N_D^{20°}$ 1.4710 to 1.4722; Hehner V. 94.9. De Negri and Fabis, as well as Crossley and Le Sueur, also examined radish seed oils with similar results.

Rape (Colza) Oil. This oil is obtained from the seeds of *Brassica rapa, napus, oleifera, glauca,* and other closely related species (often included under *B. campestris*), which yield oils having similar physical and chemical characteristics. Although these plants are botanically quite distinct, the oils are not distinguished commercially and are sold as rape oil. Some of the oil, however, is sold under the name of the country of its origin, such as Japanese, Indian, etc. The seeds from

which the commercial rape oils are obtained are extensively cultivated in Europe, India, China, and Japan. The approximate annual production of the more important producing countries up to recently has been as follows: India 2 to 2.7 billion pounds, Japan 150 million pounds, and Poland 101 to 115 million pounds. Europe produces from 300 to 350 million pounds. The oil content of these seeds ranges from 30 to 45 per cent.

The term "colza" formerly referred only to that expressed from the finest French seed, but now it generally refers to the refined oil, regardless of its source.

The oil is obtained from the seed either by expression or by extraction with volatile solvents. It is quite customary in Europe to extract this oil with petroleum ether or other solvent, but elsewhere most, if not all, of the oil is expressed. The press cake or extracted meal, if free from mustard seed, can be utilized for feeding stock.

The crude oil, depending upon the kind of seed and the method employed for its extraction, varies in color from yellow to yellowish-brown or green. It has a characteristic odor and a more or less pungent taste. In order to remove the various non-oil constituents extracted in varying quantities along with the oil, it is customary to refine the oil by agitating it with 0.5 to 1.5 per cent of sulfuric acid. Formerly concentrated acid was used, but now a solution containing about 50 per cent of sulfuric acid is preferred. After thorough agitation of the oil and acid for about an hour, the mixture is allowed to rest until the charred impurities and acid solution have settled. The oil is withdrawn from the foots and washed several times with hot water. When the wash water has been entirely separated, the oil is bright yellow. The oil is also refined by caustic soda which, unlike the acid method, has the advantage of removing the free fatty acids, instead of increasing them. This undoubtedly is the preferable procedure, as it is in the case of refining linseed oil.

Composition.—Sudborough, Watson, and Ayyar [*J. Indian Inst. Sci.*, **9A**, 25 (1926)] made an exhaustive study of Indian rape oil *(B. napus)*, which had the following characteristics: Sp. g. at 15.5° C. 0.9147; $N_D^{20°}$ 1.4728; Sap. V. 172.4; Iod. No. (Winkler) 91.6; Unsap. 0.76%.

The composition of the mixed fatty acids was as follows: Myristic 1.5, stearic 1.6, behenic 0.5, lignoceric 2.4, oleic 20.2, linoleic 14.5, linolenic 2.1, and erucic 57.2 per cent.

Y. Toyama [*Chem. Absts.*, **17**, 3106 (1923)] examined a sample of Japanese rape oil and found that the saturated acids, which amounted to 2 per cent of the oil, consisted of palmitic, stearic, behenic, arachidic, and lignoceric acids, while the unsaturated acids were oleic, linoleic, linolenic and erucic.

Hilditch, Riley and Vidyarthi [*J. Soc. Chem. Ind.*, **46**, 457T (1927)] examined a sample of English rape oil with the following results: Palmitic 1.0, lignoceric 1.0, oleic 32.0, linoleic 15.0, linolenic 1.0, and erucic 50.0 per cent. This oil was extracted with carbon tetrachloride

from English-grown rape seed. The oil had a saponification value of 178.9, an iodine value of 102.9, an acidity of 0.1 per cent as oleic acid, and contained 1.1 per cent of unsaponifiable matter. These authors have shown (*ibid.*, 462T) definitely that rape oil does not contain rapic acid, which for many years was considered to be present. It will be observed that none of the other investigators mentioned above reported rapic acid.

The composition of rape oil of German origin has been studied by K. Täufel and E. L. Bauschinger [*Z. Unters. Lebensm.*, **56**, 256 (1928)] with the following results: Erucic acid 43.5 per cent, oleic 37.8, linoleic 10.6, linolenic 3.5, saturated acids 0.8, and unsaponifiable 1.0 per cent. These authors [*Chem. Abs.*, **23**, 3363 (1929)] found that the oil contained oleo-linoleno-erucin, oleo-dierucin and trierucin.

Hilditch and Paul [*J. Soc. Chem. Ind.*, **54**, 331T (1935)] published a paper on the component fatty acids and glycerides of partly hydrogenated rape. For this investigation a sample of expressed oil from East Indian seed was used which gave an iodine number of 103.2 and a saponification equivalent of 323.0 The mixed fatty acids contained the following percentages of constituents: Palmitic 2, lignoceric 1, oleic and isoleic 17, linoleic 29, and erucic 51. No myristic acid could be detected. The authors stated that it is extremely difficult to give any definite data as regards the possible small quantities of stearic, arachidic and behenic acids which may be present in the original oil to the extent of not more than one per cent. From their investigation, it was concluded that the oil contained about 50% of di-C_{18}-erucin, 44 of mono-C_{18}-dierucin (the C_{18} acid being either oleic or linoleic) and possibly about 6% of mixed palmito-oleo (or linoleo) erucins. From their observations on the course of the hydrogenation of these unsaturated fatty acid radicals, it is believed that the oil contains both alpha and beta oleo-(linoleo) dierucins and erucodioleins (linoleins). For details and other information, the original publication should be consulted.

Hilditch and Pedelty [*Biochem. J.*, **31**, 1964 (1937)] have investigated the component fatty acids of the phosphatides of rape seed.

It is very important in future studies that the botanical species should be known from which the oil was obtained; otherwise the oil should not be studied.

The following characteristics for rape oils have been selected from the extensive investigations of Archbutt, Crossley and Le Sueur, and Lewkowitsch: Sp. g. at 15.5° C. 0.9139 to 0.9160; Sap. V. 170 to 180; Iod. No. 98 to 106; Unsap. 0.5 to 1.5%; N_D at 15° C. 1.4720 to 1.4757, at 20° C. 1.4726 to 1.4742; Hexabromide 2.4 to 3.6%; Viscosity (Redwood viscosimeter) at 21° C. 365 to 380. Authentic Indian rape oils (Crossley and Le Sueur); Sp. g. at 15.5° C. 0.9141 to 0.9171; Sap. V. 168 to 174; Iod. No. 94 to 104.8; Acid V. 1.4 to 4.0; R.M.V. 0.0 to 0.79; Viscosity at 21° C. 371 to 464.

Much information on Indian mustard and rape seed and the oils covering all phases of the industry will be found in the 20-page Bulletin on Indian Industrial Research No. 13 (1938) of the Industrial Research Bureau, Delhi, India.

Properties. Crude rape oil varies from yellow to dark brown. The color depends upon the variety and quality of the seed as well as on the method used for the extraction of the oil. The oil may or may not deposit stearin on standing at ordinary temperatures. Generally, the oil does not solidify until it is cooled below −10° C. It has a characteristic odor and flavor. In the usual classification, the oil is placed between the non-drying and semi-drying classes. Its most characteristic properties are its high viscosity and its low saponification value, which is due to the presence of a large percentage of glycerides of erucic acid. The oil does not readily thicken when heated and exposed to the air; moreover, the better grades have good keeping qualities, both of which advantages favor its use as a lubricant and for burning in lamps.

Refined Oil. Oil refined by the caustic soda process should not contain over 0.1 per cent of free fatty acids and should be entirely free from soap. Oil properly refined by the sulfuric acid method should not contain over 0.006 per cent of sulfuric acid nor over 3 per cent of fatty acids (as oleic acid), and preferably less.

Blown Oil. Large quantities of rape oil are blown in equipment similar to that used for the treatment of linseed oil (in this case mechanical agitators are seldom used), until the desired viscosity is obtained. During the blowing, as in the case of linseed oil, the iodine number is diminished while the saponification value, gravity, refractive index, acetyl value, and soluble fatty acids show marked increases.

Thomson and Ballantyne [*J. Soc. Chem. Ind.*, 11, 506 (1892)] examined rape oil which had been blown for 5 then for 20 hours and a sample of commercial blown oil for comparison.

	Original Oil	Blown, 5 Hrs.	Blown, 20 Hrs.	Commercial Blown Oil
Sp. g. at 15.5° C.	0.9141	0.9257	0.9615	0.9672
Acidity, as oleic acid	5.1	5.01	7.09	4.93
Sap. V.	173.9	183.0	194.0	197.7
Iod. No.	100.5	88.4	63.2	63.6
Unsapon.	0.65	...	0.76	2.80
Hehner V.	94.76	...	85.94	82.40
Non. vol. sol. acids / Vol. sol. acids } %	0.52	...	0.82	1.90

For other data, *see* Lewkowitsch [*Analyst*, 27, 683 (1902)], and Volume 3 of his book.

As blown oil is prepared for lubricating purposes, it is important to select oils for this treatment low in free fatty acids. If the finished product is to be used alone as a lubricant, it should not contain over 3 per cent of fatty acids and preferably less, on account of their corrosive action. When, however, blown oil is mixed with mineral oil, it has been repeatedly observed that the presence of one or two per cent of free fatty acids in this mixture greatly improves its lubricating qualities [Wells and Southcombe, *J. Soc. Chem. Ind.*, 39, 51T (1920)]. The "Germ Process" patent (Eng. Pat. 130, 377, 1918) was based upon this discovery. In the absence of mineral oil, free fatty acids do not appear to increase noticeably the lubricating properties of either animal

or vegetable oils. Only in the absence of air and moisture, which is seldom the case in the practical utilization of lubricating oils, are free fatty acids without action in contact with metals such as are used in the construction of machinery.

Tests. No specific color test for rape oil has been developed. The low saponification value and the viscosity of the oil are of value in its examination. Also the odor and taste of the unrefined oil are characteristic. In the absence of mustard, cress seed, and other closely related oils, use may be made of the separation and identification of erucic acid, which gives a lead salt having little solubility in ether and separates along with the lead salts of the higher saturated fatty acids. The solid fatty acids separated from rape oil by the lead-salt-ether method have an iodine number of over 60, while the iodine number of the solid acids when properly prepared by this method, in the case of any commercial oil (except mustard oils) with which rape may be mixed, range from 2 to about 10. The directions given in this book for the lead-salt-ether method should be followed in every detail.

See *Olive Oil* for the H. Kreis method for the detection of rape oil. Thomas and Mattikow [*J. Am. Chem. Soc.*, **48**, 968 (1926)] have proposed a method for the direct identification of rape oil by the isolation of erucic acid, but this procedure does not distinguish it from mustard seed and other related oils which contain large proportions of erucic acid.

Attention is called to the following references:

"A New Method for Testing of Rape and Mustard Seed Oils and Adulterating Oils," S. Neogi, *Analyst*, **61**, 597 (1936).

"Detection of Oils Derived from the *Cruciferae* in Edible Oils," J. Grossfeld, *Z. Unters. Lebensm.*, **73**, 409 (1937); *Analyst*, **62**, 561 (1937).

Adulterants. Rape oil, at times, is adulterated with mineral, ravison, mustard, cottonseed, sesame and other drying or semi-drying oils. The presence of mineral or rosin oils is detected by the increase in unsaponifiable matter, which in the case of pure rape oil does not exceed 1.5 per cent and is usually much less. Mineral oil also lowers the saponification value. The presence of appreciable quantities of cottonseed or other semi-drying oil raises the titer of the fatty acids (rape 12° to 18° C.), as well as the saponification value. The color tests for cottonseed and sesame oils may be used, but other proof should be obtained as to the presence of these oils in any quantity, because traces are sometimes due to the expression of rape oil in mills previously engaged in pressing cotton- or sesame seed. Ether-insoluble bromides in excess of 4 per cent would indicate the presence of linseed or fish oils. The presence of small percentages of mustard or closely related oils cannot be detected, but larger percentages of these oils would raise the iodine number and lower the viscosity. Ravison oil would also lower the viscosity of rape oil.

Uses. The cold-pressed oil is used for edible purposes in India and some of the European countries. Some is also used as a "bread oil," for oiling the loaves before baking to give them a fine appearance. Oil

refined by the caustic soda method and deodorized is also used for edible purposes. Large quantities of the refined oil, as well as the blown product, are used alone or in mixture with mineral oil for lubrication of delicate mechanism. Rape oil is used extensively for burning in lamps. For this purpose, the oil should be low in free fatty acids and free from foreign substances which, when present in small proportions often clog the wicks or otherwise interfere with the proper burning of the oil, a few hours after the lamps have been lighted. Refiltration of the oil often improves its burning qualities. The oil is also used as a wool oil, in making soft soap, and for quenching or tempering steel plates, etc.

Ravison Oil (Black Sea Rape). Ravison oil is obtained from the seeds of a variety of *Brassica campestris* from the Black Sea region. The seeds contain from 33 to 40 per cent of oil. The oil has the following characteristics: Sp. g. at 15.5° C. 0.9175 to 0.9217; Sap. V. 173 to 181; Iod. No. 109 to 122; Unsap. 1.4 to 1.8%; Viscosity (Redwood Viscosimeter) at 21° C. 329 to 334.

The composition of the oil has been investigated by Hilditch, Riley, and Vidyarthi [*J. Soc. Chem. Ind.*, **46**, 457T (1927)] with the following results, Palmitic 2.0, lignoceric 2.0, oleic 20.5, linoleic 25.5, linolenic 2.0, and erucic acid 47.0 per cent. A trace of behenic acid was also found.

The oil is similar to rape oil, but it has a higher gravity, and iodine value. The viscosity is considerably less than that of rape oil. As it has more marked drying properties, it is less suitable for use as a lubricant than rape oil. Blown ravison oil is prepared for lubrication purposes. On account of its strong taste, it is not suitable for edible purposes, unless thoroughly refined. It is used locally for various purposes, including soap making, as a lubricant, and as a burning oil, for which purpose it is not so well adapted as rape oil.

Egyptian Lettuce Seed Oil. This oil is obtained from the seed of the prickly lettuce, *Lactuca scariola,* which is cultivated in Upper Egypt. The seed contains from 33 to 37 per cent of oil. The oil which is expressed by the natives has a golden yellow color and an agreeable flavor. The characteristics are as follows: Sp. g. at 15.5° C. 0.9247 to 0.9334; $N_D^{40°}$ 1.4672; Sap. V. 190; Iod. No. 122 to 136; R.M.V. 0.1; Pol. No. 0.2; Acetyl V. 12.

Bael Seed Oil. This oil is in the seeds of the fruit from the Indian tree *Aegle marmelos* of the *Rutaceae.* The fruits are used in India for the treatment of dysentery. The seeds, each of which weighs about 0.12 gram, consist of 76.5 per cent of kernel and 23.5 of shell. The kernels contain about 45 per cent of oil.

R. Child [*J. Am. Chem. Soc.*, **57**, 356 (1935)] examined the oil with the following results: Sp. g. at 30° C. 0.9180; $N_D^{40°}$ 1.4647; Sap. V. 193.6; Iod. No. (Wijs) 108; SCN V. 70.4; Unsap. 1.58%. The oil contained the following percentages of acids: Oleic 28.7, linoleic 33.8, linolenic 7.6, palmitic 15.6, and stearic 8.3.

Grapefruit Seed Oil. Jamieson, Baughman and Gertler [*Oil and Fat Ind.*, 7, 181 (1930)] found that the air-dried seed contained 30 per cent of oil. The expressed oil gave the following characteristics: Sp. g. at 25° C. 0.9170; $N_D^{25°}$ 1.4700; Iod. No. (Hanus) 106.3; Sap. V. 194.1; Acid V. 2.5; Acetyl V. 7.7; Unsap. 0.7%; Sat. Acids 28.60%; Unsat. Acids 68.50%. The oil contained the following percentages of fatty acids: Oleic 19.66, linoleic 48.84, palmitic 19.2, stearic 7.25, and lignoceric 0.16.

The solvent-extracted meal was examined by Bidwell and Coe (*loc. cit.*) with the following results: Moisture 9.7, ash 3.8, fat 4.3, proteins 21.4, crude fiber 22.0, and nitrogen-free extract 38.8 per cent. This analysis indicates that the meal has considerable value as a feed, but owing to the bitter taste it would be necessary to add other feeding materials that would render the mixture palatable to stock.

The oil, like that of other citrus seeds, has a bitter taste which is somewhat difficult to remove by deodorization. The oil, upon saponification with caustic soda, gave a medium hard soap with good lathering properties. In recent years, some of the seeds which are separated at the canning and juice plants are crushed and pressed in Florida. It is understood that the oil, after sulfonation, is used to some extent in connection with the dyeing of cotton goods. The manufacture of the oil and its properties are discussed by A. J. Nolte and H. W. von Loesecke in *Ind. Eng. Chem.*, **32**, 1244 (1940).

Lime Seed Oil. Lime seeds, which are a waste product from the lime juice industry in the West Indies and neighboring islands, contain from 31 to 40 per cent of oil, which has a bitter unpleasant taste. It is stated that the bitterness can be removed by refining with caustic soda or by washing with alcohol. The crude oil is suitable for making soap.

The oil examined at the Imperial Institute [*Bull. Imp. Inst.*, **20**, 466 (1922)] gave the following characteristics: Sp. g. at 15°/15° C. 0.9236; $N_D^{40°}$ 1.4635: Iod. No. 109.5; Sap. V. 197.7; Unsap. 0.4%; R.M.V. 0.27; Pol. No. 48; Titer 34.9° C.; Acid V. 13.6. The press cake contains 15.1 per cent of moisture, 30.5 of crude protein, 14.27 of oil, 17 of carbohydrates and 20 of fiber. This could be used as a fertilizer or locally as a feed for stock. A. E. Collins [*Analyst*, **51**, 510 (1926)] also examined a sample of this oil. Sp. g. at 27°/15.5° C. 0.9138; $N_D^{28°}$ 1.4740; Sap. V. 193.5; Iod. No. 109.7; Unsap. 0.72%; Sol. Pt. −3° C.; Acid V. 11.2.

Lemon Seed Oil. This oil is obtained from the seeds of the lemon, which have an oil content of 30 to 35 per cent. The oil is extracted by solvents in southern Italy, where the seeds are obtained in quantity by the essential oil and citric acid manufacturers. The oil is characterized by having a bitter taste which is not readily removed. It is used in soap making. It is sometimes called "lemon pip oil."

The range of the characteristics reported by various investigators is as follows: Sp. g. at 15.5° C. 0.921 to 0.923; $N_D^{40°}$ 1.4659 to 1.4669;

Sap. V. 188 to 196; Iod. No. 103 to 109; R.M.V. 0.6; Pol. No. 0.3; Titer 32° to 38°.

Orange Seed Oil. This oil is obtained from the seeds of oranges. The seeds when dry contain from 40 to 45 per cent of oil. The freshly expressed oil has little odor or taste, but upon keeping, a bitter taste develops. It can be used in soap making. This oil is sometimes known as "orange pip oil." The press cake from citrus fruit seeds is intensely bitter.

The range of the characteristics which have been reported by various investigators is as follows: Sp. g. at 15.5° C. 0.921 to 0.925; $N_D^{40°}$ 1.4638 to 1.4647; Sap. V. 194 to 197; Iod. No. 98 to 104; Titer 34° to 35°.

Hollyhock Seed Oil. The oil and seed of *Althaea rosea* were investigated by Hiltner and Feldstein [*J. Ind. Eng. Chem.*, **13**, 635 (1921)]. The seeds contain only about 12 per cent of oil. The ether-extracted oil has a greenish-yellow oil similar to some raw linseed oils. This oil has the following characteristics: Sp. g. 15.6° C. 0.9275; $N_D^{25°}$ 1.4722; Iod. No. 119.0. The oil gave strong Halphen and Bechi tests. This was to be expected since the hollyhock belongs to the *Malvaceae* family.

Ivory Wood (Pao Marfin) Seed Oil. This oil is found in the seed of the Brazilian tree *Agonandra brasiliensis* which belongs to the *Olacaceae* family. L. Gingel and T. F. de Amorim [*Mem. Inst. Chim., Brazil*, **1929**, No. 2, 31; *Chem. Absts.*, **24**, 3668 (1930)] have examined the seeds and oil. The seeds contained 35 (kernels 65) per cent of a viscous brown oil which was found to be completely soluble in cold alcohol. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.9602: $N_D^{23°}$ 1.4925; Sap. V. 207.3; Iod. No. (Hübl) 112.3, Acid V. 66.8; Unsap. 0.6. The oil contained the following percentages of acids: Ricinoleic 44.85; oleic 11.45, linoleic 34.65, myristic 2.21, and palmitic 1.32 per cent.

Fatty acids, as glycerides, were as follows: Ricinoleic 44.85, linoleic 34.65, oleic 11.45, myristic 2.21, and palmitic 1.32 per cent.

The oil is said to undergo oxidation readily. Upon sulfonation, it yields a product similar to Turkey red oil (sulfonated castor oil). Prolonged action of sulfuric acid and partial hydrogenation give a spongy product which might be used in the preparation of a rubber "substitute."

Jute Seed Oil. This oil is obtained from the seed of *Corchorus capsularis*, which is chiefly grown for its fiber in India, parts of China, Egypt, and other countries. The oil has been examined by Nirmal-Kumar Sen [*Chem. Absts.*, **23**, 2056 (1929)] with the following results: Sp. g. at 28° C. 0.923; $N_D^{29.7°}$ 1.4615; Sap. V. 184.6; Iod. No. 102.6; Acetyl V. 27.3; R.M.V. 0.16; Acid V. 1.5; Unsap. 2.25%; Sol. Pt. −20° C.

Fatty acids, as glycerides, were as follows: Oleic acid 39.2 and linoleic acid 44.6 per cent. Small quantities of palmitic, stearic, and arachidic acids were detected.

Madia (Tar Weed) Seed Oil. This oil is obtained from the seeds of the plant, *Madia sativa,* of the *Asteraceae* family, indigenous to California and Chile. Many years ago it was introduced into Algeria, Asia Minor, Europe and elsewhere. It is a heavy-scented, hairy, sticky, annual from 1 to 3 feet high, which has narrow entire leaves and inconspicuous, pale yellow flowers. The seed contain from 30 to 35 per cent of oil for which the following characteristics have been reported: Sp. g. at 15° C. 0.925 to 0.929; Sap. V. 193 to 195; Iod. No. 117 to 129; Unsap. 0.8%; Titer 20 to 22°. The cold-pressed oil has a mild, pleasant flavor and is edible. For many years the plant was cultivated in Chile and the oil was used for edible purposes and soap manufacture.

Mlenda Seed Oil. This oil is found in the almost black oval seeds of the plant *Sesamum augustifolium.* Seed from Tanganyika, Africa [*Bull. Imp. Inst.,* **27,** 281 (1929)], contained 7.5 per cent of water and 28.9 of oil. The pale green limpid oil gave the following characteristics: Sp. g. 15°/15° C. 0.9365; $N_D^{40°}$ 1.4708; Sap. V. 181.6; Iod. No. (Hübl) 117.7; Acid V. 16.8. The oil gave the Baudouin test like that of sesame oil. The extracted meal contained 23.8 per cent of protein (sesame cake 38 to 40), 40 per cent of crude fiber (sesame cake 4.4). It is much inferior to sesame cake. In addition, tests showed the presence of alkaloidal substances. As an oil seed, it is of little value as compared with the seed of *Sesamum indicum.*

Oil of Mexican or Prickly Poppy Seed (Argemone). This oil is obtained from the seed of the annual *Argemone mexicana,* indigenous to Mexico but introduced into many subtropical and tropical countries. The seeds, which weigh about 2 milligrams, contain about 36 per cent of oil, which has a slightly acrid odor and bitter taste. The oil is employed to some extent in medicine both in India and the West Indies, and is stated to have purgative properties. In Mexico, the oil is used as an illuminant. Also it can be used for making soap. This semi-drying oil does not "dry" satisfactorily even when mixed with various driers.

The oil from seeds collected in South Africa was examined [*Bull. Imp. Inst.,* **20,** 292 (1922)] with the following results: Sp. g. 15°/15° C. 0.9220; $N_D^{40°}$ 1.466; Iod. No. 123.7: Sap. V. 192.7; Unsap. 1.14%; R.M.V. 0; Pol. No. 1.16; Titer 22.8°.

In 1941, a sizable sample of the seed, which contained 8.4% of moisture and 35.9% of oil, was pressed in our laboratory oil expeller. The oil gave the following characteristics: $N_D^{25°}$ 1.4731; Sap. V. 189.6; Iod. No. (Wijs) 127.8; SCN V. (24 hrs. at 20° C. using 0.1 N. SCN Sol.) 77.7; Acid V. 2.28; Unsap. 1.40%; Sat. acids 13.3%; Unsat. acids 80.3%.

The oil was found to contain the following percentages of acids: oleic 21.3, linoleic 58.6, hexadecenoic 0.8, myristic 0.26, palmitic 11.1, stearic 1.8, and lignoceric 0.12.

The press cake is suitable only for use as a fertilizer.

Papaw Seed Oil. This oil is from the seeds of the fruit of the

North American tree *Asimina triloba,* belonging to the family of *Anonaceae.* The seeds contain 38 per cent of oil. J. L. Riebsomer, J. Bishop and C. Rector [*J. Am. Chem. Soc.,* **60,** 2853 (1938)] have examined the oil with the following results: Sap. V. 194; Iod. No. (Hanus) 111.3; R.M.V. 1.05; Acid V. 6.4; Acetyl V. 18.11; Unsap. 0.8 per cent; Sat. acids 5.6; Unsat. acids 85.5 per cent. The oil contained the following percentages of acids: Oleic 59.4, linoleic 26.1, palmitic 2.3, stearic 1.8, and arachidic acid 1.5 per cent.

Pine Seed Oils. This oil is found in the seeds of the tree *Pinus monophylla,* which grows on the eastern slopes of the Sierra Nevada Mountains in the United States. The kernels contain about 16 per cent of oil having a mild aromatic flavor. The oil examined by M. Adams and A. Holmes [*Ind. Eng. Chem.,* **5,** 285 (1913)] gave the following results: $N_D^{15°}$ 1.4733, at 40° C. 1.4543; Sap V. 189.3; Iod. No. (Hübl) 108.

A. H. Gill [*Oil and Soap,* **10,** 7 (1933)] examined the oil of seeds from Nevada, for which the following characteristics were reported: Sp. g. at 20° C. 0.911; Iod. No. (Hanus) 102.1; Sap. V. 183.9; SCN V. 78.8; R.M.V. 0.89; Unsap. V. 1.95%; Sat. acids 8.1 and Unsat. acids 84.5 per cent. The oil contained the following percentages of acids: Myristic 5.0, palmitic 2.7, stearic 0.4, oleic 30.2 and linoleic 54.3.

The seed oil of *Pinus pumila* has been investigated by G. V. Pigulevskii and M. A. Ivanova [*J. Applied Chem. U. S. S. R.,* **7,** 569 (1934); *Chem. Abs.,* **29,** 2007 (1935)]. The seeds contained 23.8 and the kernels 51.2 per cent of oil. The characteristics were as follows: Sap. V. 191.3; Iod. No. 161.1; SCN V. 91.0. Percentages of constituents of mixed fatty acids were as follows: Oleic 17.5, linoleic 71.8, linolenic 5.5, and saturated acids 5.1.

The seed oil of the Digger pine *(Pinus sabiniana)* has been examined by J. Semb. [*J. Am. Pharm. Assoc.,* **24,** 609 (1925); *Chem. Abs.,* **29,** 7104 (1935)]. The kernels, which amount to 23 per cent of the seed, contain 53 per cent of oil. On the basis of the whole seed, the oil content is 12.2 per cent. The characteristics are as follows: $N_D^{24°}$ 1.4713; Sap. V. 189.8; Iod. No. (Hanus) 120; SCN V. 83.0; Acid V. 4.5. The percentages of the constituents of the mixed fatty acids were as follows: Oleic 50.5, linoleic 45.2 and saturated acids 4.3.

W. Peyer [*Apoth. Ztg.,* **44,** 699 (1929)] examined the seed oil of the stone pine *(Pinus pinea)* which is found in Southern Europe. It reaches a height of eighty feet. The kernels contained 5.5% of moisture, 45.6 of oil, 4.4% of ash, and 40.6 of crude proteins. The characteristics of the oil were as follows: Sp. g. at 150° C. 0.9200; Sap. V. 193.1; Iod. No. 118.0; Unsap. 1.98 per cent.

The oil from the seeds of *Pinus gerardiana,* a tree growing in northwest India and Afghanistan, has been examined by S. D. Hardikar [*J. Soc. Chem. Ind.,* **47,** 3340 (1928)]. The kernels contain 33.7 per cent of oil which give the following characteristics: Sp. g. at 32° C. 0.9144; $N_D^{32°}$ 1.4709; Sap. V. 192.4; Iod. No. (Hübl) 121.3; Unsap. 0.5%; Acetyl V. 4.07.

The oils from the seeds of various coniferous trees have been examined with regard to their more important characteristics by Grimme, *Chem. Zeit.*, **35**, 925 (1911).

Anda-assu (Princeps) Seed Oil. This oil is obtained from the seeds of the Brazilian tree *Joannesia princeps*, belonging to the *Euphorbiaceae*. The kernels, which weigh from 10 to 20 grams each, contain about 56 per cent of oil. The oil has a laxative effect about 4 times as great as that of castor oil, but in contrast to the latter it has an agreeable odor and flavor, and a low viscosity, and causes no irritation or nausea when taken. The oil has been examined by Etzel and King [*J. Am. Chem. Soc.*, **48**, 1369 (1926)] with the following results: Sp. g. at 15.5° C. 0.9257, at 20° C 0.9229; $N_D^{20°}$ 1.4750; Sap. V. 192; Iod. No. (Hanus) 115.7; Acetyl V. 8.7; R.M.V. 1.2; Pol. No. 0.35; Unsap. 1.2%; Sat. Acids 7.8%; Unsat. Acids 80.45%. L. Gurgel and F. Ramos [*Chem. Abs.*, **24**, 3667 (1920)] reported the following characteristics: Iod. No. 122.5; Sap. V. 207.3; $N_D^{28°}$ 1.4742; Unsap. 0.97%. The oil was found to contain the following percentages of fatty acids as glycerides: Oleic 42.5; linoleic 43.1, myristic 2.20, and palmitic acid 5.03.

M. Silva [*Bol. Inst. Nac. Tech.*, **2**, 5 (1937)] found that a sample of the oil gave a saponification value of 192.7 and an iodine number by the Hanus method of 138.0. A sample of the oil from Brazil examined by H. A. Gardner [*Nat. Pt. Var. & Lac. Assoc. Circ.* 481, **155** (1935)] gave an iodine number of 147.7 by the same method. As these two results are much higher than those previously reported, it would appear that further examination of the oil is desirable.

An analysis of the solvent-extracted meal gave the following percentages of constituents: Moisture 5.27, proteins 62.84, crude fiber 4.84, carbohydrates 15.44 and ash 11.7.

Rose Mallow Seed Oil. C. Barkenhouse and S. T. Thorn [*J. Am. Chem. Soc.*, **57**, 728 (1935)] examined the seed and oil of the mallow, *Hibiscus moschentos*, of the *Malvaceae*. The seed contained the following percentages of constituents: Moisture 7.35, oil 20.23, proteins 24.84, crude fiber 21.64 and ash 4.15. The oil gave characteristics as follows: Sap. V. 185.5; Iod. No. (Hanus) 107.8; SCN V. 68.29; R.M.V. 1.8; Acetyl V. 22.9; Unsap. 1.34 per cent; Sat. acids 14.13 per cent; and unsaturated acids 76.67 per cent.

The saturated acid fraction consisted largely of palmitic acid. Besides some stearic acid, a trace of arachidic acid was detected. The oil contained 33.1 per cent of oleic acid and 45.5 of linoleic acid as glycerides.

Sesame Oil. Sesame oil, also known as benne, teel, gingili, and by many other names, is obtained from the seed of a herbaceous plant, *Sesamun indicum*, of which several varieties or sub-species are known. Sesame belongs to the small family of *Pedaliaceae*, which is sometimes annexed to the *Bignoniaceae*.

Sesame plants usually grown from two to four feet high (sometimes much higher). The lower leaves are broad, coarsely toothed or lobed,

while the upper leaves are lanceolate. The flowers, which are tubular and two-lipped, are about three-quarters of an inch (1.8 cm.) long. They vary in color; some are pinkish and others are yellow. They have four stamens of unequal length. The seed pod is two-valved and contains numerous small seeds. When matured, the pods open and often scatter much of the seed.

Sesame seed are white (pale yellow), dark red, brown or black. Commercially, the seed is known as white and black. "White sesame" must contain at least 85 per cent of white seeds. When "black seeds" exceed 15 per cent, allowance is made in price in proportion to the quantity of black seeds present, but when 25 or more per cent is present, the seed is not classified as white. The white seeds yield oil superior in quality to that from the dark-colored seeds.

Since the sesame plant has been cultivated from time immemorial, its original locality is not known. Sesame seed is produced in China, India, North, East and West Africa, Japan, Java, Siam, the Levant, Egypt, Mexico, and elsewhere. Although there are no statistical data either on the acreage planted or the quantity of seed produced, China annually produces a very large quantity. It is known that only a small proportion of the Chinese production is exported. Exportation of sesame seed from Hankow has reached as high as 275 millions of pounds in a single year, but sometimes the exportation falls below 20 million pounds. The exportation of sesame oil amounts to a few million pounds. Sesame oil is the most expensive edible oil produced in China; consequently it is subject to adulteration with cheaper and often inferior vegetable oils, there being no regulatory laws. The Chinese use the oil chiefly for edible purposes and feed the press cake to cattle.

Sesame is one of the most important of the oil seeds grown in India. Several millions of acres of land are devoted to its cultivation. Like China, the larger part of the oil is used in India. The exportation of oil and seed seldom exceeds 5 per cent. The varieties with dark-colored seeds are chiefly grown, but in some localities the white seeds are produced. The oil is used in India for edible purposes, soap making, medicinal purposes, and as a burning oil.

The production of sesame seed in Japan has always been small and amounts to only a few million pounds. The arable land is limited and is needed for staple food crops. Japan imports sesame seed and produces oil not only for her own requirements, but also for exportation. About 20 per cent of the oil produced is exported.

Sesame seed is a crop of increasing importance in Mexico. The white or pale yellow seeded variety is most commonly grown. Here it has been found best to plant the seed directly after the rainy season. The seed is planted in hills arranged in rows three feet apart. The planting on the better class of plantations is made with cottonseed or corn planters. Before the plants get too large, they are cultivated two or three times with cultivators. When the plants are eight inches (20 cm.) high, they are thinned so as to leave one or two per hill. In about 14 weeks the plants begin to turn yellow, then they are cut by

hand and made into bundles, which are left on the ground for a day or two in order that the leaves may dry and fall off. Then the bundles are stacked in long rows. After standing for about two weeks, they are carefully carried in an upright position (the pods are open) to canvas spread on the ground, inverted and shaken to separate the seeds. The seed is cleaned and shipped to the oil mill. Under proper cultivation, the yield of seed per acre averages about 800 lbs., but sometimes it is much more. It is stated that the sesame plant in Mexico is not attacked by either the cotton weevil or the corn worms.

Sesame Seed. The seed is not only used for the production of oil, but in various countries it is also used to some extent in making various kinds of confectionery. Both seed and leaves are used as demulcents and for other medicinal purposes. The seeds contain from 50 to 57 per cent of oil. The brown or black seeds contain the most oil, but that from the white seeds, as previously mentioned, is much superior in quality. In pressing seeds with such a high oil content, special experience is necessary, particularly when modern hydraulic presses are employed. It is not difficult to express the oil in a satisfactory manner with a continuous expeller.

Sesame Oil. In Europe and Asia it is customary to express the oil in three stages. The first pressing is made cold. The second and third pressings are made at higher pressures and temperatures. The cold-pressed oil, after filtration, is ready for use for edible purposes. The hot-pressed oil is usually refined and deodorized before it is used for edible purposes in America and Europe. The crude oil varies from yellow to a dark amber color. The refined oil is usually pale yellow. Damaged seed is more frequently extracted with volatile solvents in Europe, to recover the oil. This oil is used to make mottled soap. The extracted meal is only used as fertilizer. The press cake obtained from the expression of sound sesame seed is a valuable cattle food.

Sesame oil is much used as a salad and cooking oil as well as in the manufacture of margarine and shortenings (lard substitutes). In some countries, notably Austria, Germany, and Belgium, it is compulsory to add 5 or 10 per cent to all butter substitutes to facilitate their detection when used to adulterate (or simulate) butter. The oil is also used in pharmacy, soap making and as a burning oil in primitive regions, besides for other minor purposes.

Composition. The oil investigated by Jamieson and Baughman [*J. Am. Chem. Soc.*, **46**, 775 (1924)] was expressed by means of an expeller from 100 lbs. of pale-yellow sesame seed grown in China and shipped from Hankow. The seed contained 55.1% of oil. The expressed oil had the following characteristics: Sp. g. 25°/25° C. 0.9187; $N_D^{20°}$ 1.4731; Acid V. 1.4; Iod. No. (Hanus) 110.8; Sap. V. 189.3; Acetyl V. 9.8; Sat. Acids 12.2%; Unsat. Acids 81.2%; and Unsap. 1.73%. The oil was found to contain the following acids: Linoleic 35.2, oleic 46.0, palmitic 7.3, stearic 4.4, arachidic 0.4, and lignoceric 0.04 per cent.

In connection with an investigation on the progressive hydrogena-

tion of peanut and sesame oils, T. P. Hilditch, M. B. Ichaporia and H. Jasperson [*J. Soc. Chem. Ind.*, **57**, 363 (1938)] found that the mixed fatty acids of the sesame oil contained the following percentages of constituents: Palmitic 9.1, stearic 4.3, arachidic 0.8, oleic 45.4, and linoleic 40.4. This oil was expressed from seed grown in Gujerat, India. It gave an iodine number of 109.6, a saponification equivalent of 294.9 and contained 1.2 per cent of unsaponifiable matter. These authors (*ibid.*, **57**, 84) showed that the oil did not contain over 1 per cent of hexadecenoic acid, which was not taken into account in this investigation.

The recorded chemical and physical characteristics of sesame oil are as follows: Sol. Pt. usually between 0° and −5° C.; Sp. g. at 15° C. 0.920 to 0.926; $N_D^{25°}$ 1.4698 to 1.4731 (at 15° C. 1.4742 to 1.4762); Unsap. 0.9 to 1.8; Iod. No. 103 to 115, and Sap. V. 188 to 193; Titer 21° to 24° C.; Neutralization V. 196 to 201. The iodine number of the unsaturated acids ranges from 129.5 to 139.9. Sesame oil is slightly dextrorotary. Utz [*Pharm. Zeit.*, **45**, 480 (1900)] found from 0.8° to 1.6° at 15° C., using a 200-mm. tube. Villavecchia and Fabris [*J. Soc. Chem. Ind.*, **13**, 69 (1894)] isolated an alcohol which melted at 139° C. and gave a specific rotation of 20° to 31° 23′, which was undoubtedly a mixture of sterols. Also they separated a substance they called "sesamin," which gave a specific rotation at 20° of +68.36°. The fact that the sesamin is sparingly soluble in ether permits of its separation by crystallization from the more soluble sterols. The viscous, non-crystallizable portion of the unsaponifiable constituents contains the substance which gives the Baudouin color test. For further information consult Tocher [*Pharm. J.*, **51**, 639 (1891); **53**, 700 (1893)] Malagnini and Armanni [*Analyst*, **32**, 391 (1907)], and Marcusson and Meyerheim, *J. Soc. Chem. Ind.*, **35**, 549 (1916).

It should be noted that frequently the milk of animals fed with sesame oil cake or meal gives a test for sesame oil. Sometimes sesame oil is adulterated. The more common oils used are rape, poppy seed, cottonseed, and peanut oils. Rape oil lowers the saponification value, poppy seed oil raises the iodine number, cottonseed, besides increasing the titer of the fatty acids, usually responds to the Halphen test, and peanut oil can be detected by separating an arachidic and lignoceric acid mixture.

The following references may be consulted for further information:

"Detection of sesame oil in chocolate," E. Gerber, *Analyst*, **32**, 90 (1907).

"Sesame and melon seed as sources of semi-drying oils (in Africa)," M. Rendt, *Chem. Absts.*, **16**, 4080 (1923). Cultivation, utilization, and expression of oil are discussed.

"Sesame," *The Oil Miller*, **18**, No. 3, 10 (1923). Climate, soil, cultivation and harvesting are discussed.

"Some color reactions of rancid sesame oil," L. F. Hoyt, *The Cotton Oil Press*, **7**, No. 7, 37-8 (1923).

"Sesame Oil and Its Possibilities," C. V. Zoul, *The Cotton Oil Press*, **7**, No. 5, 33-35 (1923).

"Colorimetry of Fatty Oils: Detection of Sesame Oil," H. Heller, *J. Soc. Chem. Ind.*, **42**, 896A (1923).

"Modification of the Sesame Oil Reaction by Treatment of the Oil with Absorbents," P. Horvig, *Chem. Absts.*, **20**, 786 (1926). Bleaching carbon and earths affect intensity of color test.

"The Production of Sesame," H. Blin, *Mat. grasses*, **18**, 7670-1 (1926). U. S. Patent 1,470,929. Yu Chen Lai. Sesame Flour and Process of Making Same.

"Sesamin and Sessamolin," W. Adriani, *Brit. Chem. Absts.*—B, **1929**, 148.

"Sesamin," J. Boeseken and W. D. Cohen, *Biochem. Zeit.*, **201**, 45 (1928).

"Sesamum," W. Bally, *Intern. Rev. Agric.*, **23T**, 129 (1932), gives a description of the crop, its cultivation, and world production.

Tests for Sesame Oil. Modified Villavecchia Test for Sesame Oil. Prepare a solution containing 2 cc. of furfural and 100 cc. of 95 per cent alcohol. Mix thoroughly 0.1 cc. of this solution with 10 cc. of strong hydrochloric acid and 10 cc. of the oil to be tested by shaking them together in a test tube for 15 seconds. Allow the mixture to stand for 10 minutes and note the color. Add 10 cc. of water, shake, and again note the color. If the crimson color disappears, sesame oil is not present. It should be observed that some olive oils, particularly those of African or Spanish origin, give pink or crimson colors, but these colors disappear when water is added.

Comments. As furfural gives a violet color with hydrochloric acid, it is necessary to use the dilute solution in the quantity specified.

The Baudouin test (originally discovered by Camoin) differs from that of the Villavecchia in that a 0.1 gram of finely powdered sugar is employed in place of the 0.1 cc. of furfural solution. The color produced is the same in both cases.

The intensity of the color is reduced by the treatment of sesame oil with animal charcoal and fuller's earth. Zimmerman [*J. Soc. Chem. Ind.*, **32**, 442 (1912)] found that both refining and deodorization of sesame oil reduced the intensity of the test. Hydrogenation also reduces the color of the test and no test is obtained with the completely hydrogenated oil until it has stood some time; then a slight test is given. In most cases rancid sesame oil responds to the test, but when it is mixed with rancid butter, soybean, cottonseed, and peanut oils, the test is weakened or prevented altogether. Substances which interfere with the test may be removed by treatment of the rancid oil with sodium hydroxide.

The Baudouin and Villavecchia tests are interfered with to some extent when applied to margarins which contain added coloring substances which give red colorations with hydrochloric acid [Arnold, *Analyst*, **39**, 86 (1914)]. This interference is removed as follows: Dissolve about 3 parts of the sample in 10 cc. petroleum ether and shake thoroughly with about an equal volume of hydrochloric acid containing stannous chloride (1 cc. of 20% stannous chloride solution per 100 cc. of hydrochloric acid), then heat in a water bath until the red coloration disappears. Cool and apply test in usual manner.

Soltsien's Test for Sesame Oil. This test is particularly useful for testing margarins for sesame oil.

Dissolve 5 cc. of the sample (melted margarin) in 10 cc. of petroleum ether in a test tube and add 2.5 cc. of stannous chloride solution

(a mixture of 5 parts of crystallized stannous chloride and 1 part by weight of hydrochloric acid is completely saturated with hydrochloric acid gas and filtered through asbestos, if necessary). Shake the mixture thoroughly until homogeneous, but not longer, and place in a water bath heated to 40° C. After the acid solution has separated, transfer the test tube to a water bath heated to 80° C., so that the acid solution is warmed without boiling the petroleum solution. In the presence of sesame oil, warming for three minutes should give a distinct red coloration.

Comments. Soltsien [*Analyst,* **31,** 266 (1906)] and others are of the opinion that the furfural and stannous chloride reactions are not due to the same substance, because thorough extraction of sesame oil with hydrochloric acid (Sp. g. 1.125) removes the substance which gives the furfural reaction, while the treated oil still responds to the Soltsien test.

Lewkowitsch states that this test is not given by rancid sesame oil. He does not recommend its use because fat extracted from cake or pastry prepared from pure butter always gives a red coloration.

Ceratotheca Sesamoides Seed Oil. The plant is related to *Sesamum indicum (Pedaliaceae).* The seed, which contains about 35 per cent of oil, resembles sesame, and the characteristics of the oil are similar to those of sesame oil. However, this oil does not give the Baudouin reaction. Bolton [*Analyst,* **44,** 233 (1919)] determined the following characteristics: Sp. g. at 15° C. 0.916; $N_D^{40°}$ 1.4656; Sap. V. 190.2; Iod. No. 110.6.

German Sesame (Cameline or Dodder) Oil. This oil is obtained from the seeds of *Camelina sativa* of the *Cruciferae.* The seed contains from 30 to 35 per cent of oil which has a pungent taste. The oil is used chiefly in making soft soap. Characteristics are as follows: Sp. g. at 15° C. 0.922 to 0.926; $N_D^{20°}$ 1.4761, $N_D^{40°}$ 1.4688; Sap. V. 185 to 188; Iod. No. 135 to 142; Titer 13° to 14°.

H. Heller [*Angew. Chem.* **46,** 441 (1933)] found that seeds which he examined from Germany contained 32.8 and 35.6 per cent of oil, whereas those from Belgium had 34.3 and those from Russia 36.9. The iodine numbers of the oils were as follows: German 127 and 129.2, Belgium 131.6, and Russian 149.7.

Spurge Nettle Seed Oil. This oil is found in the seeds of the plant *Jatropha stimulosa,* native to the southern portion of the United States. The seeds consist of 39 per cent of hull and 61 of kernel. The kernels contain about 51 per cent of oil. The oil has a mild, pleasant flavor. The expressed oil was prepared and examined by P. Menaul [*J. Agric. Research,* **26,** 259 (1923)] with the following results: Sp. g. at 15° C. 0.09257; $N_D^{15.6°}$ 1.4765; Sap. V. 186.5; Iod. No. 124.6 to 129.5; Sol. Pt. Below −15° C. The insoluble fatty acids (95.6%) consist of 15.4 per cent of saturated and 83.6 of unsaturated acids.

Sunflower Seed Oil. Sunflower seed oil is obtained from the seeds of several varieties of the plant *Helianthus annuus,* which is be-

lieved to be indigenous to Mexico. The varieties most extensively cultivated for seed are the Mammoth Russian, which has striped seeds, the Manchurian, a low plant with dark striped seeds, and another (tall plant) with black seeds. In some localities, white-seeded varieties are cultivated.

Sunflower seeds are produced in Russia, Bulgaria, China, Hungary, India, Argentina, United States, and elsewhere in smaller quantities. For a great many years, Russia has been the largest producer both of seed and oil. In recent years, the cultivation of the seed and the production of oil have been largely increased in Roumania and to some extent in Bulgaria and Hungary. It should be mentioned that since 1935 Argentina has been a very large producer of the seed for its oil. A typical analysis of American whole seed is as follows: Moisture 6.9, oil 24.7, protein 16.1, crude fiber 27.9, carbohydrates 31.3, and ash 3.1 per cent. Kernels: Moisture 4.5, oil 41.5, proteins 27.7, crude fiber 6.3, carbohydrates 16.3, and ash 3.8 per cent.

Sunflower seeds contain anywhere from 22 to 32 per cent of oil. The kernels usually are from 49 to 54 per cent of the whole seed.

In Europe, it is customary to first press the seed cold and this is followed by a hot pressing. The cold-pressed oil is usually pale yellow, with a mild taste and a pleasant flavor. It is much esteemed as a salad and cooking oil. Considerable quantities are employed in making butter substitutes. The hot-pressed oil, which has a reddish-yellow color, is used for technical purposes and as a burning oil. With the introduction of modern methods of treatment, the hot-pressed oil is refined for edible purposes. The oil "dries" more slowly than the better grades of soybean oil (H. A. Gardner, *United States Paint Mfrs. Assoc. Circ.* **136**). However, it is used in some of the Russian varnishes and the Dutch use it to manufacture an enamel paint.

The press cake is a valuable stock feed and has been used for many years in Europe. (In Russia, the sunflower stalks are burned and hundreds of tons of high-grade potash salts are extracted annually from the ashes.)

The characteristics of sunflower seed oil as determined by De Negri and Fabis, Holde, Dieterich, Thompson, Dunlop and Thorner are as follows: Sp. g. 15° C. 0.922 to 0.926; Sap. V. 189 to 194; Iod. No. 120 to 136; $N_D^{40°}$ 1.4663 to 1.684; Unsap. 0.7 to 1.20%; Sol. Pt. −16° to −18° C.; Titer 17° to 20°.

Jamieson and Baughman [*J. Am. Chem. Soc.*, **44**, 2952 (1922)] made an extensive study of sunflower seed oil from seed produced in southeastern Missouri. This oil, which was light yellow, had the following characteristics: Sp. g. 25°/25° C. 0.9193; $N_D^{20°}$ 1.4736; Acid V. 2.3; Iod. No. (Hanus) 130.8; Sap. V. 188.0; Acetyl V. 14.5; R.M.V. 0.27; Pol. No. 0.25; Unsap. 1.20%; Sat. Acids 7.1%; Unsat. Acids 86.5%. This oil was found to contain the following percentages of acids as glycerides: Oleic 33.4, linoleic 57.5, palmitic 3.5, stearic 2.9, arachidic 0.6, and lignoceric 0.4. Linolenic acid could not be detected. For details of the investigation see the original article.

Sunflower Seed and Oil in the United States. The annual production of the seed ranges from 6 to about 14 million pounds. Generally, several millions of pounds of seed per year are imported from Argentina and Europe. The principal producing localities are southeastern Missouri, southern Illinois and San Joaquin Valley, California. Circular **140** (College of Agric. Univ. Missouri, 1924) states that any soil suitable for corn is adapted to raising sunflowers. The crop is usually planted like corn, but not so deep, in rows with a corn planter provided with special seed plates. The crop is cultivated with the same implements as used for corn. When the flower heads are matured, they are cut by hand and threshed, usually by a special sunflower seed thresher. Some of these threshers are capable of separating about 25,000 pounds of seed daily. The average yield of seed produced on good land is about 650 pounds per acre, but yields up to 1800 pounds are sometimes reported. Available information (United States) indicates that sunflowers remove about as much fertility from the soil as an average crop of corn. The Missouri Agricultural Experiment Station has found that a ration of equal parts of corn and sunflower seed fed to hogs compared favorably to the United States Corn Belt ration of corn and tankage.

At times, some domestic or imported seeds are pressed for oil. In 1920, 100 tons of seed from Missouri were pressed, with a yield of over 6,000 gallons of oil. Also small quantities of the oil are imported and the oil is refined for edible purposes.

Additional references are as follows:

"Oil Seed Production in South Africa," *Cotton Oil Press,* **2,** No. 3, 29 (1919).
"Sunflower Seed Oil (Dutch Enamel)," *Oil, Paint, Drug Reptr.,* **98,** 49 (1920).
"Oil Seeds in Rhodesia," *Bull. Imp. Inst.,* **21,** 180 (1923).
"Extracting Potash from Russian Soil (by Sunflowers)," J. R. Minevitch and W. M. Malisoff, *Chem. Met. Eng.,* **30,** 501 (1924).
"Sunflower Seed Oil," J. Pieraerts, *Mat. grasses,* **17,** 7340 (1925).
"Sunflower and Safflower (Oil and Cake)," Vizern and Goullot, *Analyst,* **50,** 408 (1925).
"Review of the Sunflower (Seed) Situation," G. E. Govier, *Cotton Oil Press,* **14,** No. 1, 39 (1930).
"Oil Content of Sunflower Seeds," N. Uspenski, *Brit. Chem. Absts.,* **B, 1930,** B-154.
"Sunflower Seed from Southern Rhodesia," *Bull. Imp. Inst.,* **28,** 272 (1930).
Sunflower Oil Industry in Cuba," *Oil Miller and Cotton Ginner,* **29,** No. 5, 15 (1932).
"Sunflower Seed in Roumania and Bulgaria," *Chem. Trde. J. and Chem. Eng.,* **91,** 190 (1932).
"World Production of Sunflower Seed," *Allegem. Öl Fettzeit.,* **29,** 512 (1932), *Oil and Col. Trds. J.,* **82,** 497 (1932).
"Change in Composition of Sunflower Seed Oil During Ripening of the Seeds," K. H. Bauer and U. Kangowski, *Fettchem. Umschau.,* **41,** 1 (1934).
"Sunflower Oil," J. S. Remington, *Pt. Mfr.,* **6,** 245, (1936).
"Making Stand Oil from Sunflower Seed Oil," E. Stock, *Farben Ztg.,* **43,** 1938.
"The Sunflower (Helianthus annus) as Oil Plant," A. Fischer, *Fette und Seifen,* **46,** 88 (1939).

Tomato Seed Oil. Tomato seed oil is obtained from the seeds of the tomato *(Solanum esculentum)* which, together with the skins, are waste products in the manufacture of catsup, pulp (paste), and soup.

The seeds constitute 0.5 to 0.6 per cent of the tomato and usually contain from 18 to 23 per cent of oil. In Italy, where this oil has been produced commercially since 1911, the seeds and skins are washed, then pressed to remove as much of the water as possible and finally dried in a mechanical hot-air dehydrator. The seeds are then separated from the skins in a machine equipped with a series of sieves and fans. Fachini [*Ind. chem.*, **5**, 76 (1911); *Chem. Abs.*, **5**, 2309 (1911)] claims that the seeds can be separated from the skins simply by agitating them with water and allowing the mixture to stand until the seeds settle to the bottom of the tank.

The expressed oil is brownish or reddish in color and has a strong odor. When the crude oil is refined by caustic soda, bleached, and deodorized, a pale yellow product is obtained which is entirely suitable for edible purposes. In Italy, the crude oil is chiefly used in soap making. The press cake is either used as a food for stock or as a fertilizer. It usually contains about 37 per cent of protein [Johns and Gersdorff, *J. Biol. Chem.*, **51**, 439 (1922)].

Rabak (*U. S. Dept. Agric. Bull.*, **632**, 1917), Shrader and Rabak (*U. S. Dept. Agric. Bull.*, **927**, 1921) describe methods and equipment for the separation of the seed and the manufacture of oil and meal both by expression and extraction. Also they include estimates of the cost of equipment and manufactured products for the United States, where in all probability there are sufficient waste tomato seeds if utilized to yield about 400 tons of oil per year.

CHARACTERISTICS OF TOMATO SEED OIL

Observer	Sp. G. 15° C.	$N^{40°}_{D}$	Sap. Value	Iod. No.	Sol. Pt. ° C.	Fatty Acids M. Pt. ° C.
Kochs [a]	0.920	1.4678	183.6	117.8	—9 to —12	26-29
Battaglia [b] ...	0.922	1.4675	180.4	106.9		
Accomazzo [c] ..	0.920	...	184.	118.		
Rabak [d]	0.924	1.4661	188.6	114.2	—10	

[a] *Analyst*, **33**, 423 (1908).
[b] *Ann. Chem. Anal.*, **6**, 437 (1901).
[c] *Ind. Chim.*, **1910**, 360; *Chem. Absts.*, **5**, 1304 (1911).
[d] *U. S. Dept. Agric. Bull.*, **632**, 1917.

The following results were obtained by Jamieson and Bailey [J. Ind. *Eng. Chem.*, **11**, 850 (1919)]:

No.	Sp. G. 25° C.	$N^{25°}_{D}$	Sap. V.	Iod. No. Hanus	R.M.V. V.	Pol. No.	Acetyl V.	Sat. Acids	Unsat. Acids
1	0.9191	1.4720	187.5	121.5	..	..	18.5	16.0	77.0
2	0.9196	1.4722	187.0	117.5	..	..	11.5	15.0	77.0
3 [a]	0.9189	1.4722	187.0	122.5	..	..	11.4	16.0	79.0
4 [b]	0.9186	1.4723	186.3	122.6	..	..	10.0	14.7	80.6
5	0.9189	1.4720	192.0	122.0	0.1	0.6	13.1	17.0	77.0
6	0.9189	1.4728	192.0	125.0	0.3	0.6	14.1	16.7	77.0
7	0.9190	1.4725	192.0	125.0	0.3	0.6	12.3	15.5	79 0
8	0.9184	1.4725	192.0	122.5	0.3	..	12.8	17.2	77.6
9	....	1.4725	191.0	125.0	0.3	0.4	17.6	18.0	76.1
10 [c]	....	1.4715	188.2	122.0	..	..	20.5	15.0	80.0

[a] No. 1 refined by caustic soda.
[b] No. 3 bleached with earth.
[c] Extracted with petroleum ether.

Rabak found the oil to contain approximately 45 per cent of oleic, 34.2 of linoleic, 12.4 of palmitic and 5.9 per cent of stearic acids as triglycerides. Jamieson and Bailey isolated 0.4 per cent of arachidic acid from the oil. Battaglia also reported the presence of a small quantity of myristic acid, but made no mention of arachidic acid.

Datura Seed Oil. This oil is found in the seed of the plant *Datura stramonium* belonging to the *Solanaceae*. This plant, which is indigenous to Asia, has now spread throughout Europe. The oil content of the seeds varies from 17 to 25 per cent. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.917 to 0.923; Sap. V. 186 to 202; Iod. No. 113 to 126; Unsap. 1.0 to 2.6 per cent.

T. P. Hilditch and M. B. Ichaporia [*J. Soc. Chem. Ind.*, **55**, 189T (1936)] examined an old sample of the oil, which gave the following characteristics: Sap. Equiv. 287.0; Iod. No. 115.8; Acid V. 6.7; Unsap. 1.9 per cent. The mixed fatty acids contained the following percentages of constituents: Oleic acid 33.1, linoleic 53.6, myristic 1.3(?), palmitic 10.8, and stearic 1.2.

A. J. Lutenberg and S. L. Ivanov [*Allgem. Oel Fett-Ztg.*, **32**, 141 (1935)] examined a sample of seed which contained 28.7 per cent of oil. The characteristics of the oil were as follows: Sap. V. 190.1 (Sap. Equiv. 295); Iod. No. 126.3; Acid V. 1.5. The mixed fatty acids contained the following percentages of constituents: Oleic 33.0, linoleic 55.1, and saturated acids 11.9 per cent. It should be noted that the daturic acid ($C_{17}H_{34}O_2$) reported as being present in this oil by Gerard in 1892 was shown by P. E. Verkade and J. Coops [*Biochem. Ztschr.*, **206**, 468 (1929)] to be a mixture of palmitic and stearic acids.

Xanthocarpum (Bkatkayta) Seed Oil. This oil is found in the seeds of the plant *Solanum xanthocarpum* belonging to the *Solanaceae*. It is found throughout India. The Hindus use the plant for treatment of fevers, coughs, asthma, etc.

The seeds and oil have been examined by M. P. Gupta and S. Dutt [*J. Indian Chem. Soc.*, **13**, 613 (1936)]. The seeds, which amount to 20.7 per cent of the fruit, contain 19.3 per cent of oil. The extracted oil gave the following characteristics: Sp. g. at 27° C. 0.9240; Sap. V. 182.5; Iod. No. 124.3; Unsap. 1.2%; $[\alpha]_D^{32°} - 1.35°$. The oil was found to contain the following percentages of acids: Oleic 42.93, linoleic 36.19, palmitic 5.37, stearic 9.77 and arachidic 0.35.

Seed Oils of Various Umbelliferous Plants

Parsley Seed Oil. This oil is obtained from the seed of the plant *Petroselinum sativum*, belonging to the *Umbelliferae* family. The seeds contain about 20 per cent of oil. When the seeds are extracted, more or less non-fatty substances, depending upon the solvent used, are removed along with the oil.

Grimme [*Pharm. Zentr.*, **52**, 661 (1911)], who examined the seed oils of various *Umbelliferae*, obtained the following characteristics for parsley seed oil: Sp. g. at 15° C. 0.924; $N_D^{35°}$ 1.4778; Sap. V. 176.5;

Iod. No. (Wijs) 109.5; Unsap. 2.18%; Sol. Pt. −14° C.; Sol. Pt. −10° C.

Both the extracted and expressed oils are usually of a greenish color. They have a characteristic odor and a disagreeable sharp flavor.

T. P. Hilditch and E. E. Jones [*J. Soc. Chem. Ind.*, **46**, 174T (1927)] made an extensive study of the oil from English parsley seed and found that the fatty acids consist of 2 per cent of palmitic acid, 76 of petroselinic acid, 15 of oleic acid, 6 of linoleic, and 1 of higher saturated acids. They made a special study of petroselinic acid (M. Pt. 30° C.) and some of its derivatives and confirmed the earlier work of Vougerichten and Kohler [*Ber.*, **42**, 1638 (1909)] that the acid is a 6:7-octadecenoic (oleic) acid. They also found that the chief constituent of the unsaponifiable portion is the liquid phelonic ether myristicin $(CH_2O_2)(CH_3O)C_6H_2{\cdot}CH_2{\cdot}CH{\cdot}CH_2$, as is the case with the French oil, in contrast to the German variety of the oil, which contains a predominant quantity of apiole $(CH_2O_2)(CH_3O)_2C_6H{\cdot}CH_2{\cdot}CH{\cdot}CH_2$ in the unsaponifiable portion.

A. Steger and J. van Loon [*Analyst*, **54**, 177 (1929)] examined a sample of parsley seed oil, determining the quantity of saturated acids and the unsaturated acids using the Kaufmann thiocyanogen method. The oil contained 3 per cent of unsaponifiable matter and 2 per cent of volatile matter. The oil consisted of 4 per cent of saturated acids, 45 of petroselinic acid, 8 of oleic acid, and 9.1 per cent of linoleic acid. According to these authors, the total quantity of fatty acids amounted only to 65.2 per cent; consequently it would appear that this sample must have contained a large quantity of essential oil.

It is probable that the other oils from the seed of the *Umbelliferae*, as stated by Hilditch and Jones [*Biochem. J.*, **22**, 326 (1928)], contain glycerides of petroselinic acid.

"Seed Fats of the *Umbelliferae*, II. The Seed Fats of Some Cultivated Species," B. C. Christian and T. P. Hilditch [*Biochem. J.*, **23**, 327 (1929)] includes a study of the oils from carrot, celery, coriander, chevril, fennel, caraway, and parsnip. The fatty oils are in all cases accompanied by considerable quantities of unsaponifiable and resinous substances. The percentages of acids found are given in the following table:

COMPOSITION OF INSOLUBLE FATTY ACIDS

Oil	Palmitic Acid	Petroselinic Acid	Oleic Acid	Linoleic Acid
		Per Cent		
Fennel	4	60	22	14
Coriander	8	53	32	7
Chevril	5	41	0.5	53.5
Caraway	3	26	40	31
Celery	3	51	26	20
Parsnip	1	46	32	21

Celery Seed Oil. The cultivated celery seeds of the plant *Apium graveolens* contain about 17 per cent of oil, which has been examined

by Grimme [*Pharm. Zentr.*, **52**, 661 (1911)] with the following results: Sp. g. at 15° C. 0.9236; $N_D^{35°}$ 1.4783; Sap. V. 178.1; Iod. No. (Wijs) 948; Unsap. 0.79%; Sol. Pt. −12° C.

Anise Seed Oil. The seed of the plant *Pimpinella anisum* contain about 10 per cent of oil, which has been examined by Grimme *(loc. cit.)* with the following results: Sp. g. at 15° C. 0.9232; $N_D^{15°}$ 1.4738; Sap. V. 178.4; Iod. No. (Wijs) 108.6; Unsap. 0.96%; Sol. Pt. −3° C.

Fennel Seed Oil. The seeds of the plant *Foeniculum officinale* contain about 10 per cent of oil, which has been examined by Grimme *(loc. cit.)* with the following results: Sp. g. at 15° C. 0.9304; $N_D^{35°}$ 1.4795; Sap. V. 181.2; Iod. No. (Wijs) 99; Unsap. 3.68%; Sol. Pt. −2° C.

Dill Seed Oil. The seed of the dill, *Anethum graveolens, L.*, contains about 17 per cent of oil. The extracted product is dark green and has a strong characteristic flavor. Grimme *(loc. cit.)* reports the following characteristics: Sp. g. at 25° C. 0.9282; $N_D^{35°}$ 1.4795; Sap. V. 176; Iod. No. (Wijs) 119.6; Unsap. 1.14%; Sol. Pt. −2° C.; Sol. Pt. of fatty acids 1° to 2° C.

Carrot Seed Oil. The seeds of the carrot, *Daucus carota, L.*, contain about 13 per cent of oil, which has been examined by Grimme *(loc. cit.)* with the following results: Sp. g. at 15° C. 0.9296; $N_D^{30°}$ 1.4723; Sap. V. 179.4; Iod. No. (Wijs) 105.1; Unsap. 1.53%; Sol. Pt. −6° C.

Coriander Seed Oil. This oil is found in the seed of the plant *Coriandum sativum*. The seeds contain about 19 to 21 per cent of oil for which the following characteristics have been reported: Sp. g. at 15° C. 0.9262 to 0.9284; $N_D^{30°}$ 1.4704; Sap. V. 182 to 190; Iod. No. 93 to 100; Unsap. 2.3%. The composition of the oil is given in the table under parsley seed oil.

Cumin Seed Oil. The seed of *Cuminum cyminum, L.*, contains about 10 per cent of oil. The extracted product is a greenish brown and has a strong aromatic flavor. It was examined by Grimme *(loc. cit.)* with the following results: Sp. g. at 15° C. 0.9256; $N_D^{30°}$ 1.4720; Sap. V. 179.3; Iod. No. (Wijs) 91.8; Unsap. 2%; Sol. Pt. −8° C.; Sol. Pt. of fatty acids −4° C.

Garden Chevril Seed Oil. The seeds of *Anthriscus cerefolium* contain about 13 per cent of oil. The extracted product is greenish brown and has a strong aromatic odor and flavor. It has been examined by Grimme *(loc. cit.)* with the following results: Sp. g. at 15° C. 0.9265; $N_D^{35°}$ 1.4672; Sap. V. 183.1; Iod. No. (Wijs) 110.2; Unsap. 1.45%; Sol. Pt. −9° C.; Sol. Pt. of fatty acids 1° C.

Caraway Seed Oil. Caraway seeds of the plant *Carum carvi* contain about 15 per cent of oil. The greenish-brown oil has a strong aromatic odor and flavor. The results obtained by Grimme *(loc. cit.)* are as follows: Sp. g. at 15° C. 0.9268; $N_D^{35°}$ 1.4710; Sap. V. 178.3; Iod. No. (Wijs) 128.5; Sol. Pt. −7° C.; Unsap. 2.74%.

E. Kopp [*Chem. Absts.*, **22**, 1864 (1928)] suggests the utilization

of caraway residues after the removal of volatile oil for the production of oil.

Ajowan Seed Oil. The seeds of the plant *Ptychotis ajowan* contain from 22 to 30 per cent of oil. The oil is greenish brown and has a strong aromatic (thymol) odor and flavor. The seeds are grown and the oil is expressed in India. Formerly small quantities of the oil were exported to the United States when it was used for technical purposes, chiefly in the form of sulfonated oil. Grimme (*loc. cit.*) obtained the following characteristics: Sp. g. at 15° C. 0.9267; $N_D^{35°}$ 1.4710; Sap. V. 176.8; Iod. No. (Wijs) 108.8; Unsap. 1.14%; Sol. Pt. −20° C.; Sol. Pt. of fatty acids 3° C.

Remarks: It will be observed that these oils are characterized by the low solidification point of their mixed fatty acids. The oils in each case contain more or less of volatile or essential oil, whether they are expressed or extracted with solvents. All of them have low saponification values. As mentioned under parsley seed oil, it is probable that they all contain notable quantities of petroselenic acid.

For further information see "The Chemical Composition of Vegetable Seed Fats in Relation to the Natural Order of Plants," by T. P. Hilditch [*Proc. Royal Soc.*, **103**, 111 (1928)].

Unicorn (Devils' Claws) Seed Oil. This oil is found in the seeds of the plant *Marytynia louisiana,* which is found growing in profusion under the very dry conditions found in western Kansas and portions of Colorado, Texas, and New Mexico. The seed and oil were examined by E. H. S. Bailey and W. S. Long [*Oil Paint, Drug Reptr.*, **88**, No. 1, 17 (1915)] with the following results: The seeds were found to contain 60.8 per cent of oil, 3.7 of moisture, 4.4 of starch, 23.2 of proteins, 1.5 of crude fiber and 3.7 of ash. *Oil:* Sp. g. at 15.5° C. 0.9157; $N_D^{15.5°}$ 1.4767; Sap. V. 197; Iod. No. 122.5.

The authors state that both the oil and cake are edible, the latter for stock. The green pods are used in some localities for making pickles.

Hubbard Squash Seed Oil. The Hubbard squash *(Cucurbita maxima)* belongs to the same family as the pumpkin and watermelon. Baughman and Jamieson [*J. Am. Chem. Soc.*, **42**, 152 (1920)] examined a sample of the oil which had been expressed by H. S. Bailey, formerly in charge of the laboratory. The seed contained about 36.6 per cent of oil. The expressed oil had a dark brownish-red color, somewhat similar to crude cottonseed oil. The oil refined by caustic soda was yellow. Both the crude and refined oils had a bland fatty taste and odor.

The crude oil had the following characteristics: Sp. g. 25°/25° C. 0.9179; $N_D^{25°}$ 1.4714; Iod. No. (Hanus) 121.0; Sap. V. 191.5; Acid V. 0.50; Unsap. 1.06%; Insol. Acids 94.7%; Titer 29.8° C. The refined oil contained 18.37 of saturated and 76.45 per cent of unsaturated acids.

The composition of the oil was determined with the following results:

Acid	Per Cent
Oleic	34.99
Linoleic	41.46
Palmitic	12.12
Stearic	5.86
Arachidic	0.03

The original paper should be consulted for information on the procedure employed in this investigation.

Pumpkin Seed Oil. The seeds of the *Cucurbita pepo, Lunc,* usually contain from 30 to 35 per cent of oil. The cold-pressed oil has a greenish color with a slight fluorescence. The hot-pressed oil is dark red and is fluorescent to a marked degree. In thin layers it appears greenish yellow. Power and Salway [*J. Am. Chem. Soc.,* **32,** 346 (1910)] made an extended examination of both the seed and the oil. The oil was optically inactive and had the following characteristics: Sp. g. 20°/20° C. 0.9220; Iod. No. 119.7; Sap. V. 189.4; Acid V. 3.4. The oil was found to consist, approximately, of the glycerides of palmitic and stearic acids 30, oleic acid 25, and linoleic acid 45 per cent. Sterols melting at 140° C. and 162° to 163° C. were also isolated.

Pumpkin seed oil usually has characteristics within the following limits: Sp. g. 15° C. 0.920 to 0.925; Sap. V. 188 to 198; Iod. No. 120 to 130; $N_D^{40°}$ 1.4668 to 1.4685. Fatty acids melt 26° to 28° C.

J. L. Riebsomer and G. A. Nesty [*J. Am. Chem. Soc.* **56,** 1784 (1934)] examined a sample of the oil with the following results: Sp. g. at 20° C. 0.9159; $N_D^{20°}$ 1.4737; Sap. V. 174.2?; Iod. No. (Hanus) 116.8; Unsap. 1.58 per cent; Sat. acids 11.4 per cent. The percentages of fatty acids were as follows: Oleic 35.9, linoleic 40.4, palmitic 6.2, and stearic 5.2 per cent.

H. P. Kaufmann and H. Fiedler [*Fette u. Seifen,* **46,** 125 (1939)] examined three samples of oil from pumpkin seeds from Styria with the following range of results: Sap. V. 193.2–196.5; Iod. No. 119.9–120.8; SCN V. 72.1–73.6; Sat. acids 16.8–18%. Mixed fatty acids contained the following percentages of contituents: Oleic 26.4–27.8, linoleic 54.5–55.6, palmitic 10.4–12.4 and stearic 5.6–7.5.

The oil is prepared in Austria, Hungary, Roumania (E. W. Albrecht) [*Z. angew. Chem.,* **31,** 132 (1918)], and southern Russia. The oil is chiefly used for edible purposes, but some of the lower grade oil is used for burning purposes.

Melon Seed Oils

Watermelon Seed Oil. This oil is obtained from the seeds of the fruit from different varieties of *Citrullus vulgaris,* which is indigenous to Africa, but is now cultivated in many other regions. The seeds, in addition to being utilized for the production of oil, are used as food. They are ground and made into a kind of bread or added to soup and sauces by the natives, and in India they are used as a diuretic medicine. The seeds are known as "Nuli" or "Neri" in the Gold Coast, as "Kogai" or "Egusi" in Sierra Leone, and as "Ikpan" or "Guna" seeds in Nigeria. Depending upon the variety and locality, the seeds contain

from about 20 to over 40 per cent of oil, which is yellow or greenish in color and is used for cooking or as an illuminant.

In some localities, the ripe melons are collected and a hole made in one end of each fruit; then they are placed in a pit. After the fruit has rotted, the seeds are collected, washed, dried, and stored for later use.

The range of the characteristics for watermelon seed oil is as follows: Sp. g. at 15° C. 0.914 to 0.923; $N_D^{40°}$ 1.4630 to 1.4670; Sap. V. 190 to 198; Iod. No. 115 to 125; Unsap. 0.7 to 1.3%; Sol. Pt. −5° to −7° C.; R.M.V. 0 to 0.2; Pol. No. 0.1 to 0.4; Titer 29° to 35°.

For further information, see *Bull. Imp. Inst.*, **23,** 149 (1925).

A. J. Nolte and H. W. von Loesecke [*J. Am. Chem. Soc.*, **64,** 889 (1939)] examined the seeds and oil of the Cuban Queen variety of watermelon which is grown in Florida. The air-dried seeds contained the following percentages of constituents: Moisture 8.8, oil 26.5, proteins 17.3, and ash 2.36. The characteristics of the oil were as follows: Sp. g. at 25/25° C. 0.9197; $N_D^{20°}$ 1.4669; Sap. V. 197.4; Iod. No. (Hanus) 133.8; Acid V. 0.4; R.M.V. 0.3; Pol. No. 0.7; Acetyl V. 7.5; Unsap. 1.2 per cent; Sat. acids 14.56 and Unsat. acids 78.96 per cent.

The oil contained the following percentages of acids: Oleic 12.55, linoleic 65.85, palmitic 8.46, stearic 5.41, and arachidic 0.7.

Colocynth Seed Oil. This oil is obtained from the seeds from the fruit of the *Citrullus colocynthis,* found in Algeria, India, and elsewhere. The seeds, depending upon the source, contain from 13 to about 20 per cent of oil. The oil is yellow and has a slight but characteristic flavor. It has been investigated by Hooper (*Ann. Report of Indian Museum,* **1907-8,** 13), Grimalde and Prussia [*Boll. chim. farm.*, **48,** 93 (1909)], Power and Moore [*J. Chem. Soc.*, **97,** 99 (1910)]. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.9289, at 20° C. 0.9273; $N_D^{40°}$ 1.4682; Sap. V. 187 to 203; Iod. No. 120 to 129.3; R.M.V. 0.3; Titer 27° to 29°.

Other Melon Seed Oils. The oil from the seeds of the *Citrullus naudinianus* of West Africa was examined by Grimme [*Chem. Rev. Fett Harz Ind.,* **182,** 268 (1910)] with the following results: $N_D^{20°}$ 1.4747; Sap. V. 203; Iod. No. (Wijs) 120.3; Unsap. 4.37%; Sol. Pt. −7° C. The seeds contained 15.3 per cent of oil.

Narras Seed Oil. This oil is obtained from the seeds of the fruit of the *Acanthosicyos horrida,* which is characterized by its lack of leaves. Grimme *(loc. cit.)* examined the seeds and the oil with the following results: The kernels contain about 48 per cent oil, which give an iodine number of 116.6, a saponification value of 181.4, a titer of 26° C., and a refractive index at 20° C. of 1.4768.

Bryony Seed Oil. This oil is obtained from the seeds of the fruit of *Bryonia dioica.* The seeds contain 23.6 per cent of a viscous reddish yellow oil which gave an iodine number of 135, a saponification value of 193 and a refractive index at 25° C. of 1.4757. The oil gave no hexabromide, showing the absence of linolenic acid. The seeds are stated to be poisonous.

Hodgsonia Seed Fat. This fat is found in the seeds of the fruit of *Hodgsonia capniocarpa* of the *Cucurbitaceae*. The large vine, which is found growing on the river banks in Malaya, bears fruits six inches in diameter. They weigh between two and three pounds, and contain from four to six seeds, the average weight of which is 29 grams. The kernels, which weigh about ten grams, contain about 36 per cent of fat. C. D. V. Georgi and G. L. Teik [*Malay Agric. J.*, **17**, 392 (1929)] found that the kernels contained 46.3 per cent of moisture and 35.7 of fat, which after expression gave the following characteristics: Sp. g. at 20° C. 0.922; $N_D^{20°}$ 1.4694; Sap. V. 201.2; Iod. No. 67.1; Unsap. 0.4%; Titer 42.1.

T. P. Hilditch, M. L. Meara, and W. H. Pedelty [*J. Soc. Chem. Ind.*, **58, 26** (1939)] have made an extensive investigation of a sample of the solvent-extracted fat which gave the following characteristics: Sap. Equiv. 284.3; Iod. No. 65.5; Acid V. 0.8; Unsap. 0.3%. The fatty acids contained the following percentages of constituents: Myristic 0.60, palmitic 37.24, stearic 8.67, arachidic 0.85, hexadeceonic 0.92, oleic 22.64 and linoleic 24.49. The percentages of the four types of mixed glycerides are as follows: Fully saturated 2.5, mono-unsaturated-disaturated 60, di-unsaturated-monosaturated 24, and tri-unsaturated 13. The oleo-dipalmitins amounted to 33.1 per cent, the oleo-palmito-stearins to 27.3, and the palmito-di-oleins to 24.1 per cent. The term oleo denotes glycerides in which either oleic or linoleic acid or both are concerned.

It will be observed that the quantity of saturated acids in this fat is notably higher than that found to date in the other *Cucurbitaceae* seeds.

Senat Seed Oil. This oil is obtained from the seeds of the fruit of *Cucumis chate*, which is grown in the Sudan and occurs in other regions of Africa. According to the *Bull. Imp. Inst.*, **11**, 56 (1912), the seeds contain from 30 to 38 per cent of a yellow oil which gave the following characteristics: Sp. g. at 15° C. 0.924; Sap. V. 187 to 192; Iod. No. 117 to 128.5; Titer 30.3°.

Sativus Oil. This oil is obtained from the seeds of the fruit of *Cucumis sativus*, grown in India. The oil, which was investigated by Hooper (*Ann. Report of Indian Museum*, **1907-8**, 13), had the following characteristics: Sp. g. at 15° C. 0.924; Sap. V. 195 to 197; Iod. No. 118; R.M.V. 0.52; Titer 35.5°.

Oils from Fruit and Seed of the Commiphora Zanzibarica (Nat. Ord. *Burseraceae*). The Director of Agriculture of Tanganyika [*Bull. Imp. Inst.*, **24**, 445 (1926)] reported that the fruits of *C. zanzibarica* are produced in great profusion in his Territory. The sample submitted to the Institute consisted of fruits free from exocarp. "They were small and of oval shape with pointed ends, and had a hard thin shell (endocarp), of which nearly one-half was covered with a soft, red, firmly adhering, aril-like body (mesocarp). The endocarp had a large and a small loculus, one seed maturing in the larger one. The seeds were soft and cream coloured." The fruits averaged 0.43 gram and the seed 0.15 gram in weight. The fruits consisted of 20 per cent "aril,"

48 of shell, and 32 of seed. The seeds contained 4.8 per cent of moisture and 55.1 per cent of oil. The oil was a pale yellowish brown and had a nut-like taste. Characteristics: Sp. g. at 15°/15° C. 0.9223; $N_D^{40°}$ 1.465; Sap. V. 188.6; Iod. No. (Hübl, 17 hrs.) 106.8; Unsap. 1.28%; Acid V. 0.7; R.M.V. 0.11; Pol. No. 0.3; Titer 32.7° C. The oil resembles somewhat cottonseed oil in its characteristics.

The "aril" and shell contain 6.4 per cent of moisture and 21 per cent of oil. The oil gives the following characteristics: Sp. g. at 15°/15° C. 0.9290; $N_D^{40°}$ 1.459; Sap. V. 201.2; Iod. No. (Hübl) 57.4; Unsap. 0.64%; Acid V. 7.9; R.M.V. 0.27; Pol. No. 0.43; Titer 34.9° C. This oil is red and possesses a disagreeable odor and taste. Unless a method is found for mechanically separating the seeds from the remainder of the fruits, which is very difficult, the entire fruit would have to be extracted or pressed, and this would yield a very low grade oil, in contrast to the seed oil which could be used for edible purposes. For further details of this investigation, the original paper should be consulted.

Chapter IV

Drying Oils

Alfalfa Seed Oil. The oil content of the seeds from the plant, *Medicago sativa,* of the *Leguminosae,* appears to range from about 8.5 to 11 per cent.

The characteristics of the oil examined by C. A. Jacobson and A. Holmes [*J. Am. Chem. Soc.,* **38,** 480 (1916)] are as follows: Sp. g. 24°/24° C. 0.9147; $N_D^{17°}$ 1.4783 (at 25° 1.4750); Sap. V. 172.3; Iod. No. 154.2; R.M.V. 0.4; Acetyl V. 19.8; Unsap. 4.40 per cent. The insoluble acids consisted of 9.6 per cent of solid and 90.4 per cent of liquid acids. This investigation indicated that the unsaturated acid fraction contained 3.3 per cent of oleic acid, 73.2 per cent of linoleic acid and 23.5 per cent of linolenic acid.

H. A. Schuette, H. A. Vogel and C. H. Wartinbee [*Oil and Soap,* **15,** 35 (1938)] investigated the oil extracted by petroleum ether from 50 pounds of "Fancy Utah" seed with the following results: Sp. g. 25°/25° C 0.9253; $N_D^{20°}$ 1.4797; Sap. V. 185.2; Iod. No. (Hanus) 167.8; R.M.V. 0.6; Pol. No. 0.2; Acetyl V. 16.6; Unsap. 3.15 per cent; Sat. acids 7.11 per cent; Unsat. acids 89.90 per cent; Sol. acids as butyric 1.3 per cent; titer of fatty acids 19.7°; SCN V. of Unsat. acids 103.7 and Iod. No. 186.48. From these last two values it was calculated that the oil contained 1.4 per cent of oleic acid, 67.5 per cent of linoleic acid, and 20.8 per cent of linolenic acid. In a later communication (*ibid.,* **16,** 16) these investigators showed that this oil contains, besides palmitic and stearic acids, a small percentage of myristic acid and another acid of higher molecular weight than stearic. If the oil were produced on a commercial scale, it could probably be used in the manufacture of paints, varnishes and other products which require drying oils. Finally, they (*ibid.,* p. 233) determined that the oil contained about 1.28 per cent of myristic acid.

Afzelia Seed Oil. This oil is obtained from the seeds of the tree *Afzelia brieyi* of the *Leguminosae,* native to the Belgian Congo. The hard, black, shiny seeds with light red or yellow arilli contain about 30 per cent of oil. J. Pieraerts and L. Henreux [*Mat. grasses,* **15,** 6374 (1923)] examined a sample of the oil with the following results: Sp. g. at 19.5° C. 0.9328; $N_D^{40°}$ 1.4749; Sap. V. 184; Iod. No. 142 to 144; R.M.V. 0.56; Pol. No. 0.5 to 0.7; Acetyl V. 38 to 40; Crismer V. 60.6° to 62° C.; Titer 53° to 54.6° C.; Acid V. 3.2 to 5.1.

The seeds of *Afzelia africana* contain about 24 per cent of oil; the kernel 19 and the aril 54.1. Diedrichs and Schmittmann found that the kernel oil had a saponification value of 229 and an iodine number of

74.2, whereas the aril oil gave an iodine number of 55 and a saponification value of 210.2.

Arara Nut Oil. This oil is obtained from the seed of the tree *Joannesia heveoides,* native to Brazil. The fruit is a three-celled dehiscent capsule, which contains 2 seeds or nuts with shells about one-eighth inch thick. The kernels amount to about 45 per cent of the seeds and weigh from 24 to 28 grams. They contain about 58 per cent of oil, for which the following characteristics have been reported [*Bull. Imp. Inst.,* **26,** 417 (1928)]: Sp. g. at 15°/15° C. 0.924; $N_D^{20°}$ 1.467; Sap. V. 189 to 192; Iod. No. 130; Unsap. 0.5%; Acid V. 0.4 and 2.1.

It is stated that the oil could be used for making soap and that the seeds contain alkaloidal substances. A film of the oil on glass requires 11 days to dry. The extracted meal contains 8 per cent of moisture, 0.7 of fat, 47.4 proteins, 25.1 of carbohydrates, and 6.5 of crude fiber.

Cacahuananche Oil. See page 335.

Cedar Nut Oil. This oil is obtained from the seeds of the tree *Pinus cemba,* which is found in the Alps, Carpathian mountains and Siberia. According to a report from Moscow [*Oil Col. Trds. J.,* **78,** 1279 and 1385 (1930)], these trees cover 49.4 million acres in an area extending from the Barabuisk Steppes to Bering Straits. It is estimated that when the crop is normal, the yield of seed per acre will be about 1300 pounds. Although the oil has been expressed locally in the villages for years, steps have been taken to exploit this industry on a larger scale. The oil is used for edible and technical purposes, including the manufacture of paint and varnish, and the cake may be used as a feed for stock. The kernels from the "nuts" contain from 50 to 60 per cent of oil, for which the following characteristics have been reported: Sp. g. at 15° C. 0.930; $N_D^{15°}$ 1.485; Sap. V. 192; Iod. No. 150 to 160; Unsap. 1.3%; Sat. Acids 8%; Unsat. Acids 87%.

S. L. Ivanov and S. B. Resnikova [*Shiften Zentral Biochem.,* **3,** 239 (1933); *Chem. Abs.,* **28,** 2557 (1934)] found that the oil from the seeds produced farthest north had the highest iodine numbers. The range of the percentages of the unsaturated acids found in the oils was: Oleic 32.5 to 35.8, linoleic 31.1 to 34.2, and linolenic 16.6 to 27.8.

Chia Seed Oil. This oil is found in the seed of the plant *Salvia hispanica* belonging to the *Labiatae* family. The plant, which may reach a height of 7 feet, is native to Mexico. There it is cultivated for the seeds which are used chiefly for making a demulcent beverage. J. M. Rulfo [*Agricultura (Mexico),* **1,** 28 (1937)] discusses chia, its cultivation and production in Mexico. Also, information on chia plants, seeds, and oil will be found in *Natl. Pt., Var. & Lac. Assoc. Cir. No.* **535** (1937), by H. A. Gardner. The oil content of the seed from different sources varies from 28 to 36 per cent. The iodine number of the oil ranges from 195 to 207.

The seeds contain about 34 per cent of oil. Baughman and Jamieson [*Oil and Fat Ind.,* **6,** No. 9, 15 (1929)] expressed the oil by an expeller from a quantity of the seed obtained from Mexico by H. A. Gardner.

This oil gave the following characteristics: Sp. g. at 25° C. 0.9358; $N_D^{25°}$ 1.4838; Sap. V. 194.8; Iod. No. (Hanus) 194.8; Acid V. 1.4; Unsap. 0.7%; Insol. Hexabromide 51.2%; Sat. Acids 8.1%; Unsat. Acids 85.2%. The oil was found to contain the following percentages of acids: Linolenic 39.3, linoleic 45.2, oleic 0.7, myristic 0.14, palmitic 4.90, stearic 2.73, and arachidic 0.3 per cent. The quantity of hexabromide (51.2) found in the fatty acids is equivalent to 48.1 per cent for the oil and represents 17.6 per cent of linolenic acid; the remainder, 21.7 per cent, was considered as the *beta* form of the acid. The composition of the unsaturated acids was determined by the Kaufmann thiocyanogen method, *Z. angew. Chem.*, **42**, 20 and 73 (1929).

Gardner and Holdt (*Am. Pt. and Var. Mfrs. Assocn. Circ.* **105**) found that the oil in the raw state dried rather slowly and exhibited a tendency to form droplets. This was overcome by heating it at 210° C. for 15 minutes, and then the oil showed drying results even superior to linseed oil treated with the same quantity of drier. After heat treatment for bodying the oil, there was scarcely any change in color, which indicates that it would be suitable for light-colored varnishes.

Cockle Burr Oil. This oil is obtained from the seeds of the cockle burr plant, *Xanthium echinatum,* which is a troublesome weed in parts of the United States. The seeds contain about 30 per cent of oil. The expressed oil is pale yellow and has an agreeable taste, according to L. B. Rhodes [*J. Am. Chem. Soc.*, **42**, 1507 (1920)], who examined it. The press cake is not suitable for use as feed on account of its toxic properties. The characteristics are as follows: Sp. g. at 15.5° C. 0.9251; $N_D^{15.5°}$ 1.4773; Sap. No. 190.2; Iod. No. 140.8; R.M.V. 0.2; Acetyl V. 10.6.

From the iodine number it is evident that the product belongs to the drying class of oils.

Croton Seed Oil (Oleum Elliott). This oil, which has been named "Oleum Elliott" to distinguish it from the common croton oil, is obtained from the seeds of the tree *Croton elliotianus,* native to East Africa and belonging to the *Euphorbiaceae.* The tree grows from 30 to 50 feet high and produces seeds which have rough, hornish shells. They have a shape somewhat similar to castor seeds and contain about 60 per cent of kernels. The kernels that were examined at the Imperial Institute [*Bull. Imp. Inst.*, **13**, (1915)] contained 57.4 per cent of oil or about 34 per cent of the whole seed, whereas those examined in 1907 had only about 28 per cent. The mixed fatty acids from the oil *(loc. cit.)* were found to consist of 10 per cent of saturated acids (chiefly palmitic), 80 of linoleic acid and 10 of oleic acid. No resins could be detected in the oil, such as are found in croton oil from *C. tiglium* and to which the vesicating action of the latter oil is due.

The characteristics are as follows: Sp. g. at 15° C. 0.927; Sap. V. 191.6; Iod. No. 147; Acid V. 3.6; Titer 14° C. The commercial oil has an iodine number from 143 to 147.5 and a saponification value from 188.5 to 189.4.

The oil is yellow, almost tasteless, and has a slight turpentine odor. It is found [*loc. cit.* and *Bull.* **21**, 206 (1923)] to be a non-irritant cathartic, but entirely different in its action from ordinary croton oil. The oil, which is used to some extent in England for medicinal purposes, is dispensed in capsules [Martindale and Wescott, "The Extra Pharmacopoeia," 19th Ed., Vol. 1, 875 (1928)].

Elderberry Fruit and Seed Oils. The elderberry, of which there are several species in various parts of the world, is placed under the genus, *Sambucus* of the *Caprifoliaceae.*

The pulp of the fruit of the European species, *Sambucus racemosa,* contains about four per cent of oil. The range of the characteristics reported is as follows: $N_D^{20°}$ 1.4720–1.4770; Sap. V. 196–209; Iod. No. 81.4–98.6; R.M.V. 1.5–1.8.

The seed oil which has been examined by various investigators (amounting to 25 per cent or more of the seed) gave characteristics as follows: Sp. g. at 20° C. 0.9242–0.9439; $N_D^{20°}$ 1.4797–1.4850, at 40° 1.4655; Sap. V. 187–198; Iod. No. 161–177; R.M.V. 0.8; Pol. No. 0.8; Acid V. 3.1–29.2; Unsap. 0.6–1.1 per cent; Hexabromides about 30 per cent.

H. A. Schuette and J. W. Brooks [*Oil and Soap,* **13**, 314 (1936)] obtained the characteristics of the oil from the seed of the American elderberry, *Sambucus canadensis,* which are as follows: Sp. g. at 20° C. 0.9351; $N_D^{20°}$ 1.4712; Sap. V. 188.1; Iod. No. (Wijs) 171.1; Unsap. 1.48 per cent. Fatty acids: Iod. No. (Wijs) 175.0; SCN V. 98.9.

Seed of this species which have been examined, ranged in oil content from 22 to 28 per cent.

Fig Seed Oil. The oil to be described was from the seeds of California caprified figs. The seeds are a by-product of the manufacture of fig paste. They contained 6.30 per cent of moisture and 30.4 per cent of oil. The expressed oil was a brilliant yellow liquid, which had a mild, but pleasant, characteristic dried fig taste. Upon standing for some hours at 10° C., the oil remained entirely liquid.

Jamieson and R. S. McKinney [*Oil and Soap,* **12**, 88 (1935)] examined the expressed oil which was sent for investigation by E. M. Chase, in charge of the Fruit and Vegetable Chemistry Laboratory (of the Bureau of Chemistry and Soils) at Los Angeles, California. The characteristics of the oil were as follows: $N_D^{25°}$ 1.4775; Sap. V. 190.1; Iod. No. (Hanus) 169.4; SCN V. 108.4; Acid V. 0.87; Acetyl V. (André-Cook) 6.1; Unsap. 1.07 per cent; Sat. Acids 8.46 per cent; Unsat. Acids 85.66 per cent.

The oil was found to contain the following percentages of acids: Oleic 18.99, linoleic 33.72, linolenic 32.95, palmitic 5.23, stearic 2.18 and arachidic 1.05. It could be used for either edible or technical purposes.

A. Paizi [*Praktika, Akad. Athenon,* **1934**, 164; *Chem. Abs.,* **30**, 4028 (1936)] examined fig seed oil and obtained the following results: Sp. g. at 15° C. 0.9290; Sap. V. 219; Iod. No. (Wijs) 147.4; R.M.V. 1.04;

Pol. No. 1.52. The seeds contained 23.5 per cent of oil and the dried fruit (pulp) 5.7 per cent.

Grape Seed Oil. This oil is obtained from the seeds of numerous varieties of the grape, *Vitis vinifera.* Depending upon the variety and also to some extent upon climatic and soil conditions, the oil content of the seed ranges from about 6 to 21 per cent, the average being about 12 per cent. The oil is obtained by expression or solvent extraction of the seeds, which are a by-product of the wine and seeded-raisin industries. Another source of seed is that of the grape-juice factories in the United States, but so far no use has been made of these seeds. When the expression method is to be used it is preferable to decorticate the seeds on account of the large percentage of husks (40 to 60 per cent). This procedure not only results in a larger yield of oil, but the press cake is much more valuable for feeding purposes because of its higher protein content and much lower fiber and tannin content than that obtained from pressing the whole seed.

For many years, the oil has been prepared in France, Germany, and Italy, and more recently in Argentina, North Africa, and California.

C. Otin and M. Dima [*Allegem. Öl Fettzeit.,* **30,** 71 (1933)] examined 40 samples of Roumanian grape seeds and their oils. The seeds contained from 12.7 to 20 per cent of oil. The iodine number (Hanus) of the oils ranged from 124.8 to 142.2 and the saponification values from 186.4 to 192.4.

H. P. Kaufmann and M. Sprick [*Fette u. Seifen,* **45,** 288 (1938)] examined ten samples of German grape seed and their oils. The oil content of the seed varied from 8.2 to 10.3 per cent. The characteristics of the oils were as follows: Acid V. 12 to 12.6; Iod. No. 132.6 to 138.5; SCN V. 72.6 to 76.4; Sat. acids as glycerides 11.6 to 14.7 per cent. H. P. Kaufmann and H. Fiedler [*Fette u. Seifen,* **44,** 286 (1937)] reported the following characteristics for oil from seed of the white Riesling grape: Acid V. 0.83; Iod. No. 137.8; SCN V. 76.1; OH No. 3.4. Oil from seed of the red Trollinger grape gave the following results: Acid V. 0.85; Iod. No. 137.4; SCN V. 76.4; OH No. 3.3. For other data the original paper should be consulted.

The oil, which varies in color depending upon the quality of the seed and the methods used, from yellow to green, is chiefly used for edible purposes (usually after refining) and making soap, but some is used as an illuminant and in the manufacture of paint.

It should be kept in mind that the seed from distinctly different types of grapes may yield oils of different composition. Most of the oils that have been studied evidently belong to the semi-drying or drying classes, but a few belong to the non-drying class, as indicated by their iodine numbers, 76 to 94. In many works on the fatty oils, grape seed oil is placed under the "Castor Oil Group," because early investigators happened to examine a type of oil (which, incidently, is rare, compared with the other types) that had low iodine and saponification values and high acetyl values, similar to those of castor oil; but even

this type has no striking viscosity and is insoluble in alcohol. The iodine number of the commercial grape seed oil ranges from 125 to 142.

Investigations by E. André and H. Canal [*Bull. Soc. d'Encour l'ind. nat.*, **106**, 542 (1927)] and by L. Margaillan (*ibid.*, 560) have shown that the acetyl values of the oil from a large number of varieties of grapes vary from about 4 to 44, the usual variation being from 10 to 30, and those with higher values are rare. In this connection, Margaillan has called attention to the importance of using only oil from fresh, sound seed for this determination, because the oil from old seed not infrequently gives unduly high acetyl values on account of the decomposition of a portion of the oil with formation of mono- or diglycerides, which readily react with acetic anhydride.

André and Canal *(loc. cit.)* examined oils from 46 varieties of grapes from France and Algeria with the following results: Sp. g. at 15° C. 0.912 to 0.926; $N_D^{15°}$ 1.4738 to 1.4802; Sap. V. 176 to 190; Iod. No. (Hanus) 125 to 157; Acetyl V. 2.4 to 43. Six commercial oils gave the following characteristics: Sp. g. at 15° C. 0.909 to 0.934; $N_D^{15°}$ 1.4732 to 1.476; Sap. V. 181 to 206; Iod. No. 94 to 137; Acetyl V. 27 to 72; Acidity as oleic acid 4.4 to 59.8.

These authors [*Analyst*, **53**, 544 (1928)] also examined another group containing oils from 52 varieties of grapes. The iodine numbers were all over 130; 88 per cent of the samples giving values from 135 to 142. The acetyl values were as follows: 22 samples gave figures under 10, 17 between 10 and 20, and 2 between 20 and 35. Eleven samples had saponification values below 180. F. Rabak [*Ind. Eng. Chem.*, **13**, 919 (1921)] examined the oil expressed from American concord grape seed, which contain about 13 per cent of oil, with the following results: Sp. g. at 25° C. 0.9208; $N_D^{25°}$ 1.4720; Sap. V. 193; Iod. No. 134; Acetyl V. 9.9; R.M.V. 0; Pol. No. 0.47; Unsap. 1.61%; Sat. Acids 7.17%; Unsat. Acids 85.41%. He also has examined California raisin seed oil (*Bur. Plant Ind. Bull.* **276**). These seeds contained 14.5 per cent of oil. Sp. g. at 24° C. 0.9220; $N_D^{25°}$ 1.4702; Sap. V. 188; Iod. No. 131; Acetyl V. 16; Unsap. 0.78%; Acid V. 1.2; Sat. Acids 8.4%.

Composition. K. Täufel, F. Fischler and A. Jordan [*Allegem. Öl Fettzeit.*, **28**, 119 (1931)] found that the oil from seeds of the Malaga grape and the Riesling grape contained respectively the following percentages of acids: Palmitic 4, 2.2, stearic 3.6, 3.1, unsaturated 86.8 and 87.8. C. Otin and M. Dina [*Allegem. Öl Fettzeit.*, **31**, 107 (1934)] examined the hot-pressed oil which gave an iodine number (Hanus) of 123.7, an acid value of 4.7, and a saponification value of 184.4. The oil was reported to contain the following percentages of constituents: Oleic 31, linoleic 43.74, linolenic 0.14, palmitic 6.17, stearic 2.16, hydroxy acids 11.78, and unsaponifiable matter 0.59. Erucic acid, which earlier investigators had reported as a constituent of grape seed oil, was not subsequently detected.

California Raisin Seed Oil. Jamieson and McKinney [*Oil and*

Soap, **12,** 241 (1935)] examined a sample of raisin seeds and a sample of the expressed refined oil. Those interested in the history and development of the raisin by-product industry, which includes the manufacture of oil and meal, are referred to in A. M. Paul's excellent article in *Food Industries,* **6,** 444 (1934).

The raisin seeds, chiefly from the muscat variety of grape, contained 8.2 per cent of moisture and 17.1 per cent of oil. It is understood that the average oil content of the seed crushed for oil and meal is about 15 per cent.

In a private communication from R. F. Eaton, formerly chemist for the Calavo Growers of California, it was reported that both the freshly expressed and refined oils gave positive Kreis tests. Consequently, insofar as these oils are concerned, this test is of no value as an indication of their condition. The characteristics of the refined oil were as follows: $N_D^{25°}$ 1.4740; Sap. V. 192.1; Iod. No. (Hanus) 129.1; SCN V. 80.0; Acid V. 0.03; Acetyl V. (André-Cook) 18.8; Unsap. 0.53 per cent; Hexabromides (Steele and Washburn) 0.29 per cent; Sat. acids 8.72 per cent; Unsat. acids 86.30 per cent. The oil contained the following percentages of acids: Oleic 32.1, linoleic 51.9, linolenic 2.3, palmitic 5.98, stearic 2.67 and arachidic 0.07.

No evidence was found of the presence of erucic acid previously reported by former investigators in this oil; this confirms the conclusions of E. André and the more recent ones of K. Täufel and H. Thaler [*Fettchem. Umschau,* **41,** 196 (1934)].

In addition to making soap, much raisin seed oil has been used in the production of protective coatings for canvas (awnings, etc.). The refined oil is used for making salad dressings, certain cosmetic preparations, as well as for coating raisins, which requires about one gallon of oil per ton of fruit. This treatment improves their appearance, renders them free-flowing and less liable to insect infection; besides, it keeps them soft and pliable for a long time in comparison with the untreated fruit.

Attention is also called to the following references:

"The Utilization of Waste Raisin Seeds," F. Rabak, *U. S. Dept. Agric., Bur. Plant Ind. Bull.* **276** (1913).

"Commercial Utilization of Grape Pomace and Stems from the Grape Juice Industry," F. Rabak and J. Shrader, *U. S. Dept. Bull.* **952** (1921).

"The Grape Seed Oil Industry," L. Sinay, *Chem. Abs.,* **20,** 2420 (1926); *Oil Col. Trds. J.,* **70,** 1216 (1926).

"Raisin Oil: A By-Product of Unusual Value," A. M. Paul, *Food Industries,* **6,** 444 (1934).

"Raisin Seed Oil," P. Smith, *Chem. Met. Eng.,* **42,** 436 (1935).

"Grape Seed Oil as a Domestic Varnish Material," H. Dautz and H. Schreiber, *Farbe u. Lack,* **1936,** 17 and 27.

"A Note on Muscadine Grape Seed Oils," T. A. Pickett, *Oil and Soap,* **17,** 246 (1940) gives oil content of seeds from 5 varieties of grapes and characteristics of oils from seeds of Hunt and Scuppernong grapes.

The above-mentioned bulletins may be consulted in various libraries, particularly those of the agricultural colleges and experiment stations.

Gynocardia Oil. The oil is found in the seeds from the fruit of the tree *Gynocardia odorata,* native to Sikkim, Assam and Chittagong. It is the most common tree in the Chittagong Hill tracts and it has been observed growing to an elevation of 4000 feet. It is dioecious, and a number of trees must be planted together in order that fruits may be obtained. Prior to the year 1900, it was generally believed that chaulmoogra oil was obtained from the seeds of this tree [*Pharm. J.,* **64,** 523 (1900); **66,** 596 (1902)]. In 1905, Power and Barrowcliff [*Chem. Soc. Trans.,* **87,** 896 (1905)] showed that the oil was optically inactive, and that consequently it contained no acids of the chaulmoogric series. The tree and its fruit are described in detail by J. F. Rock (*U. S. Dept. Agric. Bull.,* **1057**). It is easy to distinguish this tree from that of *T. kurzii.* The seeds weigh about a gram and contain from 63 to 68 per cent of kernels that have 26 to 27 per cent of oil. The oil has an odor resembling that of linseed. Power and Barrowcliff *(loc. cit.)* found that the oil consisted of glyceryl esters of linolenic, linoleic, oleic and palmitic acids. They state that it contains much more isolinolenic than linolenic acid, and that but little oleic acid can be found in it. They reported the following characteristics: Sp. g. at 25° C. 0.925; Sap. V. 197; Iod. No. 152.8; Acid V. 4.9.

Perkins and Cruz [*Phil. J. Sci.,* **23,** 543 (1923)] found the following: Sp. g. at 30° C. 0.929; $N_D^{30°}$ 1.4743; Sap. V. 198; Iod. No. (Hanus) 160; Sol. Pt. 4° C.; Acid V. 1.3.

It is reported that the natives of Assam sometimes prepare this drying oil, but information is lacking in regard to the use that they make of it.

Hackberry Tree Seed Oil. The pits of the fruits of the tree, *Celtis occidentalis,* of the *Ulmaceae,* contain 25 per cent of kernels. The kernels were found to contain 43.15 per cent of oil. The whole fruits have been investigated by E. Yanovsky, E. K. Nelson and R. M. Kingsbury [*Science,* **75,** 565 (1932)].

The solvent-extracted oil has been examined by H. A. Schuette and R. G. Zchupfennig [*Oil and Soap,* **14,** 269 (1937)] with the following results: Sp. 25°/25° C. 0.9204; $N_D^{25°}$ 1.4794; Sap. V. 191.1; Iod. No. (Wijs) 150.0; SCN V. 81.97; R.M.V. 0.0; Pol. No. 0.3; Hydroxyl No. 4.9; Unsap. 1.35 per cent; Sat. acids 5.9 per cent; Unsat. acids 86.4 per cent. The insoluble fatty acids consisted of 4.90 per cent of stearic, 16.50 per cent of oleic and 70.40 per cent of linoleic acid. No other saturated acid could be detected. It will be observed that the composition of this oil is entirely different from that of elm seed oil, which contains very much less unsaturated acids and a very large quantity of capric acid.

Hemp Seed Oil. This oil is obtained from the seed of the plant *Cannabis sativa,* which is chiefly cultivated for its fiber in India, Manchuria, Europe and on a comparatively small scale in the United States. It is, however, also grown for its seed in China, Japan, France, Italy and Russia. Experiments have been made in the United States with

certain varieties of hemp particularly adapted for the production of seeds by F. Rabak [*Pt., Oil and Ch. Rev.*, **83**, No. 3, 16 (1927)] of the Bureau of Plant Industry, with the object of establishing a new oil industry in this country.

Hemp seeds contain from 32 to 35 per cent of oil. Both the extracted and expressed oils have a greenish color. In some Asiatic countries, the oil is used for edible purposes, but elsewhere it is chiefly used as a paint oil. It gives a green soft soap somewhat similar, except for color, to that made from linseed oil.

The characteristics are as follows: Sp. g. at 15.5° C. 0.9285; $N_D^{40°}$ 1.4723; Sap. V. 190 to 193; Iod. No. 150 to 166; Unsap. 1 to 1.3 per cent; Titer 15° to 16.6° C.; Hexabromides 8.8 per cent.

Kaufmann and Juschkuvetsch [*Z. angew. Chem.*, **43**, 90 (1930)] examined a sample of the oil with the following results: Iod. No. (Hanus) 167; SCN V. 101.6; Sat. Acids 9.5 per cent; Unsap. 0.97 per cent. It contains the following fatty acids: Oleic 11.8, linoleic 49.8, linolenic 22.8 per cent (α-linolenic acid 7.5).

The use of the oil in the manufacture of varnishes is discussed by Kiselef and Charof in *Chim. & ind.*, **23**, 1461 (1930). It is said to be an excellent vehicle for grinding colors [H. Friedman, *Am. Paint J.*, **20**, 48 (1936)].

Isano (Boleko) Seed Oil. This oil is found in the seeds of *Ongokea klaineana,* a member of the *Olacaceae* found in the Belgian Congo region. The seeds consist of about 68 per cent of kernel and 32 of shell. The kernels contain about 60 per cent of oil. A. Castille [*Annalen,* **543**, 104 (1939); *Chem. Abs.*, **34**, 2329 (1940)] examined a sample of the extracted oil which gave the following characteristics: Sp. g. at 20° C. 0.9826; $N_D^{20°}$ 1.5079; Sap. V. 191.4; Iod. No. (Wijs) 143; SCN V. 64; Acid V. 3.8; Unsap. matter 3.27 per cent. The oil was found to contain caproic, caprylic, lauric, palmitic, stearic, arachidic, a little oleic, and erythrogenic acids ($C_{18}H_{26}O_2$).

Erythrogenic acid is a red crystalline solid which melts at 39.5°. Esters prepared from it are colorless liquids. The lead salt is soluble in ether. Hydrogenation changes it to stearic acid. It has 5 double bonds and is stated to be a heptadeca-8, 10, 12, 14, 16-pentaencarbonic acid. Apparently, it is the major constituent of the oil.

Kentucky Coffee Nut Tree Oil. This oil is found in the seed of the tree *Gymnocladus dioica,* native to the United States. The seeds contain about 19 per cent of oil, which was examined by Barkenbus and Zimmerman [*J. Am. Chem. Soc.*, **49**, 2061 (1927)] with the following results: Sp. g. at 20° C. 0.9219; $N_D^{20°}$ 1.4769; Sap. V. 191; Iod. No. (Hanus) 137.5; R.M.V. 0.44; Acid V. 0.39; Acetyl V. 11.3; Unsap. 1.3 per cent; Sat. Acids 4.86 per cent; Unsat. Acids 89.74 per cent. Oleic 37.41, linoleic 56.37 per cent.

Lallemantia Oil. This oil is obtained from the seeds of *Lallemantia iberica,* belonging to the *Labiatae,* which grows in southeastern Europe and central Asia. The oil, which somewhat resembles linseed oil, is

used in Persia, Syria and Turkestan for edible purposes as well as an illuminant. The characteristics of the oil, which were determined by Richter, are as follows: Sp. g. at 20° C. 0.934; Sap. V. 185; Iod. No. 162.1; Sol. Pt. −35° C.; Titer 11° C.

Oil from seed grown at Krasnodar, North Caucasus, U. S. S. R. has been investigated by A. A. Lesjuis [*Oil and Fat Ind. U. S. S. R.*, **15**, No. 1, 6 (1939); *Fette u. Seifen*, **46**, 470 (1939)]. The seed kernels, which amounted to 57.7 per cent of the seed, contained from 49.5 to 51.8 per cent of oil. The oil gave the following characteristics: Sp. g. at 20° C. 0.9340; $N_D^{20°}$ 1.4840°; Sap. V. 189.9; Iod. No. 196.8; SCN V. 123.2 to 125.0; Acid V. 0.5. The oil was found to contain the following percentages of acids: Oleic 8.40, linoleic 21.80, linolenic 56.75, and saturated acids 13 per cent.

It was stated that the oil made satisfactory lacquers and varnish. D. Y. Vakulin and M. Y. Roitman [*Comp. rend. acad. sci., U. S. S. R.*, **24**, 192 (1939); *Chem. Abs.*, **34**, 4928 (1940)] reported the following range of characteristics for oils from different varieties of lallemantia: Sp. g. 15°/4° 0.9335 to 0.9399; $N_D^{20°}$ 1.484 to 1.485; Sap. V. 189.8 to 195.2; Iod. No. 177.5 to 197.

Linseed Oil. Linseed oil is obtained from the seed of the flax plant, *Linum usitatissimum,* which is extensively cultivated in Argentina, Canada, China, India, Morocco, the Soviet Republics (Russia) and the United States. It is also produced in many other countries.

The cultivation of flax for fiber and the cultivation for seed are, with the exception of certain regions in the United States and Soviet Russia, distinct industries. The varieties employed for the production of seed are distinct from those grown for fiber. The yield of seed is generally smaller in the case of the fiber varieties.

The acreage planted to flax for seed varies more or less from year to year with economic conditions. The acreage in the United States ranges from about 2.9 to 4 million acres and in Argentina from 6.7 to over 7.0 million acres. The acreage planted to flax in Canada is about 1 million, in India about 3.5 millions, and in the Soviet Republics about 3.8 millions. The annual world production of oil is about 3 billion pounds.

For many years North and South Dakota, Minnesota and Montana have been the largest producers of flaxseed in the United States. Seed are also produced in California, Idaho, Iowa, Kansas, Missouri, Oregon, Washington and Wisconsin.

The commercial production of flaxseed in Oregon began as early as 1867. During December of that year, an oil mill there began the production of linseed oil for local use. Some years later, its annual production increased to 50,000 gallons of oil. In 1888, at Portland, Oregon, a mill with 12 presses was established, and this plant, now enlarged, is still in operation. It provides a market for flaxseed produced in Idaho, western Montana, Oregon and Washington. It is interesting to note

that the expression of linseed oil on a small commercial scale was begun in New York and Pennsylvania shortly after 1800.

The recent commercial production of flaxseed in California is the result of experiments begun in 1927 by A. C. Dillman and L. G. Goar at the Imperial Valley Experiment Station, near El Centro. W. W. Weeth, who succeeded L. G. Goar at this station in 1930, was largely responsible for the rapid expansion of flaxseed culture in the Imperial Valley, where in 1934 nearly 200,000 bushels of Punjab flaxseed were harvested. The following year about 20,000 acres were planted to flax in the San Joaquin and Sacramento Valleys of California and 5,000 acres in the Salt River Valley, Arizona. In addition to the information given, much more will be found in "Flaxseed Production in the Far Western States," U. S. Dept. Agric. Farmer's Bull. No. 1793 (1937) by A. C. Dillman and L. G. Goar.

U. S. Dept. Agric. Farmer's Bull. 1328, by A. C. Dillman, entitled "Production of Seed Flax," also contains much valuable information including the diseases of flax.

Oil Content. The oil content of flax seed varies from about 32 to 43 per cent, the quantity depending in part upon the variety and in part upon seasonal influences, which cause differences from year to year.

Schindler and Washata examined 43 samples of seed from various countries and found the percentage of oil to range from 37.5 to 43.2. Sheppard [*J. Ind. Eng. Chem.*, **4**, 14 (1912)] found that the oil content of seed from the Americas, India, and Russia varies from about 37 to 41.2 per cent. According to G. H. Pichard, North American seed received at a mill in the United States for a period of 5 years ranged in oil content from 35.8 to 40.2 per cent; the average was 38.8 per cent. During the same time, seed from Argentina gave a variation from 36.9 to 39.6 per cent of oil, the average being 38.5 per cent.

J. V. Eyre and E. A. Fisher [*J. Agric. Sci.*, **7**, 120 (1915)] found the following percentages of oil in seed at different stages of development: Green seed 21.05, seed beginning to turn brown 30.08, seed all brown 38.03, and fully matured 40.88.

Methods for the refractometric determination of the oil content of flax seed and the iodine number of the freshly extracted oil will be found in the chapter on methods.

Attention is called to the following references:

Sheppard, *Ind. Eng. Chem.*, **1912**, 4, 14 (1912); Rabak, *U. S. Dept. Agric. Bull.* **655** (1918); Ivanov, *Chem. Absts.*, **21**, 3382 (1927).

"Daily Growth and Oil Content of Flax Seed," A. C. Dillman, *J. Agric. Research*, **37**, 357 (1928).

Ivanov, *Przemysl Chem.*, **13**, 167 (1929). *Oil and Fat Ind.*, **6**, No. 10, 39 (1929). Effect of geographical location on the unsaturated linkages in drying and semi-drying oils.

"Moisture Content of Flaxseed and Its Relation to Harvesting, Storage, and Crushing," A. C. Dillman, and R. H. Block, *J. Am. Soc. Agron.*, **21**, 818 (1929).

"Oil Development in the Seed of a Growing Plant (Flax)," J. V. Eyre, *Biochem. J.*, **57**, 258 (1932).

"Influence of Climate During Ripening on Quality (Composition) of the Oil of *Linum Usitatissimum*," S. Ivanov, *Allegem. Öl Fettzeit.*, **29**, 149 (1932).

"The Relation of Agronomic Practice to the Quantity and Quality of the Oil of Flaxseed," I. J. Johnson, *J. Agric. Res.*, **45**, 239 (1932).

"Climatic Influence on the Quality of Oil from Ripening Linseed," S. Ivanov and P. Klokow, *Allegem. Öl Fettzeit.*, **29**, 149 (1933).

"Factors Affecting Linseed Oil Industry," T. H. Hopper, L. L. Nesbitt and A. J. Pickney, *N. Dakota Agric. Exp. Sta. Bull.* **286** (1935).

"Survey of the Oil Content and Iodine Value of Western Canadian Flaxseed 1935 Crop," W. F. Geddes, Canadian Dept. Trade and Commerce, Ann. Rept., p. 77, 1935.

"Experimental Studies on the Physiology and Nutrition of Flax with Respect to the Formation of Fiber and Oil," K. Schmalfuss, *Bodenkunde und Pflanzenernähr*, **3**, 1 (1936); *Chem. Abs.*, **30**, 8308 (1936); Pt. 2, Field Exps., *ibid.*, **4**, 340 (1937).

"1936 Crop of North American Linseed Oil," H. A. Gardner, *Nat. Pt., Var. and Lac. Assoc. Circ. No.* **521** (1936).

"Inheritance of Quality and Quantity of Oil in Flax in Relation to Other Plant Characters," W. G. McGregor, *Canadian J. Res.*, **15**, 362 (1937).

"Environment and Nutrition of the Flax Plant in Relation to the Degree of Saturation of Linseed Oil," K. Schmalfuss, *Fette u. Seifen*, **44**, 31 (1937); *Chem. Abs.*, **31**, 4368 (1937); *Pt. Oil & Chem. Rev.*, **99**, No. 11, 25 (1937).

"The Drying Behavior and Chemical Characteristics of Royal, Redwing and Crown Flaxseed (Oils)," J. A. Anderson, Ann. Report, **13**, 41-3 (1940), Canadian Dept. Trade and Commerce.

"Western Canadian Flaxseed (and Oil)," F. H. Lehberg and J. A. Anderson, *Sci. Agric.*, **21**, 727 (1941); *Chem Abs.*, **35**, 7744.

Manufacture of Oil. Cold-pressed oil is made in the Soviet Republics, Hungary, and Eastern Germany, where it is used for edible purposes. Most of the oil obtained in the United States is expressed hot from the seed by means of open frame or box hydraulic presses. The oil expeller is very satisfactory for pressing flax seed. In many other countries, the oil is chiefly obtained by expression in open frame or cage presses, but some is extracted with solvents.

The first step in connection with any of the methods of oil extraction is to separate the foreign matter (dockage), which (aside from pieces of iron or stems sometimes present) consists of weed seed and plant débris. From an economic standpoint, the foreign seeds should be separated at the farms and fed to poultry. The removal of foreign seeds, etc., is made by specially designed screening and blowing equipment. Formerly, in the United States, for example, the "cleaned" seed contained anywhere from 3 to 6 per cent of "dockage"; further improvement has reduced it to 3 per cent and less. Additional equipment has been devised in this country which is used in conjunction with the older sieving machinery, which is stated to remove all the foreign seeds. The more common foreign seeds present are those of cow cockle, corn cockle, thistle, pig weed, smartweed, ragweed, fox tail, flat and round-seeded false flax, vetch, charlock, various mustards, wild oats and buckwheat, sunflower, and sometimes wheat.

W. H. Eastman and W. L. Taylor, *Ind. Eng. Chem.*, **19**, 896 (1927), have shown the importance of separating all the foreign seed before expressing the oil.

The cleaned seed are crushed by passing them through oil seed rolls, which are built for this purpose in stacks of five. For the best results, all the rolls should make about 150 revolutions per minute. When the crushed seeds are to be pressed in hydraulic presses (United States and elsewhere) they are heated in large steam-heated "cookers" from

about 85° to 95° C. until they are ready for pressing. Much depends upon the proper "cooking," in order to get a maximum extraction of oil of good quality and also a satisfactory cake. Insofar as the cooking of flax seed is concerned, it now largely depends upon the individual operator's experience and judgment. If the time of cooking is too short or the temperature too low, the seed tissues are not sufficiently softened, which results in a lowered yield of oil. On the other hand, too high a temperature results in a dark-colored oil which contains an excess of mucilaginous matter, and the cake may have an undesirable odor. Also the moisture content must be carefully controlled; too little makes the meal non-coherent and gives unsatisfactory cakes, while meal with excessive moisture is difficult to handle and produces tough, dark-colored cake. In order to determine when the meal is cooked and in suitable condition for pressing, the present practice is for the operator to withdraw a handful from time to time and compress it. If the meal packs in his hand in a definite manner and has a certain "feel" it is considered ready to be pressed. A measured quantity of the meal is evenly distributed by the "buggy box" upon a strip of press cloth placed on the cake former—a press operated by hydraulic or other power with a steel block, containing in its upper surface a shallow depression, the size of a single press-frame or box. It is so constructed that after the meal has been placed on the press cloth, pressure can be applied against a "head plate" for an instant to compact the meal. After the ends of the press cloth are folded over the top of the cake, it is removed with a broad steel spatula and placed in the lowest frame of the press. One after another, all the frames are thus charged. It is of importance that each of the cakes should be of uniform thickness and density in order to get satisfactory results upon pressing as well as to reduce to a minimum the wear on the expensive press cloth. The press consists of a series of 16 or more steel plates, set one above the other, about 5 inches apart when the press is wide open. These perforated or channeled plates are provided with close-fitting steel sides or frames, so that the whole machine is really a series of boxes without ends, piled one upon the other, the lowest resting on the head (curb) of the hydraulic piston. Above the top frame, a heavy iron plate is fastened to the hydraulic piston cylinder by four heavy vertical steel columns, which serve as guides for the sliding frames. The pressure system for operating the press consists of powerful pumps, pressure accumulators and a supply tank for the linseed oil used in this system. The low and high accumulators consist of weighted tanks superimposed upon pistons. The accumulators serve to maintain a uniform pressure and reduce the shock upon the pumps due to the intermittent use of the "oil pressure" in operating the presses. This pressure system is regulated by automatic control. A number of oil mills, however, operate their presses directly from the pressure pumps, which have both speed and pressure automatic controls.

When a press is filled with cakes, the pressure is applied gradually and the piston slowly forces the frames upward, each against the one

above it. The final pressure used ranges from about 3500 to 4500 pounds per square inch. The oil flows over the sides of the press into the gallery around the bottom frame and out into the settling tanks, in which the coarse particles settle to the bottom. From there, the oil is transferred to the filter supply tanks. It is now customary to filter the oil (best, after cooling to room temperature) either through cloth or paper in plate-and-frame filter presses. Oil that is filtered while warm usually deposits some "foots" upon standing a short time.

The filling of the press and pressing occupy from 20 to 30 minutes. Then the pressure is released and the cakes are removed. The press cloths are removed by machine or hand. The soft oily edges of the cakes are cut off by the trimming machine and are later pressed again. The cakes are sold as such or ground into meal, both of which are used as feed for cattle. The cake usually contains 6 to 8 per cent of oil. The average yield in America is about 16 to 17 pounds of oil and 36 pounds of cake per bushel of seed.

It should be observed that flax seed as well as the press cake contain a cyanogenetic glucoside known as Linamarin [Jorissen and Hairs, *Bull. acad. roy. belg.*, (3), **21**, 529 (1891)]. The cake, however, from "hot pressing," is innocuous to cattle. The heat apparently prevents the action of the enzyme in the seed upon the glucoside and stops the evolution of hydrocyanic acid from the cake in the presence of moisture. References: Henry and Auld, *J. Soc. Chem. Ind.*, **27**, 428 (1908); S. H. Collins and H. Blair, *Analyst*, **39**, 70 (1914); **40**, 125 (1915).

Oil expeller presses are particularly well adapted for pressing linseed and many oil mills are now using them. Recently, a cooker-expeller has been developed. The "cooker" takes the place of the "temperer" placed above the expeller, besides, eliminating the use of the seed dryers for reducing the moisture of the seed before processing.

Under the manufacture of cottonseed oil and cake, some information is given in connection with the operation of the expeller. Before the older types of expeller became hot, the press cake (unless the seed have been previously heated sufficiently to destroy the cyanogenetic glucosides) had to be returned through the expeller.

Refining. The first method employed for improving the oil consisted simply of storing it, sometimes for several years, until the mucilaginous impurities had precipitated and settled. A more rapid method, which was devised many years ago, is based on the agitation of the oil with 1 or 2 per cent of strong sulfuric acid, which chars the impurities and causes them to separate as a flocculent precipitate. The method requires care and experience, as the oil is easily damaged by using either too much or a too highly concentrated acid. It is important to avoid sulfonation of the oil as much as possible. Also in washing out the acid with water, care must be taken to avoid loss of oil through the formation of stubborn emulsions. The operation is conducted in large lead-lined wooden tanks, provided with mechanical agitators. It is advisable to determine by laboratory experiment the strength and quantity of sulfuric acid best adapted for each lot of oil to be heated. Usually,

from 18 to 25 pounds of acid are required to refine a ton of oil. The factory refining is made by spraying the acid into the agitated oil. As the acid is added, the oil gradually becomes greenish; then the mucilage coagulates and separates as brown flocks. Toward the end of this operation, a small portion of the oil is removed to a white tile and examined. As soon as the flocks or flakes separate, having a clear oil, no further addition of acid is made. At this stage, about 20 gallons of water are added (to a 10-ton batch) to swell the "flakes" and to stop further action of the acid. The oil is now allowed to stand for 18 hours or longer and then withdrawn from the acid sludge into a tank, where it is washed with 2 or 3 successive portions of boiling water. After separating the last of the undissolved water, the oil, which should be bright and clear, is pumped into storage tanks. The refined oil frequently contains somewhat more free fatty acid than the untreated oil. The refining loss usually amounts to about 1.5 per cent, but may be higher in the case of oil expressed from immature or damaged seed, which contain larger quantities of non-oil constituents than the oil from sound mature seed. Incidentally, these highly colored off-oils seldom refine to a satisfactory color. A dark oil is recovered from the acid sludge mentioned above by repeated treatment with hot water, and this is usually sent to the soapmaker.

Acid refining oil is now considered inferior to that refined by the caustic soda process, with the result that increasingly large quantities of the oil are being refined by the latter process in a manner similar to that employed in treating crude cottonseed oil. Caustic soda not only removes the free fatty acids as soap but also precipitates the mucilage and other coloring matter.

C. W. A. Mundy [*J. Oil Col. Chem. Assoc.*, **18**, 238 (1935)] states that a satisfactory varnish oil is obtained from raw oil, by heating it to about 160° C. in a vacuum deodorizer and passing super-heated steam at 250° C. through the oil. As soon as the "break" is observed in the sight glasses, the oil is pumped through one, and then a second, heat exchanger. When cooled to below 100° C., the oil is agitated, for example, with fuller's earth and filtered. He states that this oil suffers no discoloration when subjected to cooking for long periods of time. For additional details on the refining and bleaching of the oil, the original article should be consulted.

Bleaching. The refined oil may be further bleached, if desired, by heating to about 100° C. and agitating it for a short time with 2 to 5 per cent of fuller's earth, then filtering while hot through a filter press.

The raw oil may be bleached by treatment after heating with fuller's earth, prepared "silica" earths, benzoyl peroxide or by blowing air through the heated oil. Many other reagents have been proposed for this purpose, but most of them are not satisfactory. The less mucilage and moisture present, the better the oil bleaches.

When desirable, the refined, bleached oil can be chilled or "wintered" until the wax (dissolved in the oil from the seed coats) has separated;

then it can best be removed by filtration, using filter paper in place of cloth in a filter press.

Boiled Oil. Boiled oil is now quite generally prepared by heating the raw (or refined) oil in open, steam-heated kettles or tanks with small quantities of resinates, linoleates, tungates, or other compounds of lead, manganese and cobalt. As irritating, inflammable fumes are evolved, provision is made for leading them into a stack or into the furnaces of the power plant where they are burned. For the preparation of pale or bleached boiled oil, air is blown gently through the oil heated to about 125° C. in the presence of a small quantity of drier. When the temperature begins to rise above 125° C., the air pressure is reduced, the steam is shut off, and water is circulated through the steam coil, so that the temperature of the oil is gradually reduced. When the desired gravity of the oil is obtained, it is rapidly cooled to about 65° C., the remainder of the drier is added, which is followed by vigorous blowing of the oil for a short time. After settling, the oil is filtered. The raw oil should be bright and free from foots, and the minimum quantity of driers should be used in making pale boiled oil.

Formerly, the "boiling" was conducted by heating the oil, in kettles over fires, with lead and manganese oxides, and naturally, many fires resulted from this practice.

Boiled oils are sold as single, double, pale, extra pale or bleached, the names indicating differences in color, consistency and drying properties.

C. Fichandler [*Ind. Eng. Chem.*, **17**, 478 (1925)] found that kettles made of monel metal were affected less than those made of copper, which are in more general use for making boiled oil. For boiling linseed oil by means of electric heat see *Chem. Met. Eng.*, **25**, 844 (1921).

Blown Oil. Blown oil is prepared by passing air through the heated oil until the desired viscosity is reached in the presence of a small quantity of a drier such as cobalt resinate or acetate. While the oil is being blown vigorously with air, the temperature should be maintained at about 120° to 125° C. Equipment similar to that used in "boiling" is employed, and the same precautions are taken in the removal of the fumes. If a further addition of driers is to be made, the oil is rapidly cooled to about 60° C., the air blast is greatly reduced, and the cobalt linoleate or other drier is then added. To produce a pale blown oil requires much experience. Blown oil of pale color is required for making special paints, varnishes and enamels. Low-acid blown oil, for making certain lacquers, is prepared by using carbon dioxide in place of air. Blown oil is used in the manufacture of linoleum, paste paints and varnishes, including some made with tung oil.

Stand Oil. Stand oil is made by heating thoroughly settled or refined oil in covered varnish kettles to 260° to 285° C. until the desired viscosity is obtained. Aluminum kettles give the lightest-colored product. The lower the acidity, the quicker the oil will thicken. It is important to draw off the fumes in order to prevent their partial condensation

and return to the oil in the kettle, and thereby delay the thickening process.

"Top fired" oil for lithographic varnish and copper plate printing ink is made by heating the oil to the ignition point of the evolved vapors. This oil is usually pale in color and less oxidized than a "boiled" oil.

For enamel oil, a mixture of linseed and tung oil may be used in making the stand oil, which will not only thicken faster than linseed oil alone but also yields a lighter-colored product.

The losses during manufacture vary with the temperature and period of the heating, and range from about 3 to 16 per cent. Stand oil is most satisfactory for the preparation of high-gloss paints and enamels, although the cheaper blown oil is often employed for these purposes. It is also largely used in the manufacture of fair-drying and baking enamels.

For further information and details of manufacture of boiled blown and polymerized linseed oils, works especially devoted to these subjects must be consulted. However, it requires experience to obtain any of these products.

Attention is called to the following references:

"Action of Heat and Blowing of Linseed and Perilla Oils and Glycerides Derived from Them," J. S. Long, W. S. Egge and P. C. Wetteran, *Ind. Eng. Chem.*, **19**, 903 (1927).

"Rate of Molecular Weight Increase in the Boiling of Linseed and Tung Oils," J. S. Long and G. Wurtz, *Ind. Eng. Chem.*, **18**, 1252 (1926).

"Relationship During Drying Between the Acid Value of Linseed Oil and the Concentration of Cobalt Acetate," W. L. Evans, P. E. Marlingard, and S. E. Lower, *Ind. Eng. Chem.*, **18**, 1229 (1926).

"Action of Driers," Morrell and Weale; "Rubber, Resins, Paints, and Varnishes" (Baillere, Tindall and Cox, London, 1920); "The Chemistry of Drying Oils," Morrell and Wood (E. Benn, Ltd., London, 1925).

Composition. At various times different investigators have determined the quantities of the fatty acids present in linseed oil as glycerides. Since the publication of the thiocyanogen method by Kaufmann, the results of which, together with the iodine number, can be used to calculate the proportions of the unsaturated acids present, provided the quantity of saturated acids in the oil is known, much recent data for linseed oil from different sources have been published. Within the past two years, however, it has been shown that thiocyanogen does not react with either linoleic or linolenic acids in accordance with the calculated or theoretical amounts, as formerly believed (see the thiocyanogen method). Consequently, the published data on the percentages of the fatty acids are incorrect.

Rose and Jamieson [*Oil and Soap*, **18**, 173 (1941)] have investigated seven large samples of oil expressed from seed of known varieties of flax. The samples of seed were selected with a view to obtaining oils, the iodine numbers of which would extend over a considerable range in order to ascertain how such oils would differ with respect to the quantities of the individual saturated and unsaturated acids present.

The more important characteristics of these oils are given in Table 1.

TABLE 1. CHARACTERISTICS OF EXPRESSED LINSEED OILS

Oils Source of Seed	Bison No. 1 N. Dak.	Bison No. 2 N. Dak.	Bison No. 3 N. Dak.	Bison Texas	Punjab Texas	Punjab Cal.	Abyssinian Cal.
$N_D^{25°}$	1.4742	1.4772	1.4784	1.4771	1.4773	1.4787	1.4799
Iod. No. (Hanus)	140.9	156.6	161.4	169.4	164.6	179.7	190.6
SCN Value	93.8	100.3	109.3	112.8	111.0	116.5	120.7
Unsap. (%)	1.11	1.12	1.11	1.35	1.24	0.90	0.89
Sat. acids (%)...	11.97	10.45	9.00	7.03	8.72	10.13	9.32

Table 2 gives the percentages of the acids present in the oils. The percentages given for the unsaturated acids were calculated with the aid of their empirical (or determined) thiocyanogen values which were obtained under carefully controlled experimental conditions.

TABLE 2. PERCENTAGES OF ACIDS IN OILS

Oils	Bison No. 1 N. Dak.	Bison No. 2 N. Dak.	Bison No. 3 N. Dak.	Bison Texas	Punjab Texas	Punjab Cal.	Abyssinian Cal.
Oleic	35.00	28.10	37.60	34.30	36.00	26.26	21.70
Linoleic	21.65	23.10	4.56	6.12	3.30	3.54	5.34
Linolenic	25.75	32.70	43.25	46.65	46.20	54.70	58.30
Palmitic	6.29	5.94	5.93	4.38	3.84	4.98	6.87
Stearic	4.46	4.00	2.37	2.32	4.61	4.84	2.17
Arachidic	0.86	0.30	0.50	0.28	0.22	0.29	0.28
Lignoceric	0.36	0.21	0.20	0.05	0.05	0.00	0.00

Characteristics. The following range of characteristics has been selected from the results obtained by many different investigators. Oils from the more important producing countries are represented over a period of many years:

Sp. g. at 20° C. 0.927 to 0.931, at 15° C. 0.931 to 0.938; $N_D^{25°}$ 1.4786 to 1.4815, at 40° C. 1.4742 to 1.4754, at 15° C. 1.4808 to 1.4859; Sap. V. 189 to 196; Iod. No. 170 to 204; SCN V. 114 to 124.3; Unsap. 0.5 to 1.6 per cent, Acetyl V. 4 to 10; Sat. acids 8 to 12.5 per cent; Titer of fatty acids 19° to 21° C. The range of the hexabromide value as determined by modern methods is usually from about 45 to 52 per cent, but is sometimes as low as 41 per cent.

Ingle [*J. Soc. Chem. Ind.*, **30**, 344 (1911)] gives the limits for the iodine numbers by the Wijs method of oils of established purity as follows:

Oils	Iodine Numbers
Baltic (North Russian)	190 to 204
Indian	180 to 189
Argentine	175 to 186
Black Sea (South Russian)	176 to 182
North American	177 to 188
Morocco, Dutch, Turkish	185 to 202

Smith and Tuttle (U. S. Bur. Stds., *Tech Paper* **37**) studied the Hanus method and found that concordant figures are obtained when the quantity of oil taken for the determination of the iodine number does not exceed 0.259. Committee D-1 [*Proc. Am. Soc. Test. Mat.*, **21**, 3348 (1921)] studied both the Hanus and Wijs methods and concluded

that there is little difference in the accuracy, but that the Wijs method gives an iodine value 4 to 5 per cent higher than the Hanus procedure in the case of linseed oil.

Foots. The foots referred to are those which separate from the oil upon standing, and are not meal ("press foots"). Raw linseed oil contains more or less non-oil constituents, which consist of carbohydrates, proteoses, phosphatides and probably other substances. Larger quantities of these substances are present in oils obtained from immature or damaged seed than in the oil expressed from sound matured seed. Formerly, the larger part of these substances was separated from the oil by allowing it to stand for several months or longer, as previously mentioned. During the storage, the foots separated as a brown slimy precipitate (mucilage). When the oil is heated rapidly (220° to 280° C.) the mucilage coagulates and separates as a bulky flocculent precipitate known as the "break." It usually amounts to from 0.1 to 0.3 per cent by weight of the oil, but in some cases the oil contains considerably more. Properly refined oil contains none of these substances. Thompson [*J. Am. Chem. Soc.*, **25**, 716 (1903)] found in one case that the break amounted to about 0.28 per cent by weight. The ash of the break, which amounted to 47.8 per cent, was found to contain 50.85 phosphorus pentoxide. Eisenschiml and Copthorne [*Ind. Eng. Chem.*, **2**, 29 (1910)] found that the phosphorus pentoxide in the ash from foots and breaks (solvent-extracted oil) ranged from 46.5 to 81.08 per cent.

Properties. Linseed oil, in common with other drying oils, keeps practically unchanged indefinitely when stored in closed, completely filled containers from which the light is excluded. The characteristic property of the oil is its ability, upon exposure to the air, to absorb oxygen and form an elastic solid known as linoxyn. Reid [*J. Soc. Chem. Ind.*, **13**, 1020 (1894)] states that if a film of linoxyn is exposed to the air for several years, it gradually softens and ultimately becomes a fluid mass, which is readily soluble in alcohol in contrast to linoxyn. The composition of this product, which is called superoxidized oil, still remains unknown.

Genthe [*Z. angew. Chem.*, **19**, 2087 (1906)] found that linseed oil exposed to the air absorbed 22.6 per cent of its weight of oxygen, but when exposed in an atmosphere of oxygen to ultraviolet rays, it absorbed 34 per cent. Coffey [*J. Chem. Soc.*, **119**, 1152 (1921)] has shown that linseed oils absorb a mean of 28.7 per cent of oxygen, while the fatty acids of the oil absorb about 30 per cent. When the oil is "dry" there is a position of equilibrium where the gain in weight is approximately equal to the loss in weight because of the volatilization of carbon dioxide, moisture, and organic compounds. Therefore, the weight of oxygen absorbed by the oil is considerably greater than the observed gain in weight.

During the drying of the oil it has been found that there is a maximum increase in volume at the setting or solidification point, which is followed by a gradual contraction with an increase in density. This is very noticeable in the drying of thick oil or paint films by their wrinkling.

Another important property is the ability of the oil to polymerize with an increase of viscosity in proportion to the degree of polymerization. Polymerization begins when the oil is heated to about 200° C., but at higher temperatures it proceeds much more rapidly. The higher the iodine value, the more rapidly will the oil polymerize. As it does so, the iodine and hexabromide values diminish. Morrell [*J. Soc. Chem. Ind.*, **36**, 105 (1915)] found that oil thickened (polymerized) from 260° to 280° C. contained two modications, both of which were soluble in petroleum ether, but only one in acetone. The original oil had an iodine value of 185, an acid value of 0.4, and a molecular weight of 805. The acetone-insoluble portion of the thickened oil had a molecular weight of 1788 to 2517 and an acid value of 0.2, while the acetone-soluble portion had an acid value of 7.5 to 8.0 and a molecular weight of 904 to 975. As all traces of linoleic and linolenic acids had disappeared, Morrell concluded that linkage changes must have occurred during the thickening of the oil prior to polymerization.

Numerous theories have been proposed from time to time to explain the changes which take place during the drying or solidification of films of linseed and other drying oils (such as the auto-oxidation, Blom's micelle and Auer's gas coagulation theories), but according to Eibner and Munzert [*Chem. Umschau*, **34**, 183:206 (1927)] these are inadequate. These authors also state that polymerization does not occur with fatty oils except at high temperatures and that all drying oils are improved by conversion into "stand oils," as they are more difficult to saponify and develop less acidity on drying.

Space does not permit of a discussion of the very numerous investigations which have been made or the theories advanced in connection with the chemical and physical changes which take place during the drying of linseed oil, alone or in the presence of driers, or the changes taking place during the preparation of boiled, blown oil, etc. However, much remains to be investigated before these changes can be entirely understood and the final products known. The following references contain much information:

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Uses of Oil. The cold-pressed oil is used for edible purposes in Russia and nearby countries. The hot-pressed oil is used chiefly in the manufacture of paints, varnishes, printing inks, soft soap, waterproofings, oil-cloth and linoleum. In the Soviet Republics, Bulgaria, Hungary and some other countries, cold-pressed linseed oil is used for edible purposes. Acid-refined oil is useful in "wet pulping" of white lead, for grinding pigments in paste form, and the production of thick lithograph varnishes. Alkali-refined oil is used in the manufacture of paints, enamels, lacquers and varnish. Much oil is also used for making linoleum, oil-cloth, waterproofings, printing ink and soft soap.

Adulterants. Linseed oil is sometimes adulterated with vegetable oils such as soybean, rape, sunflower, safflower, and candlenut, as well as with rosin, mineral, and fish oils. However, boiled linseed oil is more frequently adulterated than raw oil. Tests for the more common adulterants are given below. It should be noted that the iodine numbers of some fish oils are as high as that of linseed oil. When the hexabromide test is applied to a mixture of fish and linseed oil, the quantity obtained is sometimes greater than that from pure linseed oil, due to the octo-bromides of the fish oil. In any case it is preferable to take the melting points of the ether-insoluble bromides and note whether or not they darken. In the absence of fish oil, linseed oil in admixture with most other oils, gives an abnormally small quantity of hexabromides.

Rosin and Mineral Oils. Rosin and mineral oils increase the quantity of unsaponifiable matter over that normally present in linseed oil. When appreciable quantities of rosin oil are present, the flash point of the mixture will be lower than that of pure linseed oil, which is approximately 240° C. The flash point of rosin oil ranges from about 155°

to 160° C. Use is made of the Lieberman-Storch test for rosin or rosin oil, but according to H. Wolff [Chem. Umschau., **34**, 17 (1927)] some pure linseed oils give this test.

Rape and Mustard Oils. When appreciable quantities of rape or mustard seed oils are present in admixture with linseed oil, a lower saponification value will be obtained (in the absence of mineral oil). The presence of these oils should be confirmed by the separation and identification of erucic acid (see Rape oil). Also see the following test.

Test for Cottonseed Oil. The following method has been proposed by P. Torelli [*Oil Col. Trds. J.*, **66**, 954 (1924)]. Add 8 cc. of 2 per cent alcoholic silver nitrate (alcohol 99 per cent) to 20 cc. of the oil to be tested and heat for 10 minutes in a boiling water bath. Cottonseed oil gives a black color, mustard oil a dirty greenish one. The author has had no experience with this test.

Oxidized Fatty Acids. Saponify a 5-gram sample in a 200-cc. Erlenmeyer flask with 5 cc. of (1 : 1) potassium hydroxide solution and 10 cc. of alcohol. Heat carefully until the alcohol is expelled. Dissolve soap in 75 cc. of hot water and transfer solution to a separatory funnel. Rinse the flask several times with hot water and transfer the washings to the funnel. Decompose the soap with a slight excess of hydrochloric acid. Cool and add 100 cc. of petroleum ether. After shaking, allow mixture to stand until it has separated into 2 layers. Withdraw the lower aqueous layer. The oxidized acids, depending upon the quantity, will be found as an insoluble precipitate adhering to the sides of the funnel or as a sediment in the petroleum ether. Withdraw the petroleum ether into a filter, if necessary, to prevent loss of any precipitate, and wash funnel (and filter) several times with petroleum ether to remove the soluble acids. (When the quantity of oxidized acids is large, it is necessary to dissolve them in alkali, and after acidification, extract again with petroleum ether to remove all the unoxidized fatty acids.) Dissolve the insoluble oxidized acids in hot alcohol and transfer the solution to a weighed flask. Evaporate the alcohol, dry at 100° C., and weigh the residue. Calculate the percentage of oxidized acids.

Test for Boiled Oil. Reference: *Sci. Amer.*, **131**, Sept. No., 189 (1924). Reagent: Dissolve 1 cc. of freshly distilled aniline in 10 cc. of carbon tetrachloride in a flask and add a few drops of bromine previously dissolved in several volumes of carbon tetrachloride. Then add aniline, cautiously while shaking the solution, until the separated bromide dissolves. To 5 cc. of the sample of oil to be tested, add a few drops of the reagent and shake. A deep brown color indicates a boiled oil. No color is given by a raw oil.

Some other tests will be given in connection with the following United States Government Specifications:

Master Specification (No. 4a) for Oil, Linseed, Raw. This specification covers two types of raw linseed oil: A. normal iodine number; B. high iodine number.

Raw linseed oil shall be pure oil expressed from flax seed, and shall conform to the following requirements:

	Maximum	Minimum
Foots:		
Heated oil, per cent by volume	1.0	...
Chilled oil, per cent by volume	4.0	...
Specific gravity 15.5°/15.5° C.	0.936	0.931
Acid number	5.5	...
Saponification number	195.0	189.0
Unsaponifiable matter	1.5	...
Iodine number	...	177.0

Color: Not darker than a freshly prepared solution of 1 gram potassium bichromate in 100 cc. pure sulfuric acid sp. g. 1.84.

When high iodine number type of raw linseed oil is specified by purchaser, the iodine number must be not less than 188 and the oil shall conform to all the other requirements.

Deliveries will in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

Sampling:—The method of sampling given under (a) below should be used whenever it is feasible to apply it. To meet conditions when (a) is not applicable, method (b), (c) or (d) is to be used according to the special conditions that obtain.

(a) *During Loading of Tank Cars or Filling of Containers for Shipment at the Factory:*—The purchaser's inspector shall draw a sample at the discharge pipe where it enters the receiving vessel or vessels. The total sample shall be not less than 5 gallons and shall be a composite of small samples of not more than 1 pint each, taken at regular intervals during the entire period of loading or filling.

The sample thus obtained shall be thoroughly mixed, and from this composite sample three portions of not less than 1 quart each shall be placed in clean, dry glass bottles or tin cans which must be filled with the sample and securely stoppered with new clean corks or well-fitting metal covers or caps. These shall be sealed and labeled distinctly by the inspector, and one delivered to the buyer, one to the seller, and the third held for check in case of dispute.

(b) *From Loaded Tank Cars or Other Large Vessels:*—The total sample shall not be less than 5 gallons and shall be a composite of numerous small samples of not more than 1 pint each, taken from the top, bottom, and intermediate points by means of a glass or metal container with removable stopper or top. This device attached to a suitable pole is lowered to the various desired depths when the stopper or top is removed and the container allowed to fill. The sample thus obtained is handled as in (a).

(c) *Barrels and Drums:*—Not less than 5 per cent of the packages in any shipment or delivery of barrels and drums shall be sampled. The packages shall be shaken, rolled, and stirred to mix the contents thoroughly. The samples from the individual containers shall be taken through the bunghole or holes not less than 1¼ inches in diameter bored in the head or side for the purpose. The apparatus for drawing the sample shall consist of a glass tube about 1 inch in diameter and somewhat longer than the length or diameter of the oil container, a conical stopper that will fit the glass tube and is not more than ½ inch long fastened to a stiff metal rod not more than ¼ inch in diameter and not less than 4 inches longer than the glass tube. The stopper is lowered by the rod until it rests on the bottom of the cask, the tube slipped down slowly over the rod, and finally pressed on the stopper. By holding tube and rod, the column of oil can then be removed. This process is repeated until the required amount of samples is obtained, which shall be not less than 2 gallons. This is mixed and handled as in (a).

(d) *Small Containers, Cans, Etc., of 10 Gallons or Less:*—Small containers, cans, etc., of 10 gallons or less, should be sampled while filling by method (a) whenever possible. When method (a) is not applicable, it is mutually agreed that: In all cases the total sample taken shall not be less than 3 quarts. This shall be obtained by taking at least one package from each lot of not more than 300 packages. The sample thus taken shall be thoroughly mixed and subdivided as in (a).

Testing

All tests shall be made on oil that has been thoroughly agitated before removal of a portion for analysis. (a) Foots.—General test:—With all materials at a temperature between 20° and 27° C. mix by shaking for exactly one minute in a

graduated tube, 25 cc. of the well-shaken sample of oil, 25 cc. of acetone, and 10 cc. of acid calcium chloride solution (*see* Reagents). Then clamp tube in an upright position and allow to settle for 24 hours. The temperature during this period should be between 20° and 27° C. The graduated tube shall be not less than 70 cc. capacity and shall have at least 50 cc. graduated in 0.1 cc. The diameter of the tube shall be such that the 50 cc. graduated portion shall be not less than 40 cm. or more than 60 cm. in length. The volume of the stratum lying between the clear calcium chloride solution and the clear acetone and oil mixture is read to 0.1 cc. or fraction thereof. This reading multiplied by 4 expresses the amount of foots present as percentage by volume of the oil taken.

Heated Oil.—Heat a portion of the oil to 65° C., hold it within 2° C. of that temperature for 10 minutes, then cool it to room temperature (20° to 27° C.). Promptly make the general foots test as described above.

Chilled Oil.—Heat a portion of the oil to 65° C., hold it within 2° C. of that temperature for 10 minutes, then place it in a clean dry bottle, stopper tightly, and place in a cracked-ice and water mixture (0°) for exactly 2 hours. At the end of this time place the bottle in a large bath of water at 25° C. and keep it there for 30 minutes, then promptly make the general foots test as described above.

Specific Gravity.—Determine at 15.5/15.5° C. by any convenient method that is accurate within two points in the fourth decimal place.

Acid Number.—Weigh from 5 to 10 grams of the oil. Transfer to a 300-cc. Erlenmeyer flask. Add 50 cc. of a mixture of equal parts by volume of 95 per cent ethyl alcohol and C. P. reagent benzol. (This mixture should be previously titrated to a very faint pink with dilute alkali solution, using phenolphthalein as an indicator.) Add phenolphthalein indicator and titrate at once to a faint permanent pink color with standard sodium or potassium hydroxide solution. Calculate the acid number (mg. KOH) per gram of oil.

Saponification Number.—Weigh (accurately) about 2 grams of the oil and transfer to a 300-cc. Erlenmeyer flask. Add (exactly) 25 cc. of alcoholic sodium or potassium hydroxide solution. Put a condenser loop inside the neck of the flask and heat on a steam bath for one hour. Cool, add phenolphthalein as indicator, and titrate with 0.5*N* sulfuric acid. Run two blanks with the alcoholic alkali solution. These should check within 0.1 cc. of 0.5*N* sulfuric acid. From the difference between the number of cubic centimeters of acid required for the blank and for the determination, calculate the saponification number (mg. of potassium hydroxide required for 1 gram of the oil).

Unsaponifiable Matter.—Weigh 8 to 10 grams of the oil and transfer to a 250-cc. long neck flask. Add 5 cc. of a concentrated solution of sodium hydroxide (equal weights of alkali and water) and 50 cc. of 95 per cent ethyl alcohol. Put a condenser loop inside the neck of the flask and boil for two hours. Occasionally agitate the flask to break up the liquid, but do not project the liquid onto the sides of the flask. At the end of two hours remove the condenser and allow the liquid to boil down to about 25 cc. Transfer to a 500-cc. glass-stoppered separatory funnel, rinsing with water. Dilute with water to 250 cc., add 100 cc. of redistilled ether. Stopper and shake for one minute. Let stand until the two layers separate sharp and clear. Draw all but one or two drops of the aqueous layer into a second 500-cc. separatory funnel and repeat the process, using 60 cc. of ether. After thorough separation, draw off the aqueous solution into a 400-cc. beaker, then transfer the ether solution into the first separatory funnel, rinsing down with a little water. Return the aqueous solution to the second separatory funnel and shake out again with 60 cc. of ether in a similar manner, finally drawing the aqueous solution into the beaker and rinsing the ether into the first separatory funnel. Shake the combined ether solutions with the combined ether rinsings and let the layers separate sharp and clear. Draw off the water and add it to the main aqueous solution. Shake the ether solution with two 25-cc. portions of water. Add these to the main water solution. Swirl the separatory funnel so as to bring the last drops of water down to the stopcock and draw off until the ether solution just fills the bore of the stopcock. Wipe out the stem of the separatory funnel with a bit of cotton on a wire. Draw the ether solution (portionwise, if necessary) into a 250-cc. flask and distill. While still hot, drain the flask into a small weighed beaker, rinsing with a little ether. Evaporate this ether, cool the beaker, and weigh. (The unsaponifiable oil from adulterated drying oils may be volatile and as a consequence may evaporate on long heating. Therefore heat the beaker on a warm plate, occasionally blowing out with a current of dry air. Discontinue heating as soon as the odor of the ether is gone.)

Iodine Number.—Determine the iodine number by the Wijs method, allowing the Wijs solution to react for one hour.

Loss on Heating at 105° to 110° C.—Place 10 grams of the oil in an accurately weighed 50-cc. Erlenmeyer flask and weigh. Heat in an oven at a temperature between 105° and 110° C. for 30 minutes, then cool and weigh. Calculate the percentage loss. This determination shall be made in a current of carbon dioxide.

Color.—Prepare a fresh solution of 1 gram of pure potassium bichromate in 100 cc. pure concentrated colorless sulfuric acid (sp. g. 0.184). Place the oil and color solution in separate thin-walled clear glass tubes of the same diameter (1 to 2 cm.) to a depth of not less than 25 cm. and compare the depths of color by looking transversely through the columns of liquid by transmitted light.

Reagents

Acetone.—United States Pharmacopoeia grade.

Acid Calcium Chloride Solution.—Saturate with calcium chloride a mixture of 90 parts water and 10 parts concentrated hydrochloric acid.

Standard Sodium Hydroxide Solution.—Prepare a stock concentrated solution of sodium hydroxide by dissolving the hydroxide in water in the proportion of 200 grams to 200 cc. of water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 175 cc. and dilute to 10 liters with freshly boiled distilled water. Preserve in a stock bottle provided with a large guard tube filled with sodium lime. Determine the exact strength by titrating against pure benzoic acid, using phenolphthalein as indicator (*U. S. Bur. Stds. Sci. Paper* 183). This solution will be approximately one fourth normal, but do not attempt to adjust it.

Alcoholic Sodium Hydroxide Solution.—Dissolve pure sodium hydroxide in pure ethyl alcohol in the proportion of about 22 grams per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow.

Half Normal Sulfuric Acid Solution.—Add about 15 cc. of sulfuric acid (sp. g. 1.84) to distilled water, cool and dilute to 1000 cc. Determine the exact strength by titrating against freshly standardized sodium hydroxide or by any other accurate method. Either adjust to exactly half normal strength or leave as originally made.

The complete master specifications (4a and 475a) can be purchased from the Superintendent of Documents, U. S. Govt. Printing Office, Washington, D. C.

U. S. Master Specification (No. 475a) for Oil, Linseed, Boiled. The specification covers two types of boiled linseed oil: A—kettle boiled, and B—quick-process boiled linseed oil.

Boiled linseed oil shall be pure linseed oil that has been treated (preferably by heating—kettle boiled) with compounds of lead and at the option of the manufacturer with suitable compounds of other drying metals, so as to produce a product that will dry rapidly. It shall be clear, free from sediment, and shall meet the following requirements:

	Maximum	Minimum
Time of drying on glass, hours	18.0	...
Loss on heating at 105° to 110° C., per cent	0.2	...
Specific gravity at 15.5°/15.5° C.	0.945	0.937 [1]
Acid number	7.5	...
Saponification number	195.0	189.0
Unsaponifiable, per cent	1.50	...
Iodine number, Wijs	...	170.0
Ash, per cent	0.5	...
Lead, per cent	...	0.5

[1] When quick process, not kettle-boiled, oil is called for in contract, the minimum specific gravity shall be 0.931.

Methods of Sampling and Testing. With the exception of the methods given below, the methods to be used are those given under the specification for the raw oil.

All tests shall be made on oil that has been thoroughly agitated before removal of a portion for analysis.

Ash.—Weigh a porcelain crucible or dish. Add 10 to 25 cc. of oil, carefully weighing the amount. Place on a stone slab on floor of a hood. Ignite by playing the flame of a burner on the surface of the oil and allow to burn quietly until most of the oil is burned, then transfer to a muffle or over a flame and continue heating at a low temperature (not over a dull red heat) until all carbonaceous matter is consumed. Cool, weigh, and compute the percentage of ash.

Lead.—Dissolve the ash (from previous determination) in dilute nitric acid to which a little hydrogen peroxide has been added and determine lead by the sulfate or any other equally accurate method.

Time of Drying on Glass.—Flow the oil over a perfectly clean glass plate. Place plate in a nearly vertical position in air that is between 15° and 35° C. and of humidity between 48 and 60 per cent saturation. After about two hours, test the film at intervals with the finger at points not less than 2½ cm. from the edges. The film will be considered dry when it no longer adheres to the finger and does not rub up appreciably when the finger is lightly rubbed across the surface.

Jamieson and Baughman [*Oil and Fat Ind.*, 3, 307 (1926)] have proposed a gravimetric method for the determination of the "break" or the "break" and "foots" which can be completed in about 6 hours. The neutral glycerides and free fatty acids are determined [*Cotton Oil Press*, 6, No. 4, 33 (1922)] and the sum of their percentages is deducted from 100 to get the percentage of the "break" and "foots," if present. The break from 8 samples of linseed oil free from "foots" ranged from 0.25 to 0.67 per cent. There is no apparent relation between the results obtained by this method and the volumetric method previously described. Further study is necessary to determine the suitability of the gravimetric procedure as a routine method.

British Standard Specification for Raw Linseed Oil. This specification was prepared by the British Engineering Standards' Association in 1926.

Sp. g. at 15.6° C. not less than 0.931 nor more than 0.935.
Refractive Index at 20° C. not less than 1.4805 nor more than 1.4824.
Iodine Value (Wijs) not less than 175.
Saponification Value not less than 188 nor more than 192.
Unsaponifiable Matter not more than 1.50 per cent.
Acid Value shall not exceed 4.
Color. Oil shall not be darker in color than a freshly made solution of 0.1 gram iodine and 1.0 gram pure potassium iodide in 100 cc. of water.
Drying Time. Oil shall become surface dry in not more than 4 days at a temperature from 15.6° to 21.1° C.
Oil held from 15.6° to 21.1° C. for a period of 24 hours shall be free from turbidity and visible impurities.
Methods of analysis are included in the specification.

Manihot (Ceara Rubber) Seed Oil. This oil is obtained from the seeds of the tree *Manihot glaziovii*, belonging to the *Euphorbiaceae*. The tree is native to Brazil and has been cultivated on the east and west coasts of Africa. The seeds, which have a thick, hard, woody shell, weigh about 0.5 gram. Depending upon their source, they contain from 25 to about 45 per cent of kernels. The kernels usually contain from 35 to 42 per cent of oil. The oil is greenish yellow and has a slight bitter taste.

The characteristics reported by various investigators are as follows: Sp. g. at 15° C. 0.9238 to 0.9258; $N_D^{15°}$ 1.4750, at 40° C. 1.4670 to 1.4678; Sap. V. 189 to 193; Iod. No. 135 to 138; Unsap. 0.5 to 0.9 per cent; R.M.V. 0.4 to 0.7; Acid V. 0.6 to 1.7; Titer 20.5° to 23.5°.

Grimme [*Chem. Zeit.*, **43**, 505 (1919)] examined the oil from East African seed with the following results: Sp. g. at 15° C. 0.9235; $N_D^{40°}$ 1.4674; Sap. V. 187.5; Iod. No. 142; R.M.V. 0.35; Unsap. 0.76 per cent; Acid V. 1.68; Titer 21.5°.

The oil can be used in mixture with linseed oil for the manufacture of paint, etc.

Grimme also examined the oil from the seeds of *Manihot dichotoma*. The kernels contained 46.1 per cent of oil with the following characteristics: Sp. g. at 15° C. 0.9265; $N_D^{40°}$ 1.4661; Sap. V. 188.6; Iod. No. 133; R.M.V. 0.5; Unsap. 0.82; Acid V. 1.6; Titer 22°.

The kernels from the seeds of the *Manihot piauhyensis* contain 48 per cent of oil, which gave the following characteristics: Sp. g. at 15° C. 0.9225; $N_D^{40°}$ 1.4681; Sap. V. 187.7; Iod. No. 144.4; R.M.V. 0.42; Unsap. 0.78 per cent; Acid V. 1.6; Titer 20°.

It will be observed that both of these oils are similar to that of manihot oil and they could be used for the same purposes.

Mercuriales Seed Oils. These oils are found in the seeds of the plants from species of *Mercurialis* of the *Euphorbiaceae*, found growing in various parts of Europe. The oils from three species have been studied by P. Gillot [*Bull. mat. grasses inst. Colonial Marseille*, **No. 2**, 59-63 (1927)]. The *M. annua*, which is abundantly distributed in Europe, is known in France as the "foirole" and is regarded as a weed, but it is believed to be suitable for cultivation on a large scale for the production of oil. It is an annual and can be grown in temperate climates. On this account, together with the high oil content of the seed, it is considered the most promising of the species described. The weight of 1000 seeds varies from 1.4 to 3 grams and the seeds contain about 38 per cent of oil.

The *M. perennis* produces rhizomes and is long-lived. It grows in cool, shady places. It does not lend itself to extensive cultivation and yields only a small number of seeds. The seeds contain about 26 per cent of oil.

The *M. tomentosa*, which is long-lived and has stiff branches like a shrub, is found only in the region bordering the Mediterranean. The weight of 1000 seeds is from 3 to 6 grams and the oil content is about 36 per cent. The seeds of these 3 species yield yellow odorless oils with a sweet flavor.

The more important characteristics are as follows:

Oil from	Sp. G. at 15° C.	$N_D^{15°}$	Iod. No. (Wijs)	Br. Glycerides (Hehner-Mitchell)
M. annua	0.935 to 0.937	1.4848 to 1.4861	205.9 to 215.5	65 to 80
M. perennis	0.934 to 0.937	1.4846 to 1.4857	203.6 to 203.8	54 to 58
M. tomentosa ..	0.934 to 0.935	1.4840 to 1.4852	201.5 to 208.1	52 to 56

These oils show a marked homogeneity. The extreme values given by the different oils prepared by expression and extraction from 1913 to 1923, scarcely exceed the difference usually found in an oil of a given species, produced under various climatic and soil conditions. These oils are distinguished from most other vegetable oils by their density, indices of refraction, and high iodine numbers.

All these oils were found to "dry" much more rapidly than linseed oil, as expected from their very high iodine numbers. On exposure to the sun, the oil from *M. annua* dried in about 3 hours; in the laboratory it requires from 24 to 26 hours. All the oils give a firm elastic and adherent film, particularly suitable for the manufacture of paints, varnishes, etc.

Another strong drying oil is obtained from the seeds of *Euphorbia esula,* a native of Europe, and this has also been studied by P. Gillot, [*Mat. grasses,* **21,** 8391 (1929)]. The very small seeds contain about 31 per cent of oil, for which the following characteristics are reported: *Expressed Oil:* Sp. g. at 15°/15° C. 0.9385; $N_D^{15°}$ 1.4855; Sap. V. 196.2; Iod. No. (Wijs) 207.2; Acetyl V. 12.5; Unsap. 0.93 per cent; Acid V. 4.4; R.M.V. 3.0; Pol. No. 0.5; Sol. Pt. −30° C.; Insol. bromo-glycerides 52.3 per cent; Crismer (Alco. d. 7967) 64° C. The extracted oil gave similar results.

The oil has a purgative action when taken internally. It will be observed that these figures are closely similar to those for the oils from the mercuriales seeds. The writer has no information at hand regarding either the cultural or harvesting possibilities of this plant, the stem of which appears to lie on the ground.

The plant *Euphorbia platyphylla,* which is common in France, yields seeds which contain 33 per cent of oil. The weight of 1000 seeds is 2.13 grams; a liter 622 grams. Gillot [*Mat. grasses,* **20,** 8110 (1928)] reported the following characteristics: Sp. g. at 15° C. 0.9355; $N_D^{15°}$ 1.4830; Sap. V. 191.1; Iod. No. (Wijs) 211.6; Acetyl V. 6.2; Unsap. 0.72 per cent; Crismer (Alco. d. 7967) 66°; Sol. Pt. −30° C.; Acid V. 1.0; R.M.V. 0.3; Pol. No. 12; Insol.-bromo-glycerides (Hehner-Mitchell) 67.96 per cent. It is a strong drying oil similar to that from *M. annua* and has purgative properties.

Another plant, *Euphorbia amygdaloides,* which grows pretty much all over France, yields seeds which contain from 22 to 30 per cent of oil. The weight of 1000 seeds is 3.7 grams. The plant is found on argillaceous soils in the woods. Gillot [*Mat. grasses,* **19,** 7806 (1927)] examined the oil with the following results: Sp. g. at 15° C. 0.936; $N_D^{15°}$ 1.4836; Sap. V. 194; Iod. No. (Wijs) 192.1; Acetyl V. 5.8; Unsap. 0.88 per cent; Sol. Pt. −30° C.; Crismer (Alco. d. 7967) 64° C.; Insol.-bromo-glycerides (Hehner-Mitchell) 39.66 per cent. The oil, which has excellent drying properties, is similar to that from the seeds of *E. helioscopia.* The oil has a purgative action.

The plant *Euphorbia helioscopia* is a weed found throughout France. The seed pods at maturity burst open and more or less scatter the seeds.

The seeds contain 30 to 33 per cent of oil, which has been examined by Gillot [*Mat. grasses,* **18,** 7503 (1926)] with the following results: Sp. g. at 15°/15° C. 0.9346; $N_D^{15°}$ 1.4847; Sap. V. 191.1; Iod. No. (Wijs) 204.4; Acetyl V. 5.6; Unsap. 0.78 per cent; Insol.-bromo-glycerides (Hehner-Mitchell) 58.4 per cent. The pale yellow oil has strong drying properties. It also has a purgative action. This oil is similar to those from the seeds of *mercurialis* species.

The seeds of the plant *Euphorbia verrucosa* contain about 26 per cent of oil, which has been examined by Gillot [*Mat. grasses,* **20,** 8166 (1928); *Chem. Abs.,* **22,** 2676 (1928)] with the following results: Sp. g. at 15°/15° C. 0.9356; $N_D^{15°}$ 1.4829; Sap. V. 190.4; Iod. No. (Wijs) 209; Acetyl V. 10.4; Unsap. 1.04 per cent; Crismer (Alco. d. 7967) 65° C. The oil has very strong drying properties. For other details the original paper should be consulted.

Another strong drying oil is obtained from the seed of *Euphorbia cyparissias.* The seeds contain over 33 per cent of oil, which has been examined by Gillot [*Mat. grasses,* **19,** 7971 (1927)] with the following results: Sp. g. at 15°/15° C. 0.9396; $N_D^{15°}$ 1.4835; Sap. V. 196; Iod. No. (Wijs) 204.8; Acetyl V. 7.2; Unsap. 0.94 per cent; R.M.V. 3.5; Acid V. 32; Insol.-bromo-glycerides (Hehner-Mitchell) 47.67 per cent. The oil has a purgative action.

The seeds of the plant *Euphorbia paralias,* which is found on the dunes of Pornichet and La Baule in France, contain about 38 per cent of oil. The plant, seeds and oil have been described by Gillot [*Mat. grasses,* **20,** 8307 (1928); *Chem. Abs.,* **23,** 478 (1929)]. The characteristics are as follows: Sp. g. at 15°/15° C. 0.9368; $N_D^{15°}$ 1.4845; Sap. V. 194; Iod. No. (Wijs) 196.3; Acetyl V. 10; Unsap. 1.55 per cent; Acid V. 3.4; Crismer (Alco. d. 0.7967) 62° C.; R.M.V. 2.5; Pol. No. 5; Insol.-bromo-glycerides (Hehner-Mitchell) 43.6 per cent.

The oil is very limpid, without characteristic odor, and has a sweet taste, but like the others, has a purgative action. As would be expected, it has marked drying powers.

The seeds of the small annual plant, *Euphorbia exigua,* of the *Euphorbiaceae,* which is found in France, contain about 34 per cent of oil which has been examined by Gillot [*Bull. Sci. Pharmacol,* **40,** 449 (1933)] with the following results: Sp. g. 15/15° C. 0.9368; $N_D^{15°}$ 1.4858; Sap. V. 191.5; Iod. No. (Wijs) 212.5; Acetyl V. 7.0; Unsap. 0.94 per cent; Insol.-bromo-glycerides 69.9 per cent.

Those interested in the *Euphorbia* species, which have been studied by Gillot, should consult the original references for descriptions of the plants, fruits, and seeds. In view of the fact that quite a number of these species are weeds in France and other parts of Europe, a careful investigation of these plants is desirable, before a decision is made in regard to their possible introduction into other countries for the purpose of cultivating them on a commercial scale for the production of oil.

Manketti Nut Oil. This oil is found in the kernels of the nuts from the tree *Ricinodendron rautanenii,* of the *Euphorbiaceae,* native to

Southwest Africa. According to the examination made at the Imperial Institute [*Bull. Imp. Inst.*, **15**, 35 (1917)] the fruits consisted of 13 per cent of husk, 20 of mesocarp, and 67 of nuts, of which the hard, thick shell amounted to about half the weight of the fruit, and the kernels to 10 per cent. The fruits weigh from 7.5 to 10 grams. The kernels, which weigh about 0.7 gram, contain from 50 to 57 per cent of a bright yellow oil with a pleasant odor and taste. Although the oil is edible and can be used for making soap and paint, the difficulty of extracting the kernels and the small proportion of kernels is a serious obstacle which has so far prevented the preparation of the oil on a commercial scale. The press cake is said to be unsuitable for feeding purposes. The oil has been examined by various investigators and the range of the characteristics found is as follows: Sp. g. at 15° C. 0.929 to 0.931; $N_D^{40°}$ 1.4807; Sap. V. 191.5 to 195; Iod. No. 129 to 137; R.M.V. 0.8 to 1.2; Pol. No. 0.4 to 0.6; Unsap. 0.85 per cent; Titer 35° to 39° C.; no hexabromides.

Nsa-sana (Essang) Oil. This oil is found in the seeds from the tree *Ricinodendron africanum* (*heudoletii*) of the *Euphorbiaceae*. The tree, which varies from 30 to 70 feet in height, is found in the Congo, Nigeria, the Spanish island Fernando-Po in the Gulf of Guinea, and possibly elsewhere. The hard, thick shell nuts, which weigh about 2 grams, contain from 25 to about 30 per cent of kernels. The oil content of the kernels ranges from about 40 to 49 per cent.

The characteristics of the oil are as follows: Sp. g. at 15° C. 0.934 to 0.937, at 20° 0.932 to 0.935; $N_D^{19.5°}$ 1.5026; Sap. V. 184 to 194; Iod. No. 146 to 148; Titer 34.5 to 35.7° C.

A. Steger and J. van Loon [*Rec. trav. chim.*, **54**, 988 (1935)] examined a sample of solvent-extracted oil which gave the following characteristics: $N_D^{25°}$ 1.5054; Sap. V. 193.2; Iod. No. (Wijs), 240 hrs. 192; SCN V. (48 hrs.) 86.6; R.M.V. 0.4; Acid V. 0.0, Unsap. 0.5%; volatile 1.2%. The investigators reported that the oil contained the following percentages of acids: Saturated 9.7, oleic 16.0, linoleic 11.0, linolenic 10.0 and elaeostearic 46.0. L. J. N. van der Hulst, by means of absorption spectra measurements, estimated that the oil contained 51 per cent of elaeostearic acid as glyceride.

Exposure to direct sunlight, or heating the oil with traces of iodine or sulfur, causes it to solidify gradually. As in the case of tung oil, this solidification is due to the formation of β-elaeostearic acid from the much lower-melting α form.

It is reported that after the oil is heated for one hour at 280° C. in an atmosphere of carbon dioxide, it will give a hard, transparent, water-resistant film.

Apparently, the only use made of this oil, which is prepared locally in very small quantities, is reported to be for edible purposes by the natives. Whether or not it would be possible to produce the oil on a commercial scale for technical purposes remains to be determined.

N'Gart Oil. This oil is obtained from the kernels of the fruit of the climbing plant, *Plukenetia conophora*, which is cultivated in some

parts of the Cameroons by the natives, who extract the oil and use it for edible purposes. The fruit, which is about the size of a walnut, contains a thin-shelled seed or "nut" in which is a round kernel weighing 4 or 5 grams. The kernels contain from about 50 to 60 per cent of a pale yellow oil having a taste similar to that of linseed oil. The oil has been examined by Krause and Diesselhorst [*Chem. Rev. Fett. Hartz, Ind.*, **16,** 200 (1909)], Lewkowitsch [*J. Soc. Chem. Ind.*, **31,** 545 (1912)], P. Mühle and A. Hämmelman [*Farben Ztg.*, **18,** 2175 (1913)].

The range of the characteristics is as follows: Sp. g. at 15.5° C. 0.936 to 0.939, at 17.5° C. 0.9354; $N_D^{15°}$ 1.4835, at 17.5° C. 1.4830, at 40° C. 1.474 to 1.4753; Sap. V. 190 to 192; Iod. No. (Wijs) 198 to 204; (Hübl-Walker) 195; Unsap. 0.2 per cent; Titer 24° to 25° C.; Sol. Pt. −16° to −20° C.; Hexabromides 47.7 per cent.

When the oil is heated to 300° to 310° C. for 6 hours, it polymerizes to a solid, rubber-like mass (*cf.* tung, sterculia, safflower oils). The oil is said to dry more quickly than linseed oil, if the free fatty acids are previously removed. Krause and Diesselhorst *(loc. cit.)* heated the oil with 3 per cent of lead-manganese drier, and a film dried completely in 18 hours.

Niger Seed Oil. This oil is obtained from the shiny black achenes, commonly known as seeds, of the plant *Guizota abyssinica* of the *Compositae* family, indigenous to various parts of tropical Africa. It has been cultivated for many years in East Africa, India and elsewhere. The weight of the so-called seeds averages 0.035 gram and the seeds contain from 38 to 50 per cent of oil. In Europe and India, it is customary to make two pressings of the seed, one cold and the other hot. Smetham [*Analyst,* **35,** 54 (1910)] examined a sample of press cake with the following results: Moisture 8.9, oil 14.0, crude protein 34.0, crude fiber 9.3, carbohydrates 21.8, and ash 11.95 per cent. The cake may be used as a food for stock or as a fertilizer.

The oil has been examined by Crossley and Le Sueur [*J. Soc. Chem. Ind.*, **17,** 992 (1898)], Utz [*Chem. Rev. Fett. Hartz, Ind.*, **18,** 106 (1911)], and other investigators. The characteristics of this oil are as follows: Sp. g. at 15° C. 0.924 to 0.927; $N_D^{15°}$ 1.4708, at 40° C. 1.4670 to 1.4689; Sap. V. 189 to 193; Iod. No. 126 to 134; R.M.V. 0.1 to 0.6; Unsap. 0.5 to 1.2 per cent; Sol. Pt. −6° to −8° C. Vuablart [*J. Soc. Chem. Ind.*, **30,** 965 (1911)] states that the oil gives but very little ether-insoluble bromides.

D. L. Sahasprabuddhe and N. P. Kale [*J. Univ. Bombay,* **1,** Pt. 2, 37 (1932); *Chem. Absts.*, **27,** 2054 (1933)] examined a sample of the oil, which gave an iodine number of 126.4. They reported that the mixed fatty acids contained the following percentages of constituents: Oleic 31.0, linoleic 54.3, lauric and myristic 3.3, palmitic 8.4, stearic 4.9 and arachidic 0.5. These figures total over 102.

N. L. Vidyarthi and M. V. Mallya [*J. Ind. Chem. Soc.*, **17,** 87 (1940)] made an extensive investigation of an oil which gave the following characteristics: $N_D^{25°}$ 1.472; Sap. V. 189.7; Iod. No. 129.2; Acid V.

8.5; Unsap. 3.65 per cent. The mixed fatty acids contained the following percentages of constituents: Capric, caprylic, lauric and myristic acids 1.7, palmitic 5, stearic 2, arachidic, behenic and lignoceric 0.2, oleic 38.9, and linoleic 51.6. Percentages of glycerides in the oil were reported as follows: tri-linolein 2, oleo-di-linolein 40, di-oleo-linolein 30, myristo-di-linolein 2, palmito-di-linolein 6, palmito-oleo-linolein 11, stearo-di-linolein 2, and stearo-oleo-linolein 4. The myristo glycerides include those of capric, caprylic, and lauric acids, whereas the stearo-glycerides include those of arachidic, behenic, and lignoceric acids, the total of which amount to less than one per cent.

The oil has little odor and a pleasant nutty taste. The cold-pressed oil is used for edible purposes as is the refined, hot-pressed oil. It is also used for making soap, as an illuminant, and sometimes as an adulterant of rape oil. The addition of appreciable quantities of niger seed oil may be detected by the increase of the iodine number over that for rape oil, but there is no specific test known for the oil.

E. Stock [*Farben Ztg.*, **40**, 476 (1935); *Brit. Chem. Abs.*, B **1935**, 732] prepared varnishes using boiled and stand oils made from niger seed oil which gave an iodine number of 138.9, an acid value of 5.8 and contained 0.5 per cent of unsaponifiable matter. From experiments made with the varnishes, it was concluded that the oil could be used as a drying oil.

Osage Orange Seed Oil. This oil is found in the seeds from the fruit of the tree *Toxylon pomiferum*, native to the United States. The seeds contain from 40 to 42 per cent of oil, which has been examined by J. C. McHargue [*Ind. Eng. Chem.*, **7**, 612 (1915)] with the following results: Sp. g. at 15° C. 0.929; Sap. V. 192; Iod. No. 134 to 136. This oil is not a commercial product.

Oiticica Oil. This oil is found in the seeds of the large tree *Licania rigida* belonging to the *Rosaceae*. In many instances, the older literature and works dealing with oiticica oil stated that it came from the seeds of *Couepia grandiflora, Moquilea tomentosa,* or that it was obtained from various other trees.

The *Licania rigida,* native to northwestern Brazil, is found chiefly in the states of Bahia, Ceara, Parahyba, Piauhy, and Rio Grande do Norte. Depending upon the locality, they vary in height from 40 to about 100 feet. During August they blossom and harvesting of the fruit begins in December. The matured fruit consists of a thin, friable husk or shell in which is inclosed a single reddish-brown seed, or kernel, one to two inches long and from 0.5 to 0.8 inch in diameter. The kernels, which constitute 60-70 per cent of the fruit, vary in weight from 2 to 8 grams, the average being about 3.5 grams. Their oil content ranges from 55 to 62 per cent.

Characteristics of Oiticica Oil. Sp. g. 15°/15° C. 0.9630 to 0.9697; $N_D^{25°}$ 1.5130 to 1.5158, at 40° 1.5070 to 1.5140; Sap. V. 186 to 195; Iod. No. (Wijs) 140 to 152; R.M.V. 0.56; Unsap. 0.4 to 0.9 per cent;

SCN. V. 75 to 80; Sat. acids 10.7 to 11.6 per cent; Unsat. acids 82.4 to 84.1 per cent; Titer 44.8 to 47.4°. Browne heat (gel) test at 280°–300° 18–24 minutes.

A much greater variation of the characteristics will be found in the recorded values of the older literature than those given here. This is partly because of the methods used, but not infrequently it is caused by the great differences in the quality of the samples of oil under examination. Iodine numbers determined by the Hanus or Hübl methods, with few exceptions, are very much higher than those with the Wijs reagent. Slight variations in the weight of the oil taken in the case of the Hanus reaction caused marked differences in the results obtained [R. S. McKinney and G. S. Jamieson, *Oil and Soap,* **13,** 10 (1936)].

It should be noted that the heat-treated liquid form of oiticica oil on the market generally gives a Browne heat test within 16 minutes or less.

Raw oiticica oil, upon standing a short time after expression at ordinary temperatures, is either in the form of a soft, cream-colored fat or partially liquid. Heating it at 220–225° C. for about an hour renders the oil permanently liquid, if kept under suitable storage conditions.

Composition of Oiticica Oil. McKinney and Jamieson [*Oil and Soap,* **13,** 10 (1936)] examined a sample of untreated expressed oil having the following characteristics: $N_D^{25°}$ 1.5145; Sap. V. 192.0; SCN V. 76.2; Unsap. 0.57%. The calculated iodine number was 218. It was found to contain the following percentages of acids: Saturated 10.7, oleic 5.9 and licanic 78.2. Linoleic acid was not detected in this oil.

R. S. Morrell and W. Davis [*J. Oil Col. Chem. Assoc.,* **19,** 359 (1936)] concluded from their investigation that the oil contains at least 4.7 per cent of elaeostearic acid. The figures (78.2%) for licanic acid given above include any elaeostearic acid present in the oil.

A. Machado [*Rev. Soc. Brazil Quim.,* **7,** 73 (1938); *Chem. Abs.,* **32,** 8803] reported the following percentages of acids in the oil: Licanic (couepic) 75.4, oleic 4.2, palmitic 6.1, stearic 5.2, and 2.4 of hydroxy acids. Evidently, no attempt was made to determine the elaeostearic acid. It was stated that the oil gave an iodine number of 152.4, a saponification value of 187.7, and a refractive index of 1.5158.

W. B. Brown and E. H. Farmer [*Biochem. J.,* **29,** 631 (1935)] were the first to show that the triply unsaturated licanic acid was a keto-octadecatrienoic acid. Previously F. Wilborn and A. Lowa [*Farben Ztg.,* **35,** 388 (1929)] and some later investigators considered that it was probably an isomer of elaeostearic acid.

Properties of Oiticica Oil. Exposure to air causes this strong drying oil to undergo oxidation. Direct sunlight quickly transforms the alpha-licanic acid into the much higher-melting beta form. This results in the complete solidification of the oil. Tung, Japanese tung, and bagilumbang *(Aleurites trisperma)* oils behave in the same manner. A similar property is the formation of a wrinkled film by the raw untreated oil when exposed in the customary manner. Although in physical charac-

teristics and behavior the oil resembles tung oil, experience has shown that in making varnishes, for example, it cannot in all cases be treated in the same manner. Consequently, it was only through much study and experimentation that ways were discovered by which satisfactory products could be made with oiticica oil. Varnishes made with the oil are reported to give films about as hard as those of tung oil varnish, but upon aging, they have a greater tendency to become brittle, besides being somewhat less waterproof. However, they are distinctly more gasproof. Much use has already been found for this valuable drying oil and more can be expected as its properties become better understood by manufacturers. For varnish and other protective coatings, it may be used alone or along with other drying oils.

In the 72-page illustrated Circular No. 470 (Nat. Pt., Var. Lac. Mfrs. Assoc., 1934), by H. A. Gardner, will be found the history of the earlier and later attempts, which finally resulted in the establishment of the oiticica oil industry in Brazil, which since that time has continued to progress. It includes also much other information of interest about the tree and the oil and numerous abstracts of papers dealing with the characteristics and composition of the oil, as well as an article by J. B. de M. Carvalho, Rio de Janeiro.

By 1940, there were 19 oil mills in northeast Brazil having a capacity for handling over 78,000 metric tons of oiticica seed a year, producing about 25,000 metric tons of oil. Fourteen of these oil mills are in the state of Ceara, 3 in Paraiba, and 2 in Rio Grande do Norte. Two mills solvent-extract the oil, and the others express it either by hydraulic or expeller presses. A selected list of the later references includes:

"Brazilian Oiticica Oil," R. Lude, *Fettchem. Umschau.*, **42**, 4 (1935).

"Oiticica Fat and Its Fundamental Difference from Tung Oil," C. P. A. Kappelmeier, *Fettchem. Umschau*, **42**, 145 (1935).

"Oiticica Oil," Anon., *Paint Manufacture*, **6**, 116 (1936).

"Oiticica Oil," E. Stock, *Farben Chem.*, **7**, 45 (1936). Discusses the manufacture of stand oil and varnish.

"Oiticica Oil: A New Product from Brazil," M. E. Marvin, *Drugs, Oils and Pts.*, **51**, 520 (1936). Also see C. P. Holdt, *ibid.*, p. 64.

"Composition of Oiticica Oil," H. P. Kaufmann and J. Baltes, *Ber.*, **69**, 2679 (1936),

"Identity of the Oiticica Tree and Uniformity of the Oil," C. P. Holdt, *Drugs, Oils and Paints*, **52**, 316 (1937).

"Oiticica Oil: Preparation of Stand Oil," Anon., *Oil and Col. Trds. J.*, **92**, 828 (1937). Also gives formulas for several varnishes.

"Cicoil," C. P. Holdt, *Drugs, Oils and Pts.*, **54**, 86 (1939).

"The Story of Oiticica Oil," *Drugs, Oils and Pts.*, **54**, 310 (1939).

"Laboratory-Controlled Uniform Quality Raw Liquid Oiticica Oil," C. P. Holdt, *Am. Pt. J.*, **23**, No. 22, 50 (1939).

"Continuous Laboratory Method for Bodying Oiticica Oil," V. Marchese, J. Mattiello and L. T. Work, *Pt. Ind. Mag.*, **55**, No. 4, 122 (1940).

"Behavior of Oil-Resin Combinations," *Oil, Pt. and Drug Reptr.*, **138**, No. 19, 50 (1940).

"Drying Oils, etc.," G. Eisenschiml, *Pt., Oil and Chem. Rev.*, **103**, No. 8, 32, (1941). Discusses facts about use of oiticica oil.

Perilla Oil. This oil is obtained from the seeds of the annual *Perilla frutescens (ocymoides)* and *P. frutescens nankinensis* of the

Labiatae family, which are cultivated in northern India, Japan, Chosen (Korea), Manchukuo (Manchuria), and elsewhere, in smaller quantities. The oil of commerce appears to be chiefly obtained from the seeds of *P. frutescens.* In Japan the average yield of seed is reported to be about 560 pounds of seed per acre, but yields up to 1,500 pounds have been obtained. Seed of good quality *(P. frutescens)* weigh about 37 pounds per bushel. Considerable information on the cultivation and production of the seed in Manchukuo, Chosen and Japan, as well as statistical data on temperatures and rainfall during the growing season, areas planted, yields and exports of seed will be found in the (*Nat. Pt. Var. and Lacquer Mfrs. Assoc. Circ.* **524** 1937) by H. A. Gardner.

Experiments on the cultivation of the seed have been made in the East African Protectorate, South Africa, Cyprus, and Rhodesia [*Bull. Imp. Inst.,* **24,** 205 (1926)], but as yet no perilla industry has been established in these regions nor in the United States, where similar experiments have been made (*Am. Pt. and Var. Mfrs. Assoc. Circs.* **52, 257, 506, 565** and **571**). One of the several difficulties encountered in connection with the cultivation of this crop is that of harvesting the seed before they fall to the ground, which occurs quickly after maturity is reached. Also, it should be noted that the seed do not all mature at one time. In many of the localities in this country where experimental plantings were first made, the plants for one reason or another failed to mature the seed, and in some instances, they did not even blossom before killing frosts arrived. It still remains to be determined whether or not it is feasible to produce this crop here on a commercial scale.

The average oil content of commercial perilla seed is about 38 per cent. Seed from different sources vary in oil content from about 30 to about 51 per cent.

Characteristics: Sp. g. at 15° C. 0.930 to 0.937; $N_D^{15°}$ 1.4826 to 1.4856, at 20° 1.4830 to 1.4841, at 25° 1.4800 to 1.4820, at 40° 1.4735 to 1.4785; Sap. V. 188 to 197; Iod. No. 185 to 208; Unsap. 0.6 to 1.3 per cent; Hexabromides (Eibner-Muggenthaler) 45 to 54 per cent. C. A. Lathrop [*Ind. Eng. Chem.,* **24,** 826 (1932)] gives data on density, refractive index, acid value, saponification, and the iodine number by both the Wijs and Hanus methods for three samples each of Manchukuo and Chosen oils. The average difference between the results with the Wijs and Hanus methods was 5.9; the smallest, 4.4.

Composition. The most extensive investigation of the composition of the oil was that made by H. P. Kaufmann [*Allgem. Öl Fettzeit.,* **27,** 39 (1930); *Chem. Abs.,* **24,** 2000 (1930)]. He examined two samples of oil and reported the following percentages of acids: Saturated 6.3 and 7.2, oleic 3.7 and 10.1, linoleic 41.9 and 31.9, linolenic 41.7 and 46.4. The iodine number of the oils was 204 and they contained about 0.7 per cent of unsaponifiable matter.

The American Society for Testing Materials specifications for raw perilla oil are as follows:

	Maximum	Minimum
Foots, %	2.5	...
Loss on heating 105-110° C., %	0.2	...
Specific gravity 15.5°/15.5° C.	...	0.932
Acid number	5.0	...
Iodine number (Hanus)	...	191.
Unsaponifiable matter, %	1 5	...

The British Standard Specification (No. 654–1936) is as follows:

	Maximum	Minimum
Moisture, %	0.2	...
Specific gravity 15.5°/15.5° C.	0.936	0.932
Refractive index at 20° C.	1.484	1.481
Iodine number (Wijs)	...	193.0
Acidity, as oleic acid, %	3.0	...
Unsaponifiable matter, %	1.5	...

Color. Not darker than a freshly prepared solution of $1.0_g K_2Cr_2O_7$ in 100 ml. of pure H_2SO_4 (sp. g. 1.84).

The oil shall be the product obtained by expression or extraction and shall be free from admixture with other oils or fats. The oil, when kept at a temperature of 15° to 20° C. for a period of 24 hours, shall be clear, free from sediment or other insoluble matter.

Properties. Perilla oil somewhat resembles linseed oil in odor and taste. The crude oil is usually deep yellow or greenish. Most samples, when spread on a smooth surface, creep and form drops and streaks while drying. This tendency, which appears to be due to the high surface tension of the oil, is overcome by heating it for several hours at about 250° C. or converting it into boiled, blown or polymerized oil and by mixing the raw oil with linseed or other drying oil. Perilla oil upon drying produces a hard, brilliant, tough waterproof film. The dried film is considerably harder than that of linseed oil. The films from raw or bodied perilla oil discolor more upon aging than those of linseed oil. M. Toch [*J. Oil Col. Chem. Assoc.*, **9**, 309 (1926); with T. T. Long, *Ind. Eng. Chem.*, **18**, 1285 (1926)] states that the oil polymerizes when heated above 260° C., and in factory practice the volatile matter amounts to about 5 per cent by volume of the oil treated. Perilla does not polymerize at as low a temperature as linseed. When heated to about 300° C., polymerization proceeds rapidly, with an increase in gravity and refractive index, and a marked reduction in the iodine value. Toch gradually heated 100 gallons of the oil in a Monel metal kettle to almost 305° C. and maintained that temperature for 4 hours. The gravity increased from 0.9316 to 0.9711 and the refractive index at 25° C. from 1.480 to 1.4915, while the acid value increased from 0.85 to 10.37. The iodine number (Wijs) decreased from 204 to 140. Gardner (*Am. Pt. and Var. Mfrs. Assoc. Circ.* **106**) heated a sample of raw perilla oil quickly to 310° C. with no apparent change except a slight darkening in color. The oil showed no break or turbidity, which is one of its characteristics. Further heating (325° to 350° C.) caused the oil to become very dark (the presence of drier causes even more pronounced darkening).

When Gardner passed air through the oil heated to about 250° F. a clear, light-colored bodied product was obtained; but in the presence of a drier the oil becomes dark in color. In most instances, the blown samples had better drying properties than the raw oil. The blown oil is noted for its rapid drying and the hardness of the resulting film. When used in paints and varnishes, the films are reported to be more resistant to weathering than those made from linseed oil. In connection with the use of the oil for paint and varnish, cobalt driers and manganese resinate appear to give the best results.

Uses. The countries in Asia which produce perilla seed use the oil both for edible and technical purposes. There it has long been used in waterproofing paper, etc., and in making the cheaper grades of lacquer varnishes. In America and Europe the oil is used in the manufacture of paints, varnishes and printers' ink. In this country the oil is mixed with soybean oil, and after suitable heat treatment, is used for making varnish and other protective coatings.

Attention is called to the following references:

"Polymerization of Perilla Oil," K. H. Bauer and F. Hugel, *Chem. Umschau*, **32**, 13 (1925).

"Influence of Agronomic Factors on the Cultivation of Perilla," E. Lynbarskii, M. Z. Delo, No. 11, 63 (1932); *Chem. Abs.*, **28**, 4927 (1934).

"Final Ripening and Harvesting for *Perilla ocymoides*," M. S. Dumin, N. S. Torman, R. M. Erastova and E. A. Buikova, *Chem. Abs.*, **30**, 7887 (1936).

"Perilla Oil: Assuming Leadership Based on its Special Features," O. Eisenschiml, *Am. Paint J.*, **20**, 16 (1935).

"Perilla: Manchuria, Foreign Crops and Markets," **33**, 145 (1936).

"Perilla Oil," J. van Loon, *Verfkronick*, **9**, 64 (1936).

"Perilla Oil," C. W. A. Mundy, *Oil Col. Trdes. J.*, **91**, 917 (1937).

"Perilla Seeds: Harvesting in China, Foodstuffs Around the World," **3**, No. 24, 3 (1939).

"Safety Precautions to Observe When Preparing Stand Oil from Perilla," K. Bauer, *Farben Ztg.*, **43**, 1252 (1938).

"Production of Stand Oil from Perilla Oil," W. Meyer, *Farben-Chem.*, **10**, 54 (1939).

"Heat Processing of Perilla Oil to Produce Stand Oil," W. Meyer, *Farben-Chem.*, **10**, 54 (1939); *Chem. Abs.*, **33**, 9015 (1939). Discusses fire risks and precautions to be taken.

"Tung, Oiticica and Their Mixtures with Perilla Oil," H. Kemner, *Farbe u. Lack*, **1939**, 171; *Chem. Abs.*, **33**, 9015 (1939), shows that from 30 to 50 per cent of these oils could be replaced by perilla oil without impairing water resistance of varnish films.

Poli Oil. This oil is obtained from the seeds of the plant *Carthamus oryacantha*, which is found in northwest India. Barnes and Single [*Analyst*, **41**, 72 (1916)] found the following characteristics: Sp. g. at 15.5° C. 0.927; $N_D^{40°}$ 1.4755; Sap. V. 174.2; Iod. No. 167.4; R.M.V. 0.6.

Crossley and Le Sueur [*J. Soc. Chem. Ind.*, **991** (1898)] obtained a saponification value of 189.4 and an iodine number of 135.5. It would appear that there is need for further examination of this oil.

The oil is used locally by the natives for edible purposes. It is stated that the plant is a troublesome weed in India, and this should be carefully considered before introducing it into other countries.

Pimento Seed Oil. This oil is obtained from the seed of the pimento, a cultural variety of *Capsicum annuum*. The seeds contain

about 18 per cent of oil. Large quantities of the seed are separated at the canning factories and a sizable sample of the oil pressed from a 70-ton lot of seed from Griffin, Ga., was examined by H. C. Ebert and H. S. Bailey [*Cotton Oil Press,* **7**, No. 12, 35 (1924)] with the following results: Sp. g. at 20° C. 0.9228; $N_D^{20°}$ 1.4750; Sap. V. 171.4; Iod. No. (Wijs) 134.4; Titer 21.2° C.; Sat. Acids 12.6 per cent; Unsat. Acids 82.9 per cent. These results were determined on the refined oil. Both the crude oil and that refined by caustic soda are red. It is readily bleached by the customary treatment with fuller's earth. It is believed that the oil from sound seed, after suitable refining, would be suitable for edible purposes. The crude oil would yield a red-colored soap.

Pomegranate Seed Oil. This oil is found in the seeds from the fruit of the tree *Punica granatum* belonging to the *Punicaceae*. The seeds contain about 7 per cent of oil. Apparently, the characteristics of the oil (if determined) have not been published. Y. Toyama and T. Tsuchiya [*J. Soc. Chem. Ind., (Japan),* **38**, 182B (1935)] isolated an acid (Punicic) from the oil which is a stereoisomer of elaeostearic acid. This has been confirmed by E. H. Farmer and F. A. van den Heuvel (*J. Chem. Soc.* **1936**, 1809) who reported that the acid melted at 44° C., as did that isolated by the previous investigators.

Poppy Seed Oil. This oil is obtained from the seed of various varieties of the plant *Papaver somniferum,* which has been cultivated for centuries in Europe, China, India, Asia Minor, Egypt, and elsewhere. The seeds, which are white, brown, bluish gray or bluish black, contain from about 44 to over 50 per cent of oil. The white seeds are considered to yield the finest oil. It is customary to make a cold pressing, then a hot pressing. The press cake, which is rich in proteins, is used as a feed for stock. Considerable quantities of the oil are expressed in France and Germany. The cold-pressed oil from sound seed varies from pale to golden yellow, and it is used chiefly for edible purposes, but some is used in making artists' paint, etc. [*cf.* Eibner and Wibelitz, *Chem. Abs.,* **18**, 3728 (1924)]. The hot-pressed oil could be refined and used for edible purposes, but it is largely used for making soap.

The usual range of the characteristics are as follows: Sp. g. at 15° C. 0.924 to 0.927; $N_D^{20°}$ 1.4751, at 40° C. 1.467 to 1.470; Sap. V. 189 to 196; Iod. No. 132 to 140; Unsap. 0.5 per cent; Sol. Pt. −15° to −20° C.; Titer 16° to 19° C. The oil gives no ether-insoluble hexabromides. The oil usually contains less than 7 per cent of saturated acids, which probably consist chiefly of palmitic and stearic acids. The unsaturated acids probably consist of oleic and linoleic acids, as the oil gives no insoluble hexabromides.

Eibner and Wibelitz (*loc. cit.*) reported that the oil examined by them contained 28.3 per cent of oleic acid, 29.5 of α-linoleic, 29 of β-linoleic, and 7.2 per cent of saturated acids.

There is no characteristic test for this oil. Sometimes it is adulterated with cheaper oils, such as peanut, sesame, etc. Quite often, however, poppy seed oil contains very small quantities of sesame oil from being pressed in oil mills which have previously pressed sesame

seed. This should be taken into account when positive Baudouin or Villa Vecchia tests are obtained (because they are obtained when an oil contains a per cent or less of sesame oil).

Po-Yoak (or Yok) Seed Oil. This oil is found in the seeds from the fruit of the West African tree *Afrolicana elaeosperma,* belonging to the *Rosaceae.* This tree was formerly believed to be a Parinarium species because its fruits closely resembled those of certain Parinarium trees [*Bull. Imp. Inst.,* **33,** 271 (1935)]. The tree is common at Grand Bassa, Liberia and is found also in the French Cameroons, Nigeria, and Bonthe Island, Sierra Leone. Culture experiments made on Bonthe Island have shown that the growth of the tree is slow. Those 5 years old were only 8 feet high and had not fruited.

The warty, ovoid, one-seeded fruits vary in weight from about 7 to about 11 grams. On the outside of the thin shells is a tough layer about one millimeter thick which usually decays in a short time after the fruits fall to the ground. The kernels, which amount to from 61 to 69 per cent of the fruit, contain 55 to 58 per cent of a viscous, golden-yellow oil. The moisture content of the kernels ranges from 6 to 9 per cent. The range of characteristics of the oil is as follows: Sp. g. at 15/15° C. 0.9535 to 0.9690; $N_D^{40°}$ 1.5020 to 1.5110; Sap. V. 188 to 192.3; Iod. No. (Wijs, 3 hrs.) 139.9 to 150.9, Hübl (17 hrs.) 156.9 to 157.1: Unsap. 0.3 to 1.0 per cent. Some samples formed a gel when heated to and held at 300° C. for 16 to 20 minutes, whereas others held at this temperature for 30 minutes did not solidify. This difference in behavior still remains unexplained.

A. Steger and J. van Loon [*Rec. trav. chim.,* **57,** 620 (1938)] extracted with petroleum ether 40.6 per cent of oil from the kernels and 3.6 more using ethyl ether. The oil gave the following characteristics: Sp. g. 78°/4° C. 0.9250; $N_D^{18°}$ 1.5209; Sap. V. 192; Iod. No. (Wijs 1 hr.) 160; SCN V. (6 hrs.) 76.2; R.M.V. 0.43; Acid V. 1.35; Unsap. 0.58 per cent.

It was found to contain 3 parts of licanic (couepic) acid to 2 parts of elaeostearic acid, 9 to 10 per cent of oleic and 11.8 per cent of saturated acids. They stated that exposure to light caused the oil to solidify, but that solidification took place much quicker in the presence of a trace of sulfur or iodine. For other details, the original paper should be consulted.

This strong drying oil is not produced commercially.

Akaritton Oil. This oil is found in the seeds from the fruit of the tree *Parinarium laurinum* which belongs to the *Rosaceae.* The tree is found in Samoa, Pellew, and the western Caroline Islands.

M. Tsujimoto and H. Kayanagi [*J. Soc. Chem. Ind. (Japan),* **36,** 110B (1933); *Chem. Abs.,* **27,** 3099 (1933)] examined the kernels from the pits of fruit from Pellew Island. They varied in weight from 57 to 68 grams and contained 15 per cent of oil and 45 of moisture. The oil gave the following characteristics: Sp. g. at 50° V. 0.9370; $N_D^{50°}$ 1.5610; Sap. V. 186.8; Iod. No. (Wijs) 214.1; Acid V. 1.31; Unsap. 1.15

per cent; M. Pt. 49–50° C. From the oil, they isolated an unsaturated acid which melted at 83-84°. By treatment with a trace of iodine and exposure to direct sunlight, the acid was changed into a form which melted at 95–96° C. As hydrogenation converted it into stearic acid, these investigators believed that the acid was isomeric with elaeostearic acid, but after making ozone oxidation experiments [*ibid.*, **36**, 673B (1934)] they concluded that the acid was probably identical with the licanic acid of oiticica oil. E. H. Farmer and E. Sunderland (*J. Chem. Soc.*, **1935**, 759) found that this acid, which they separated and purified, melted at 83.5° C., contained 4 double bonds and had the formula $C_{18}H_{28}O_2$. Kaufmann, Baltes and Funks [*Fette u. Seifen*, **45**, 302 (1938)] named it Parinaric acid. They isolated the acid and after making absorption spectra measurements, concluded that it contained 4 conjugated double bonds.

Farmer and Sunderland found that their sample of kernels contained about 44 per cent of a butter-like fat, which gave a refractive index of 1.5565 at 25° C.

Neou Oil. This oil is found in the seed of the fruit from the tree *Parinarium macrophyllum*, which belongs to the *Rosaceae*. The tree is found in Gambia, Gold Coast, northern Nigeria, Senegal, and Sierra Leone. The fruit, known as the gingerbread plum, is a drupe. The pit, which is called a nut, varies in weight from 7 to 22 grams. It has a very hard shell, inside of which are one or two kernels imbedded in a soft, light-brown fibrous mass. The kernels, which amount to from 6 to 15 per cent of the nut, contain from about 60 to 70 per cent of oil.

A. Steger and J. van Loon [*Rec. trav. chim.*, **53**, 197 (1934)] examined the nuts (and oil) which were obtained from Sierra Leone. The kernels, which amounted to 9 per cent of the nuts, contained 65.2 per cent of oil. The extracted oil gave the following characteristics: $N_D^{70°}$ 1.4741; Sap. V. 190; Iod. No. (Wijs 2 hrs.) 135; SCN V. 78.3; R.M.V. 0.33; Acid V. 0.25; Unsap. 0.9 per cent. Calculations indicated that the oil contained the following percentages of acids: Oleic 21, linoleic 32, an isomer of elaeostearic 30, and saturated acids 10.3. However, W. B. Brown and E. H. Farmer [*J. Chem. Soc.* **1935**, (761)] have shown that the acid is α-elaeostearic and that no isomeric acid is present in the freshly extracted oil. They concluded that the oil investigated by Steger and van Loon contained a notable quantity of α acid which had changed to the much higher-melting β form, and that this was the reason the previous investigators had believed that the acid was probably identical with couepic (licanic) acid.

The commercial production of the oil does not appear feasible on account of the great difficulty of cracking the nuts and the small proportion of kernels to be obtained from them.

Castanha de Cotia Kernel Oil. K. A. Pelikan and J. F. Gerkens [*Oil and Soap*, **16**, 11 (1939)] have examined the nuts, kernels, and oil. The nuts, which came from Brazil, were 3 to 4 inches long and from 2 to 2.5 inches in diameter. They are probably from a tree belonging to the genus *Parinarium* of the *Rosaceae* family. Each nut contains

a single kernel, about the size of that of a Brazil nut. The nut consists of 23 per cent of kernel and 77 of shell, which is both hard and tough. The kernels contained 1.75 per cent of moisture and 74.2 of oil. The extracted oil gave the following characteristics: Sap. V. 194.2; Iod. No. (Hanus, 1 hr.) 153.5; Acid V. 0.72; Diene V. 33.5 and 33.9; Unsap. 0.54 per cent; Hexabromides 0.0; Browne Heat Test, no gelation after 1.5 hours. Exposure to direct sunlight for several days caused the oil to solidify gradually to a white mass. Boron fluoride ethyl ester caused a rapid solidification of the oil. It is probable that the oil contains either elaeostearic or a related acid; this can be determined only by further investigation.

Rabbits Fruit (Nut) Oil is obtained from the nuts of a small tree (a *Heistera* species) which grows in quantity on the foothills of the Cordilleras in the Magdalena Valley [*Bull. Imp. Inst.*, **20**, 150 (1922)]. The nuts, which weigh from 10 to 12 grams, consist of 66 per cent of kernel and 34 of shell. The kernels contain about 60 to 62 per cent of viscous oil, which was examined at the Imperial Institute with the following results: Sp. g. 15/°15° C. 0.9940; $N_D^{40°}$ 1.502; Iod. No. 140; Sap. V. 187.8; Acetyl V. 128; Unsap. 2.1 per cent; R.M.V. 0.2; Pol. No. 0; Acid V. 4.2.

Although the oil has a high iodine number, it was found that even when treated with litharge, it did not dry after standing 2 weeks. Heating the oil for 4 hours at 200° C. gave a product resembling somewhat polymerized tung oil. Whether or not this oil would be suitable for any technical purpose remains to be determined. The high acetyl value would indicate the presence of a considerable quantity of hydroxy fatty acids.

Para Rubber Seed Oil. This oil is obtained from the seed of the tree *Hevea brasiliensis* of the *Euphorbiaceae,* native to Brazil, which is now extensively cultivated in many tropical regions, including Borneo, Ceylon, the Malay States, Sumatra, etc. The seeds usually weigh from about 2 to 4 grams. The kernel, which amounts to about 50 per cent of the seed, contains from 42 to 50 per cent of oil, an active lipolytic enzyme, and a cyanogenetic glucoside [Dunstan, *Chem. Soc. Proc.*, **9**, 168 (1907)]. The oil is obtained from the seeds of the cultivated trees either by expression or solvent extraction and usually has a very dark red color [*Agric. Bull. Malay States,* **6**, 231 (1918)]. The cake or extracted meal is used as a fertilizer or feeding stock. The oil is chiefly used in the manufacture of soap, but it can be used as a paint oil, particularly after it is refined. Most, if not all, of the commercial oil is high in free fatty acids, because of the poor keeping qualities of the seed. Usually the quantity of free fatty acids is so large that it is not feasible to refine the oil. The oil is said to be a fairly good drying oil and gives a hard, transparent film.

The range of the characteristics observed is as follows: Sp. g. 15° C. 0.924 to 0.930; $N_D^{40°}$ 1.4665 to 1.4685; Sap. V. 186 to 195; Iod. No. 133 to 143; R.M.V. 0.3 to 0.5; Unsap. 0.5 to 0.8 per cent; Titer 33° C.; Hexabromides 12 to 15 per cent.

S. S. Pickles and W. P. Heyworth [*Analyst,* **36,** 491 (1911)] examined a sample of oil extracted with petroleum ether, which gave an iodine number of 133.3. The insoluble fatty acids consisted of 14 per cent of saturated and 86 of unsaturated acids. The saturated acid fraction consisted of palmitic, stearic and an unidentified acid. The unsaturated fraction was stated to consist of 32.6 per cent of oleic, 50.9 of linoleic, and 2.5 of linolenic acid.

Jamieson and Baughman [*Oil and Fat Ind.,* **7,** 419 (1930)] examined the oil which they expressed from 100 lbs. of kernels imported from Sumatra. It gave an iodine number (Hanus) of 135.2, a thiocyanogen number of 88.2, a hexabromide number of 15.7, acid value of 40.9, and a saponification value of 191.8. It contained 16 per cent of saturated and 78.4 per cent of unsaturated acids. The oil contained the following percentages of acids: Oleic 27.3, linoleic 31.5, linolenic 19.6, palmitic 7.00, stearic 8.74, and 0.26 of arachidic. In this country most of the oil is extracted by solvents, but some is expressed. The oil is chiefly used by the soap makers. The press cake and extracted meal are used as fertilizer or feed for stock [A. T. Pope, *Oil, Paint, Drug Reptr.,* **118,** No. 10, 20 (1930)].

Attention is called to the following references:

"Storage of Rubber Seeds," C. D. V. Georgi, V. R. Greenstreet, and G. L. Teik, *Malayan Agric. J.,* **20,** 164 (1932); *Chem. Abs.,* **26,** 4727 (1932).

"Products from Rubber Seed. II. Applications and Economics," T. R. Dawson and T. H. Messenger, *J. Res. Assoc. British Rubber Mfgrs.,* **1,** No. 6, 45 (1932).

"Para Rubberseed Oil as a Substitute for Linseed Oil in Foundry Core Binders," A. Wilson Greene and J. M. F. Leaper, *Oil and Soap,* **10,** 28 (1932).

Funtumia Seed Oil. This oil is found in the seeds of *Funtumia elastica,* native to the west coast of Africa. The seeds, which weigh about 0.05 gram, contain about 30 per cent of oil. Ridial and Acland [*Analyst,* **38,** 250 (1913)] examined a sample of the oil with the following results: Sp. g. at 15° C. 0.9320; $N_D^{15°}$ 1.4788; Sap. V. 185; Iod. No. 138.

Kickxia Seed Oil. This oil is found in the seeds of *Kickxia elastica.* The seeds contain 28 and the kernels 54.8 per cent of oil. Sprinkmeyer and Diedrichs [*Z. Nahr. Genussm.,* **27,** 120 (1914)] reported the following characteristics: Sp. g. at 15° C. 0.9327; $N_D^{25°}$ 1.4768, at 40° C. 1.4716; Sap. V. 180; Iod. No. 131; R.M.V. 0.66; Pol. No. 0.3; Acid V. 3.33; Titer 23°.

Mexican Rubber Tree Seed Oil. This oil is found in the seeds of *Euphorbia elastica,* a native of Mexico. According to H. Okada [*Apoth. Zeit.,* **25,** 1014 (1910)], the seeds contain 32 per cent of kernels which contain 58 per cent of oil. The expressed oil gave the following characteristics: Sap. V. 195.4; Iod. No. 110.4; Acid V. 2.4. It is evidently a semi-drying oil.

Passion Fruit Seed Oil. The seeds of the *Passiflora edulis* amount to about 7 per cent of the fruit. The air-dried seeds contain from 7.9 to 8.5 per cent of water and 18.2 to 22.4 per cent of oil. The seed are

a by-product of the passion fruit juice industry of Australia, California, and elsewhere. The composition of the fruit is described by W. R. Jewell [*J. Dept. Agric. (Victoria),* **31**, 609 (1933)]. H. D. Poore ["Fruit Products," *J. Am. Vinegar Ind.,* **14**, 264 (1935)] discusses passion fruit products, giving also a brief history of the industry.

Jamieson and R. S. McKinney [*Oil and Soap,* **11**, 193 (1934)] examined a sample of the laboratory-expressed oil received from E. M. Chace, in charge of the Laboratory of Fruit and Vegetable Chemistry, Bureau of Chemistry and Soils, Los Angeles, California. The seed from which the sample was expressed contained 7.92 per cent of moisture and 18.17 of oil. When this pale yellow, limpid oil was held for some hours at 10° C., there was no separation of "stearine." It had a mild, pleasant taste.

The characteristics were as follows: Sp. g. 25°/25° C. 0.9207; $N_D^{25°}$ 1.4737; Sap. V. 190.4; Iod. No. (Hanus) 140.4; SCN V. 81.2; R.M.V. 0.11; Pol. No. 0.21; Acetyl V. (André-Cook) 8.1: Unsap. 0.62 per cent; Sat. acids 8.88 per cent; Unsat. acids 84.31 per cent; Iod. No. (Rosenmund-Kuhnhenn) of unsaponifiable 146.2.

The iodine number of the oil indicates that it belongs to the lower range of the drying oil class. This sample of oil was found to contain the following percentages of acids: Oleic 19.0, linoleic 59.9, linolenic 5.4, palmitic 6.78, stearic 1.76 and arachidic 0.34 per cent.

Seed from Kenya, Africa [*Bull. Imp. Inst.,* **35**, 22 (1937)] contained 8.5 per cent of moisture and 22.4 per cent of oil. The oil gave characteristics as follows: $N_D^{20°}$ 1.4761; Sap. V. 190.9; Iod. No. (Wijs) 141.2; Acid V. 0.3; Unsap. 0.8 per cent. The percentages of the constituents of the meal were as follows: Moisture 10.2; oil 7.0; proteins 11.3; crude fiber 52.1; carbohydrates 17.9; ash 1.5 per cent. It was stated that on account of the high fiber content of the cake (or meal made from it) it was not suitable as a cattle food and possibly of little or no use as a fertilizer material. The investigators also reported the absence of alkaloids and cyanogenetic glucosides.

The oil, if produced in quantity, could be used for either edible or technical purposes.

Safflower Seed Oil. This oil is obtained from the seed of *Carthamus tinctorius,* a plant which for many years has been extensively cultivated in India, Egypt and Turkestan. It is also grown on a limited scale in Russia (the Caucasus) and in some other European countries. During recent years [*Paint, Oil, Chem. Rev.,* **81**, No. 7, 10 (1926)] it has been introduced as an oil-seed crop into the northwestern section of the United States by the Department of Agriculture under the direction of Frank Rabak. Experimental plantings are being made in Minnesota, North Dakota, South Dakota, and Montana. The results already obtained indicate that it is well adapted to the agricultural conditions of that section of the country, both as regards dry-land and irrigation farming, and that it may be grown in the same manner and handled with the same farm machinery as is now employed for other

small grain crops. Safflower is especially suited to sandy or clay loam soil, but light sandy or heavy soil is undesirable. The plant requires about the same quantity of moisture as flax and apparently is more resistant to frost. Under normal conditions, the yield per acre is from 20 to 30 bushels of seed, but under controlled irrigation much larger yields may be obtained. A bushel of seed weighs about 45 pounds.

The oil content of the seed range from 24 to 36 per cent. The kernels amount to about 50 per cent of the seed. The oil may be expressed from the seed in hydraulic presses or expellers, or extracted by solvents. On account of the high fiber content of the seed coats, it is necessary to decorticate the seeds in order to get a press cake or meal comparable with that of linseed in composition. It is suitable for feeding stock.

The oil is used for edible and technical purposes. It has good drying properties and is suitable for use in the manufacture of paints, varnish, linoleum, etc. ["Safflower Seed Oil," by F. Rabak, *Oil, Paint, Drug Reptr.*, **111**, No. 5, 83 (1927)]. A valuable property of the oil is its ability to prevent "after yellowing" of white or pale-tinted paints, which are used for interior decoration.

It may be of interest to note that "roghan" or "afridi wax," which is used in India in the preparation of afridi wax cloth, is prepared by heating safflower oil in earthenware vessels for about 2 hours at a temperature of about 300° C.; then it is poured into water, which causes the oil to solidify to a gelatinous mass. When the oil is heated for about 2.5 hours between 307° and 310° C., it suddenly polymerizes to a very stiff elastic solid. Unlike polymerized tung oil, this product is soluble in turpentine and some other solvents.

Attention is called to the extensive studies and investigations on safflower plants, the seed and oil by A. Howard and J. S. Remington [*Agr. Research Inst. Bull.*, **124** (1921), Pusa, India].

The usual range of the characteristics is as follows: Sp. g. at 15.5° C. 0.925 to 0.928, at 25° C. 0.9243; $N_D^{40°}$ 1.4679 to 1.4693; Iod. No. 140 to 150; Sap. V. 188 to 194; Unsap. 0.5 to 1.3 per cent; Acetyl V. 12.5; Titer 16° to 17° C.; Hexabromides 0.4 to 1.6 per cent.

Jamieson and Gertler [*Oil and Fat Ind.*, **6**, No. 4, 11 (1929)] examined a sample of expressed American safflower seed oil with the following results: Sp. g. at 25° C. 0.9243; $N_D^{25°}$ 1.4744; Sap. V. 190.5; Iod. No. (Hanus) 149.3; R.M.V. 0.2; Pol. No. 0.1; Acetyl V. 12.5; Unsap. 0.59 per cent; Acid V. 5.6; Hexabromides 0.4 per cent; Sat. Acids 5.93 per cent; Unsat. Acids 87.7 per cent. The oil contained the following percentages of fatty acids: Oleic 24.58, linoleic 63.00, linolenic 0.14, myristic 0.04, palmitic 3.93, stearic 1.49, arachidic 0.4, and lignoceric acid 0.06. H. P. Kaufmann and H. Fiedler [*Fette u. Seifen*, **44**, 420 (1937)] reported the following results: Sap. V. 186.2; Iod. No. 150.1; SCN V. 84.7; Acid V. 0.5; OH No. 2.0; Hexabromides 0.81; Unsap. 0.53 per cent; Sat. acids 7.90 per cent. Fatty acids as glycerides: Oleic 16.6, linoleic 69.8 and linolenic 5.7.

J. van Loon [*Verfkroniek*, **10**, 80 (1937); *Drugs, Oils and Pts.*, **52**,

280 (1937)] found that his sample of oil contained the following percentages of acids as glycerides: Saturated 8.6, oleic 16.7, linoleic 71.3, and linolenic 3.4. The percentages of constituents in whole seed and decorticated seed press cakes were respectively as follows: Moisture 4, 9; oil 6, 7; crude fiber 43, 21; proteins 19, 38; ash 3, 8. Apparently, other constituents were not determined.

"Safflower Seed," *Bull. Imp. Inst.*, **20**, 27 and 94 (1922).
"Safflower Oil," S. Ivanov, *Chem. Umschau.*, **35**, 293 (1928).
"Safflower Seed Oil," D. Wakulin, *Chem. Umschau.*, **36**, 300 (1929). This article discusses oil content of seed from Turekstan, Saratow, and Samara, and gives characteristics of the oils.
"Safflower as a Possible Replacement Crop in the Northern Great Plains," W. A. Taylor, *Drugs, Oils and Paints*, **49**, 59 (1934).
"Safflower, a Possible New Oil-Seed Crop for the Northern Great Plains and the Far Western States," F. Rabak, *U. S. Dept. Agric. Circ. 366* (1935).
"Safflower Oil," J. S. Remington, *Pt. Mfgr.*, **6**, 50 (1936).
"Safflower, a Neglected Protective Coating Vehicle," L. L. Carrick and H. K. Nielson, *Am. Pt. J.*, **22**, 20, 24, 26, 28 (1938); *Chem. Abs.*, **32**, 8804 (1938).
"Some Studies in the Drying of Safflower Oil Films," L. L. Carrick and A. T. Murfin, *Am. Pt. J.*, **24**, No. 3, 53 (1939).

Salvia Sclarea Seed Oil. The *Salvia sclarea* of the *Labiatae* is native to the Orient. The seeds contain 29 per cent of oil. When extracted it is yellowish green and has a mild aromatic flavor. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.9303; $N_D^{15°}$ 1.4829; Sap. V. 193; Iod. No. 141; R.M.V. 1.1. References: Berlingozzi and Badolato, *Bull. Chim. Farm.*, **63**, 721 (1924).

Salvia Spinosa Seed Oil. The *Salvia spinosa,* also belonging to the *Labiatae,* is found in Arabia, Egypt and Persia. The seeds contain about 20 per cent of oil having the following characteristics: Sp. g. at 15° C. 0.9298; $N_D^{15°}$ 1.4799; Sap. V. 193; Iod. No. 159; R.M.V. 1.3. It does not solidify at −15° C.

Sandal Seed Oil. This oil is found in the seed of the sandal tree, *Santalum alba,* belonging to the *Santalaceae.*

The Indian seeds contain from 43 to over 50 per cent of oil. Y. V. S. Iyer [*Analyst,* **60**, 319 (1935)] examined the oil from six samples of seed with the following results: Sap. V. 185 to 197; Iod. No. (Wijs) 138 to 153; Acetyl value 20.8 to 24.3; Unsap. 16.8 to 18.8 per cent.

More recently, the oil has been investigated by M. K. Madhuranth and B. L. Manjunath [*J. Ind. Chem. Soc.*, **15**, 389 (1938)]. The seed contained 44 per cent of a viscous oil. The characteristics of the oil are as follows: Sp. g. at 25° C. 0.9356; $N_D^{30°}$ 1.4891; Sap. V. 176; Iod. No. (Hanus) 153; SCN V. 151; R.M.V. 0.9; Acetyl V. 22.0; Acid V. 29; Unsap. 8.8 per cent. When the oil was saponified a white, elastic, sticky, insoluble substance remained which was removed by filtration. This substance, which amounted to 5.2 per cent of the original oil, apparently was not further investigated. The mixed fatty acids were separated into solid (51 per cent) and liquid (49 per cent) fractions, the latter consisting chiefly of oleic acid. The solid fraction consisted of a triolefinic acid ($C_{18}H_{30}O_2$), for which the name Santalbic has been

proposed, and a very small quantity of palmitic acid. The purified acid, which melted at 41–2°, gave a *p*-phenyl-phenacyl ester melting 56–7°. It gave an iodine number (Hanus) of 133 (calculated as 274), a thiocyanogen value of 130, and a Diene value of 8.4 by the Ellis and Jones method. It yields stearic acid upon hydrogenation. It differs from punicic acid (M. P. 44°) in that it could not be changed to a beta form. It is obvious that further study should be made of this acid.

The oil and protein content of sandal seeds have also been investigated by M. Sreenivaya and N. M. Narayana [*J. Ind. Inst. Sci.*, **19A**, 1, (1936)].

It has been reported that the large-scale expression of the oil has been solved and that now the chief difficulty is the high cost of collecting the seeds.

Soy (Soya) Bean Oil. This oil is obtained from the seed of the numerous cultivated varieties of the legume *Soja (Glycine) max*, a plant native to China, Chosen (Korea), and Manchukuo (Manchuria). Soybeans are cultivated in many other localities, including the United States, some parts of Africa, Europe, Japan, India, and the Netherlands Indies. At the present time China, Manchukuo, and the United States are the largest producers.

Like most important food plants, the early history of the soybean is obscure. It was probably used, and perhaps even cultivated, by primitive man. The records of 5000 years ago mention its cultivation. As a result of this long period of cultivation, many hundreds of varieties of soybeans are known. Some mature early, while other varieties require 150 days or more. The cultivated soybeans are erect plants, growing to a height, in some cases, of over three feet. The hairy pods are borne in clusters of 3 to 5 and range from 1.5 to 3.5 inches long. Most varieties have 2 or 3 seeds in a pod, but some have 3 or 4. The seeds are yellow, green, brown, or black and vary considerably in size. The oil content ranges from about 11 to 25 per cent, but the varieties raised in sufficient quantity for the extraction of oil average 16 to 19 per cent. However, through plant breeding in the United States and Manchuria, one or more varieties have been developed, the seeds of which contain 22 per cent or more of oil, and in some localities such seeds are grown for the production of oil and cake. The quantity of oil in seed of the same variety is subject to marked variation when grown in different regions. Some variation, as would be expected, is due to differences in soils and in seasons, but more is due to the difference in climate. For example, soybeans of a given variety have a higher oil content when grown in the southern-producing localities of both Manchuria and the United States than those obtained from the northern portions of those countries. On the other hand, the iodine numbers of the oils from the north are higher than those from the same variety of beans growing in warmer localities.

For many centuries, soybeans have been cultivated in China. They are extensively grown in 12 of the provinces. The annual crop of beans produced in these provinces is estimated to be about 75 million bushels.

Practically all the beans produced in China are used by the Chinese. The Chinese, like the Japanese and other Oriental peoples, make a large variety of food products from the soybean, which they consume in enormous quantities. The oil is one of the staple foods, particularly of the lower classes, who consume large quantities of the crude product. Most of the oil is expressed in primitive wooden-wedge presses. Some of the oil is used in the manufacture of soap, certain kinds of paint, and waterproofings. In South China, press cake is used for fertilizing the sugar cane fields.

In Manchuria, the cultivation of soybeans is largely centered in the Liao and Sungary Valleys, where several million acres are devoted to this crop. The average yield per acre is reported as being from 20 to 22 bushels of beans. Of the annual crop, which is stated to be about 130 million bushels, about 40 per cent is retained for use in Manchuria. Although much oil is still produced in primitive mills, that exported since 1918 is chiefly from the well-equipped modern mills in Darien and other important oil centers. Up to the present time, very little soybean oil has been obtained by solvent extraction in Manchuria. Two of these plants were established some years ago, but neither one has been operated to capacity. The South Manchurian Railroad, with its experts and well-equipped laboratories and experiment stations, is taking a leading part in the development of the soybean industries in Southern Manchuria.

Japan has over a million acres of land devoted to soybean cultivation and produces about 500,000 tons of seed per year. The yield per acre averages about 16 bushels. Most of the domestic beans are utilized for food purposes. Japan also imports beans, oil and press cake. Soybeans constitute one of the most important articles of food and are used in many different forms. Large quantities of both beans and press cake are consumed in the form of soy sauce, vegetable milk and cheese, miso, tofu (curd), malto, etc. Japan is a large producer of oil, which is chiefly used for edible purposes. The inedible press cake is extensively employed for fertilizing the rice fields.

In northern India, where the soybean has long been cultivated as a forage crop and as food for the natives, it is still of little commercial importance. The cultivation of soybeans in parts of Europe and South Africa has notably increased during recent years. By 1940 Roumania had 395,360 and Bulgaria 98,840 acres planted to soybeans, whereas in 1938 their respective acreage was 139,000 and 30,550.

The soybean has been a farm crop of some importance in the United States since about 1880. Large quantities continue to be grown as a cover crop for the enrichment of the soil and forage purposes, but from about 1920 on, the production of beans for oil and other purposes has steadily increased. It is interesting to note that by 1936 there were 35 soybean mills, 15 firms making flour, 20 making food products, and 50 engaged in manufacturing various industrial products from soybeans. The production of soybeans in 1930 was 363,000 tons, whereas that for 1941 was 3,201,360 tons. Illinois ranks first in soybean production,

and is followed by Indiana, North Carolina, Missouri and Iowa. Many other states produce them in smaller quantities.

The soil requirements for the production of soybeans are about the same as for corn (maize), the best results being obtained with sandy or clay loams which contain a fair quantity of potash, lime, and phosphate. Depending upon the soil and the variety of bean planted, the yield per acre varies from a few up to 30 bushels of beans. The average yield per acre in this country is probably between 16 and 18 bushels. A bushel of beans weighs about 60 pounds.

Harvesting and Storage of Beans. When the beans are thoroughly matured they should be harvested as soon as possible, to avoid injury by frosts. Whenever possible, they should be harvested with a "combine." Care should be taken not to fracture the seed coats. Cracked seed coats permit fungus attack of the beans which results in the deterioration of the oil and proteins. If such seeds become wet, their vitality is largely destroyed. Beans which contain much over 10 per cent of moisture should be dried in a grain dryer before being placed in storage. Beans with 12 or 14 per cent of moisture have been successfully stored over considerable periods, but this practice has frequently resulted in the heating of the beans, with serious losses. As in the case of other seeds, soybeans should be stored in dry, well-ventilated seed houses or silos which are constructed so as to be mouse- and rat-proof.

Manufacture of Oil and Meal. In the United States, there are a small number of sizable solvent-extraction plants and several hydraulic press mills, besides 30 or more mills equipped with oil expellers engaged in processing soybeans for oil and meal. At the present time in Europe, most of the oil is obtained by solvent extraction. In China, it is expressed by primitive and hydraulic presses. Most of the modern mills and one or two solvent-extraction plants are located in Manchuria. In the hydraulic press mills, the beans are freed from foreign matter, crushed and heated in the cookers, formed into cakes and pressed. In the case of the expeller mills, the beans, after cleaning, are crushed by means of slightly fluted rolls; the coarsely crushed meal is passed through a steam-heated dryer to reduce the moisture content to 2 or 3 per cent, and is then conveyed to the steam- (80 to 100 lbs.) heated temperer, where it is mixed with sufficient water to produce a satisfactory cake when pressed. The preliminary drying of the crushed beans is essential for efficient extraction of the oil. In the United States, the press cake has an oil content from 4.5 to 5 per cent. The press cake is broken and ground to a meal, and then sacked. At some mills the beans are decorticated mechanically and the separated hulls are ground with the press cake. The oil from the expellers is passed through a slowly revolving oil reel, which retains the coarser part of the press foots; the larger part of the oil drains through the wire screen of the reel. The separated foots are fed back to the expellers. The oil is agitated with 0.2 to 0.4 per cent of a siliceous filter aid, pumped through a filter press and transferred to storage tanks.

Practically all the oil expressed in the United States shows a "break"

when heated. The substances which cause the "break" can be completely removed by refining the oil with caustic soda. The oil obtained by solvent extraction usually gives no "break."

For many years in Europe discontinuous or batch solvent extractors of various types have been used, but more recently several different kinds of continuous solvent extractors have been designed and installed, particularly for processing soybeans for oil and meal. In the United States, there are several installations of imported continuous solvent-extraction plants, besides a number of others of American origin. For extraction, the beans are cleaned, dried and flaked. The general principle upon which the operation of continuous extractors is based is to introduce the flaked meal by a conveyor in a thin layer into the extraction column, where it meets with a counter-current of solvent. The extracted meal and oil-laden solvent are continuously passing out of the system. The solvent which is distilled from the extracted oil and that recovered by steaming the meal is returned to the solvent storage tanks. After steaming the meal, it is dried without delay to the desired moisture content. This meal, which contains about one per cent of oil, is used both for edible and technical purposes. The solvent extraction of soybeans is discussed by W. E. Meyerweissflog, *Oil and Soap,* **14,** 10 (1937). A method for the extraction of fatty oils with alcohol has been devised by T. Inaba and K. Kitagawa [*Brit. Chem. Abs.,* **B 1935,** (318)]. Alcoholic extraction plants for soybeans have been established in Japan, Chosen, and Manchuria [*Oil Col. Trdes. J.,* **89,** 291 (1936)].

Although various agents have been suggested in connection with the recovery of the phosphatides from the oil, probably water is now most generally used. Introduction of steam into the oil hydrates the phosphatides, causing them to precipitate. They are in the form of an emulsion which is separated from the oil by high-speed centrifuges. The emulsion, which contains about 30 per cent of oil, is placed under diminished pressure and heated until the moisture has been removed by distillation. Depending upon the use, the product may or may not be further treated. The phosphatides as separated usually contain from 30 to 35 per cent of lecithins, and even more cephalins. Commercially, this mixture is known as soybean or vegetable lecithin (different preparations are sold under trade names) and is used as an emulsifying, wetting and stabilizing agent in various products which include leather and textile finishes, margarines, shortenings, certain kinds of candy, and pharmaceutical preparations. Attention is called to "Lecithin—Its Manufacture and Use in the Fat and Oil Industry" by J. Eichberg, [*Oil and Soap,* **16,** 51 (1939)] which gives 43 references. Over 20 of these deal with patents. G. A. Wieschahn [*Oil and Soap,* **14,** 119 (1937)] gives a review on soybean phosphatides and their uses, citing 64 references.

Soybean meal contains anywhere from 41 to 50 per cent proteins and sometimes more. In North America and Europe, it is largely used for feeding livestock, but in the Orient it is used very extensively as a fertilizer material. However, the use of the flour made from the meal

for human food is now increasing at a notable rate in all countries. Also in the United States, much meal is used in the manufacture of adhesives, sizing for paper and plastic compositions for making various molded articles. The production of a textile fiber from the meal is a new use. The nutritive value of soybean meal is discussed by J. W. Haywood [*Oil and Soap,* **14,** 317 (1937)].

Depending upon the oil content of the beans and the methods used, the yield of oil from a ton of beans varies from 250 to about 400 pounds of oil and the meal from 1400 to 1600 pounds.

Soybean oil is refined in the same manner as cottonseed oil. Abstracts of patents covering the treatment of the refined oil to delay "reversion" flavor will be found in *Oil and Soap,* **15,** 273 (1938), and **16,** 45 (1939).

For further information on soybeans, their production and utilization in various countries, consult:

"The Soy Bean," by Piper and Morse, McGraw-Hill Book Co., New York, 1923.

"Selection for Quality of Oil in Soy Beans," L. J. Cole, E. W. Linstrom and C. M. Woodworth, *J. Agric. Research,* **35,** 75 (1927).

"Soy Bean Production in Illinois," *Ill. Agric. Exp. Sta. Bull.,* **310,** (1928) by Hackleman, Sears, and Burlison.

"The Soya Bean," E. Bowdidge, Oxford Univ. Press (1935).

"Soybean Varieties for Hay, Seed and Oil Production," C. K. McClelland, *Arkansas Agr. Exp. Sta. Bull.* **334** 3–44 (1936).

"The Soybean. A Plant Immigrant Makes Good," W. L. Burlison, *Ind. Eng. Chem.,* **28,** 772 (1936).

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F. B. **372** (1909), "Soy Beans," by C. V. Piper and H. T. Nelson.

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Many experiment stations, agricultural colleges and other libraries contain copies of these and other bulletins issued by the United States Department of Agriculture which may be consulted.

Soybeans. The analysis of a large number of samples of soybeans grown in the United States gives the following percentages of constituents: Moisture 5.5 to 9.4, oil 12 to 24, and proteins 30.0 to 50.0. The average oil content of beans crushed for oil is 18 per cent and the proteins 42 per cent. In the case of soybeans it has been found that in order to convert the percentage of nitrogen into terms of proteins, it should be multiplied by 6.38.

Soybeans give upon ignition from 3.3 to 6.4 per cent of ash. Ash analysis indicated that they contain the following percentages of constituents: Lime (CaO) 0.50 to 0.63, magnesia (MgO) 0.45 to 0.55, potash (K_2O) 2.0 to 2.6, soda (Na_2O) 0.19 to 0.46, and phosphorus pentoxide (P_2O_5) 1.5 to 2.2.

G. S. Jamieson and R. S. McKinney [*Oil and Soap,* **12,** 70 (1935)] examined 23 samples of soybeans, including 18 different commercially grown varieties, and found that they contained from 0.078 to 0.150 per cent of phosphatide phosphorus which, calculated in terms of lecithins, gave respectively from 2.00 to 3.82 per cent (18 of the samples varied from 2.00 to 2.55 per cent).

Many investigators have examined the nitrogen-free extract, which amounts to from 22 to 29 per cent. J. P. Street and E. M. Bailey [*J. Ind. Eng. Chem.,* **7,** 853 (1915)] made a quantitative study of this extract. It is interesting to note that soybeans as a rule contain little or no starch. The amount found depends on the variety as well as on the maturity of the beans; the immature seeds generally contain somewhat more starch.

The proteins of soybeans appear to vary from 31 to about 40 per cent. T. B. Osborne and L. B. Mendel [*J. Biol. Chem.,* **32,** 369 (1917)] have shown that the proteins are adequate for prompting the growth of animals and that the beans contain ample quantities of fat- and water-soluble vitamins. Much of the flour is now being used in various food products for general use.

Soybeans are a very good source of vitamin B_1 and B_2 (Riboflavin). The beans of some varieties are a fair source of vitamin A, whereas those of other varieties are deficient in it. Dry, matured beans have little, if any, vitamin C, and but little D. The presence of a notable quantity of vitamin K (antihemorrhagic vitamin) in the oil has been shown by H. J. Almquist and E. L. R. Stokstad [*J. Nutrition,* **14,** 235 (1937)].

Soybean Oil. The oil usually varies in color from yellow to dark amber depending upon the method of extraction and the variety as well as the quality of the beans. The range of characteristics reported for crude soybean oil are as follows: Sp. g. at 15° C. 0.922 to 0.925, at 25°/25° C. 0.9179 to 0.9245; $N_D^{15°}$ 1.4765 to 1.4775, at 20° 1.4742 to 1.4763, at 25° 1.4722 to 1.4750, at 40° 1.4675 to 1.4736; Sap. V. 189.9 to 194.3; Iod. No. 103 to 152 (but the range for most of the commercial oils is from

124 to 136); SCN V. 77.0 to 85; R.M.V. 0.2 to 0.6; Pol. No. 0.2 to 0.6; Unsap. 0.50 to 1.8 per cent; Phosphatides 1.0 to about 3 per cent; Sat. acids 11 to 13.5 per cent; Flash Pt. 300 to 315° C.; Fire Pt. 350° to 355° C. Much data on the smoke, flash, and fire points of crude and refined soybean, and other vegetable oils by S. B. Detwiler and K. S. Markley will be found in [*Oil and Soap,* **17,** 39 (1940)].

"Tentative specification (D124-37) for Raw Soybean Oil" [*Am. Soc. Testing Materials Standards, Part II.* **1136** (1939)].

	Minimum	Maximum
Sp. g. 15.5°/15.5° C.	0.924	...
Acid number	...	3 0
Saponification number	190.0	...
Unsaponifiable matter, per cent	...	1.5
Iodine number (Wijs)	131.0	...
Loss on heating 105–110° C., per cent	...	0.2
Foots, per cent	...	2.5

Appearance. Clear and transparent at 65° C.

Color. Not darker than a freshly prepared solution of 1.0 g $K_2Cr_2O_7$ in 100 ml. of pure H_2SO_4 (sp. g. 1.84) or its equivalent in iron-cobalt solution or in Lovibond glass 2.5.

Specification is subject to annual revision.

Federal Specifications (Tentative) give sp. g. at 15.5/15.5° C. 0.924 to 0.930, Iod. No. (Wijs) not less than 130, Sap. V. not less than 189, Unsap. not over 1.5 per cent, Acid V. not over 3.0, loss on heating not over 0.2 per cent and "break" not to exceed 0.02 per cent by weight.

Dall Acqua [*J. Soc. Chem. Ind.,* **40,** 153A (1921)] states that soybean oil has different electrical properties from those of other seed oils. It discharges an electroscope of the Elster and Geitel type in less than a second while other oils require at least 15 and usually more seconds.

Seltimj [*Analyst,* **38,** 36 (1913)] suggested a color test. The test is made by shaking 5 cc. of the oil with 2 cc. of chloroform and 3 cc. of a 2 per cent aqueous solution of uranium nitrate. This gives an intense yellow emulsion. Newhall [*Ind. Eng. Chem.,* **12,** 1174 (1920)] in making the test, added a little gum arabic. He found that bleached or deodorized soybean oil did not give the test and that linseed oil gave brownish emulsions. The test is not sufficiently characteristic for soybean oil so that reliance can be placed on its use [Utz, *J. Soc. Chem. Ind.,* **41,** 222A (1922)].

Analysis of Crude Soy Bean Oil for Neutral Glycerides. Jamieson and Baughman [*Cotton Oil Press,* **6,** No. 4, 33 (1922)] examined 4 samples as follows:

No.	Acidity as Oleic Acid	Neutral Oil	Fatty Acids	Other Substances	Refining Loss (NaOH)
			Per Cent		
1	0.28	99.48	0.40	0.12	3.19
2	0.34	98.96	0.86	0.18	3.52
3	0.34	98 81	0.99	0.20	3.89
4	1.54	97.67	1.87	0.46	6.52

The percentages of fatty acids given in column 4 are larger than those in column 2. This is partly because some of the fatty acids are

liberated from the lecithins, cephalins and similar substances during the analysis. The figures in column 5, which are the differences between the total loss and the weight of the fatty acids of column 4, include any traces of moisture present in these samples as well as the inosite phosphates, peptones, resins, mucilaginous substances, etc., which are present in most if not all seed oils. Some oils like crude cottonseed, pumpkin and squash seed oils, contain notable quantities of these substances.

Composition of Soybean Oil. The oil expressed from mammoth yellow soybeans grown in the United States, which gave an iodine number of 128 by the Hanus method, was examined by W. F. Baughman and G. S. Jamieson [*J. Am. Chem. Soc.*, **44**, 2947 (1922)] who reported the following percentages of constituents: Oleic 32.0, linoleic 49.3, linolenic 2.2, palmitic 6.5, stearic 4.2, arachidic 0.7, lignoceric 0.1, and unsaponifiable matter 0.6. E. S. Wallis and G. H. Burrows [*J. Am. Chem. Soc.*, **46**, 1949 (1924)] found the following percentages: Oleic 33.6, linoleic 51.8, linolenic 2.3, palmitic 6.8, stearic 4.4, and arachidic 0.7. It should be noted that prior to 1926 when Kaufmann described his thiocyanogen method, investigators could estimate the quantity of linolenic acid in an oil only from the amount of the ether-insoluble hexabromide obtained, and this accounts for the low results.

W. Kimuro [*J. Soc. Chem. Ind. (Japan)*, **33**, S. B., 325 (1930); *Chem. Abs.*, **25**, 428 (1931)] calculated with the aid of the iodine and thiocyanogen values that the mixed fatty acids contained the following percentages: Oleic 259, linoleic 58.8, linolenic 3.8, and saturated acids 11.8. H. P. Kaufmann [*Allegem. Öl Fette Ztg.*, **27**, 325 (1930)] reported the following results for the mixed fatty acids from Manchurian soybean oil: Oleic 21.0, linoleic 54.5, linolenic 8.1, and saturated acids 15.1 per cent.

Recently, a very extensive investigation has been made by T. P. Hilditch and H. Jasperson [*J. Soc. Chem. Ind.*, **58**, 187 (1939)] using the fatty acids from 1140 grams of alkali-refined oil. They reported the following percentages of constituents: Sat. acids below myristic acid 0.2, myristic 0.08, palmitic 9.74, stearic 2.39, arachidic 0.94, tetradecenoic 0.05, hexadecenoic 0.42 (includes some hexadecadienoic acid $C_{16}H_{28}O_2$), oleic 28.71, linoleic 50.42, and linolenic 6.46. The glyceride structure of soybean and other oils is discussed by T. P. Hilditch and E. C. Jones [*J. Soc. Chem. Ind.*, **53**, 13T (1934)].

F. G. Dollear, P. Krauczunas, and K. S. Markley [*Oil and Soap*, **15**, 263 (1938)] examined the oils from the Dunfield variety of soybeans, grown during 1936 and 1937. The oil (1936 crop) gave an iodine number of 102.9, whereas the 2 samples of oil from the 1936 crop grown in different regions gave iodine numbers of 124 and 127. These two oils contained respectively 3.6 and 6.0 per cent of linolenic acid, whereas the other oils contained 2.9 per cent. For other data, the original paper should be consulted. Also attention is called to their contribution of the chemical composition of some high iodine number, "Soybean Oils" [*Oil and Soap*, **17**, 120 (1940)] which also gives much analytical data for the beans.

Composition of Soybean Phosphatides, Fatty Acids. An investigation of the alcohol-soluble (lecithins) and insoluble (cephalins) phosphatides has been made by T. P. Hilditch and W. H. Pedelty [*Biochem. J.*, **31**, 1964 (1937)] with the following results:

Alcohol-soluble fraction: Phosphorus 3.82 and nitrogen 1.56 per cent: iodine number 83.5 and saponification equivalent 254.4; mixed fatty acids, which amounted to 70 per cent, gave an iodine number of 128.6 and a saponification equivalent of 277.5. They contained the following percentages of constituents: Palmitic 17.15, hexadecenoic 5.47, oleic 18.81, linoleic 52.40, linolenic 3.65, as C_{20} Unsat. acids 1.49, and 1.03 of unsaponifiable matter. These results, as stated by the investigators, must be regarded as less reliable than those found for the alcohol-insoluble fraction (110 grams), as only 35 grams of the alcohol-soluble phosphatides were available for study.

Alcohol-insoluble fraction. Phosphorus 3.7 and nitrogen 1.4 per cent; iodine number 94.2 and saponification equivalent 242.7. The mixed fatty acids (69 per cent) gave an iodine number of 131.9 and a saponification equivalent of 283.2. They contained the following percentages of constituents: Palmitic 11.47, stearic 3.87, as arachidic 1.37, hexadecenoic 8.37, oleic 5.42, linoleic (includes a little linolenic acid) 61.83, as C_{20} Unsat. acids 5.36, and 2.31 of unsaponifiable matter. For details and literature review, the original contribution should be consulted.

Uses of Soybean Oil. The crude (raw) oil is used for making foundry cores (metal molding), factice which is compounded with rubber for the manufacture of hose, mats, and other articles, and for making soaps which include liquid shampoo and hand soap, soft or paste soaps for hospital use and washing automobiles. Mixtures of fats containing from 20 to 25 per cent of highly hydrogenated soybean oil are at times used for making hard soaps. The oil, after "boiling," "blowing," or other treatment, is used along with linseed, perilla, oiticica, dehydrated castor, or tung oils in the manufacture of paints, varnishes, baking japans for automobiles and refrigerators, for various "air drying" synthetic finishes, linoleum, oil cloth, and printing inks. For some of these purposes the crude oil (usually freed from "break") is used, whereas for others only the alkali-refined product is desirable. White or tinted paints made with soybean oil do not yellow with age as is the case with those which contain only linseed, perilla or other strong drying oils. The proportion of soybean oil to stronger drying oil which is used for making paints and other coatings varies from 10 to about 50 per cent, but from 15 to 25 per cent of the oil is more commonly used. The refined deodorized oil is used as a salad and cooking oil, and in the manufacture of margarine and shortening (along with cottonseed or other oil).

Unless the alkali-refined oil is skillfully deodorized, its flavor "reverts," developing a characteristic fishy taste upon standing a short time.

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"Phosphatides From Soybean Oil." M. H. Thornton and H. R. Kraybill, *Ind. Eng. Chem.,* **34,** 625 (1942).

Stillingia Oil. This oil is obtained from the kernels from the seeds of the tree *Stillingia sebifera* (*see* Chinese vegetable tallow), native to China. The kernels contain over 50 per cent of oil. In China, after the removal of the tallow from the mesocarp (or white layer in which the seed is enclosed), the seeds are crushed and the oil expressed. It is said to be used locally for the most part as a burning oil. Only small quantities of the oil produced are exported for the manufacture of paint and varnish.

The characteristics of the oil are as follows: Sp. g. at 15° C. 0.9395 to 0.9458; $N_D^{25°}$ 1.4818; Sap. V. 203 to 210; Iod. No. 170 to 187; R.M.V. 0.9; Titer 12° to 13° C.; Hexabromides 25.8 per cent; $(\alpha)_D^{16°} - 18.6°$; Unsap. 0.45 to 1.4 per cent. The outstanding characteristic of this oil is its negative optical rotation.

References: Lewkowitsch [*Analyst*, **29**, 112 (1904); Nash, *ibid.*, **29**, 110 (1904); Diedrichs, *Z. Nahr. Genussm.*, **27**, 132 (1914)].

Jamieson and R. S. McKinney [*Oil and Soap*, **15**, 295 (1938)] examined the oil expressed by them from a composite sample of seed from California, Florida and Texas, as well as a sample of the oil imported from China and for which they are indebted to E. Schuelke and the Murray Oil Products Company. The following characteristics of the oils were determined.

	Chinese Oil	American Oil
Refractive index at 25° C.	1.4817	1.4830
Iodine number (Hanus)	169.0	176.1
Thiocyanogen value	100.7	102.7
Saponification value	206.2	211.7
Acid value	3.7	3.1
Acetyl value (André-Cook)	...	8.5
Reichert-Meissl value	1 64	0.60
Polenske number	0.97	0.60
Unsaponifiable matter	0.78%	0.61%
Saturated acids	8.67%	6.19%
Unsaturated acids	85.70%	88.60%
Total neutral oil	97.5%	97.6%

These oils were found to contain the following percentages of acids.

Acids	Chinese Oil	American Oil
Oleic	10.4	7.7
Linoleic	49.9	56.3
Linolenic	25.4	24.6
Palmitic	5.9	4.4
Stearic	2.6	1.4
Arachidic	0.14	0.34

H. P. Kaufmann and Bao-Wei King [*Fette u. Seifen*, **46**, 388 (1939)] reported the following characteristics: Sap. V. 205.2; Iod. No. 176.4; SCN V. 101.4; Unsap. 3.0 per cent; Acid V. 2.4; Sat. acids 5.7 per cent. The mixed fatty acids contained the following percentages of constituents: Oleic 8.8, linoleic 62.7, linolenic 22.2, and saturated acids 6.2. The oil can be used in the manufacture of paints, varnishes and other products requiring a drying oil. The low acidity of the crude oil imported from China is noteworthy. Also, it is obvious that both of these oils contain but very small quantities of non-oil constituents.

Belladonna Seed Oil. This oil is found in the seeds of the plant *Atropa belladonna* belonging to the *Solanaceae*. It is a European plant which reaches a height from 3 to about 5 feet. The seed contain about 30 per cent of oil. The characteristics of the expressed oil are as follows: Sp. g. at 15° C. 0.9250 to 0.9256; $N_D^{25°}$ 1.4726; Sap. V. 191.2; Iod. No. 145; R.M.V. 2.86; Pol. No. 0.45.

T. P. Hilditch and M. B. Ichaporia [*J. Soc. Chem. Ind.*, **55**, 189T (1936)] examined a sample of oil which gave the following characteristics: Sap. Equiv. 296.7; Iod. No. 146.5; Acid V. 28.0; Unsap. 2.5 per cent. The percentage composition of the fatty acids was found to be as follows: Oleic 25.5, linoleic 66.8, palmitic 5.9, and stearic acid 1.8.

The oil is edible, as it contains none of the alkaloids of the plant.

Hyoscyamus Seed Oil. This oil is found in the seed of the plant *Hyoscyamus niger* belonging to the *Solanaceae*. The plant, which is native to Europe, grows to a height of about 5 feet. The seeds contain about 30 per cent of oil. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.9239 to 0.9390; $N_D^{15°}$ 1.4788; Sap. V. 171–188; Iod. No. 131 to 143; R.M.V. 0.9 to 1.06; Pol. No. 0.45 to 0.57; Unsap. 0.7 to 1.9 per cent; Sat. Acids 7.2 per cent.

T. P. Hilditch and M. B. Ichaporia [*J. Soc. Chem. Ind.*, **55**, 189T (1936)] examined a sample of oil which gave the following characteristics: Sap. Equiv. 290.3; Iod. No. 151; Acid V. 27.; Unsap. 0.3 per cent. The percentage composition of the fatty acids was as follows: Linoleic 82.0, oleic 11.1, palmitic 6.5, and stearic 0.4. It will be observed that these investigators found a notably higher iodine number than that previously reported.

Paprica Seed Oil. This oil is found in the seed of the plant *Solanaceae capsicum*, a 3-foot annual belonging to the *Solanaceae*. The seed contain from 28 to 30 per cent of oil. The characteristics of the oil are as follows: Sp. g. at 15° C. 0.9138 to 0.9316; N_D^{20} 1.4732 to 1.4784; Sap. V. 185 to 195; Iod. No. 133 to 144.

Apparently, no investigation on the composition of the oil has been made.

Thistle (Cardo) Seed Oil. This oil is found in the seeds of the *Cynaria cardunculus* of the *Compositae* family, which is widely distributed in the pampas regions of South America. G. Eckstein [*Industria y Quim.*, **3**, 81 (1940); *Chem. Abs.*, **35**, 8332 (1941)] reported that the seeds which he examined contained the following percentages of constituents: moisture 8.5, oil 23.0, proteins 17.8, fiber 15.2, and ash 3.3. The characteristics of the oil were $N_D^{25°}$ 1.4732; Sap. V. 188.1; Iod. No. (Wijs) 133.4; SCN V. 76.7; Acid V. 0.4; Unsap. 0.63 per cent, and Hexabromides 3.9 per cent. The percentages of acids were as follows: oleic 24.2, linoleic 64.6, linolenic 1.5 and saturated 9.7.

In Uruguay, successful experiments were made several years ago on the expression and refining of the oil for edible use. The thistle floss or down separated from the seeds was suggested as a substitute for kapok as a filling for pillows and cushions.

Tobacco Seed Oil. This oil is obtained from the seed of varieties of the plant *Nicotina tobacum*. The seeds contain from 33 to 38 per cent of oil. The oil is yellow, odorless and free from harmful substances. According to T. Paris [*Chem. Abs.*, **16**, 4080 (1922)], the oil is expressed and used in Bulgaria for edible purposes. It also can be used for soap making and as a burning oil. The characteristics of the

oil are as follows: Sp. g. at 15° C. 0.9232 to 0.9250; $N_D^{25°}$ 1.4739 to 1.4828; Sap. V. 186 to 197; Iod. No. 131 to 142; R.M.V. 0.06 to 0.3; Pol. No. 3; Unsap. 1 to 1.2 per cent; Sat. Acids 9 to 10 per cent; Unsat. Acids 82 to 84 per cent.

M. P. Peatnizki (*Brit. Chem. Abs.* **B, 1930,** 429) stated that the oil which he examined contained the following percentages of fatty acids: Oleic 21.7, linoleic 60, palmitic, etc., 9.6. The extracted meal was examined by T. Paris with the following results: Proteins 28.63, oil 1.64, carbohydrates 31.41, cellulose 19.9, and ash 6.59 per cent. It is said that the cake or meal can be used as a feed for stock.

The seed oils from tobaccos grown in Wisconsin have been investigated by W. L. Roberts and H. A. Schuette [*J. Am. Chem. Soc.*, **56,** 207 (1934)]. The range of the characteristics of these oils was as follows: Sp. g. 20°/20° C. 0.9235-0.9260; $N_D^{20°}$ 1.4755-1.4763; Sap. V. 189.1-190.7; Iod. No. (Wijs) 142.7–146.7; R.M.V. 0.26–0.28; Pol. No. 0.11–0.13; Unsap. 1.24–1.25 per cent; Solid Pt. −14 to −16°; Sat. acids 7.7–8.0 per cent; Unsat. acids 86.5–86.7; Titer of fatty acids 18.1–18.2°.

The average percentages of the acids found in the oils are as follows: Oleic 16.2, linoleic 70.4, palmitic 3.1 and stearic 4.8 per cent.

Philippine tobacco seed oil has been investigated by A. O. Cruz and A. P. West [*Phil. J. Sci.*, **61,** 161 (1936)] with the following results: Sp. g. 30/30° 0.9130; $N_D^{30°}$ 1.4714; Iod. No. (Hanus) 135.8; Sap. V. 190.5; Unsap. 1.41 per cent; Sat. acids 10.0 per cent; Unsat. acids 82.9 per cent. The oil contained the following percentages of acids in terms of glycerides: Oleic 26.4, linoleic 70.2, myristic .05, palmitic 7.0, stearic 3.0, and arachidic 0.34 per cent. In recent years, considerable quantities of tobacco seed oil have been produced in Greece from the seed not required for planting purposes.

M. Brambilla and G. Balbi [*Chimica e Industria*, **20,** 548 (1938). *Chem. Abs.*, **33,** 1522 (1939)] discusses the use of tobacco seed oil in paints and varnishes.

Tung (Chinese Wood) Oil. Tung oil is obtained from two species of Aleurites, a small genus belonging to the *Spurge* family (*Euphorbiaceae*). Both of these species, *A. fordii* and *A. montana*, are natives of China. A large part of the oil exported from China is expressed from the seeds of the *A. fordii*, which is more widely distributed than the *A. montana*, and grows in central and western China. The less hardy *A. montana* is found in southwestern China from Fukien southward to Tonkin. In China, *A. fordii* is known as the tung oil tree, and the *A. montana* as the wood oil tree. The trade makes no distinction between the oil from these species and the oil exported is frequently a mixture of the two. As the oils from these two species are similar in composition and properties, little or nothing would be gained by keeping them separate. The *Aleurites montana* and its seed oil will be discussed under Abrasin Oil.

Tung Oil Trees. In China, both the *A. fordii* and *A. montana* are

short-lived trees; the former lives for about 30 years and the latter somewhat longer. The trees seldom exceed 30 feet in height and average much less in China because of the poorness of the soil on which they grow. Many are on heavy clay and rocky hillsides, the better lands having to be utilized for growing food crops.

Aleurites fordii, Hemsl. A much-branched deciduous tree; bark is smooth and pale gray; leaves ovate-cordate, some 3-lobed; flowers appearing before leaves on previous year's growth, in numerous, few-flowered cymose corymbs, bell-shaped, 1 to 1.5 inches in diameter, white, stained with pink, yellow markings at base of petals; central terminal flower of each cyme is female, others generally male; stamens 8 to 10, ovary 3- to 5-celled and sometimes more; fruit, 2 to 3 inches in diameter, is smooth, subglobose, green, passing to dull brown when ripe; seeds 3 or more, compressed, broadly obovoid, about 1 inch long and broad; seed coats ridged and warty.

Aleurites montana E. H. Wilson. A deciduous tree; leaves ovate, acuminate, usually 5-lobed, expanding before tree blooms, inflorescence, terminal, few- to many-flowered raceme or corymb, on current season's growth; flowers similar but slightly smaller than those of *A. fordii*; fruit, egg-shaped, 2 to 2.5 inches long and about 1.5 inches wide; pointed at apex and flattened at base; surface of fruit with 3 longitudinal and many transverse ridges; mesocarp thick and woody; seeds, usually 3, compressed, broadly obovoid, warty, about 1.5 inches long and one wide.

Under favorable conditions of soil and climate both species are rapid growers. The *A. fordii* begins to bear fruit when about 3 years old and sometimes earlier. The *A. montana* does not grow quite so rapidly as the *A. fordii* and begins to bear about the fourth or fifth year. When the trees in China are 9 or 10 years old, they bear from 1 to 5 bushels of fruit. The seeds constitute slightly over half the weight of the matured fruit, the kernels about 30, and the oil about 20 per cent. The seeds are commonly called "nuts." The oil content of the kernels ranges from about 40 to 58 per cent, depending on their moisture content. Kernels from thoroughly matured seeds usually contain about 50 per cent of oil. A bushel of the air-dried mature fruits weighs 25 to 27 pounds. A ton of them will yield about 320 pounds of oil and 900 pounds of press cake. A 100 pounds of fruits will yield from 2 to 2½ gallons of oil.

From about 1923 tung tree planting on a commercial scale has been in progress in the United States. In the beginning this was confined to Florida and came about through the activities of the then recently formed American Tung Oil Corporation, which was organized primarily to demonstrate the possibility of growing tung trees for fruit on a commercial scale. From its demonstration farm near Gainesville, it supplied both seed and seedlings besides information on tung tree culture to those who became interested in establishing groves. At about this time (1923) the University of Florida Agricultural Experiment Station at Gainesville became more actively interested in studying the tung tree and it is still engaged with investigations dealing with the various prob-

lems arising in connection with this industry. Much valuable information is to be found in this Station's bulletins on the tung tree.

As interest in tung tree culture extended into other southern states, their respective Agricultural department and experiment station personnel took steps to cooperate with this movement, and they also have issued several publications on the tung tree.

To assist further with the development of the tung oil industry, Congress in 1938 passed a bill and appropriated funds for the establishment and operation of tung tree and oil regional laboratories under the direction of the Bureau of Plant Industry and the Bureau of Chemistry and Soils which is known now as the Bureau of Agricultural Chemistry and Engineering. Both Bureaus have established laboratories at Gainesville, Florida, and at Bogalusa, Louisiana. In addition to these the Bureau of Plant Industry has another at Cairo, Georgia. These units are now actively engaged in the investigation of various agronomical and chemical problems confronting the American tung oil industry.

Up to 1928 all the seed which had been produced were required for planting purposes, but that year a sufficient quantity of them was available so that the Alachua Tung Oil Company near Gainesville, Florida, was able to produce over a thousand gallons of oil. In 1932 over 16,000 gallons of tung oil were produced in Florida. Shortly afterward, some of the older groves in the other states came into bearing. From the 1938 crop harvested from 48,700 acres of trees in Louisiana and Mississippi, 947,000 pounds of oil was produced. At the same time 20,500 acres of trees located in Florida and Georgia gave a crop of fruits from which 1,785,000 pounds of oil were obtained. Some years the yield of oil has been greatly reduced because of the destruction of the flower buds by freezing after they had become swollen by a very early spell of warm weather.

It may be of interest to some readers to mention that tung trees grow well in a number of different types of soils. They thrive best in well-drained, deep, slightly acid soils which are supplied with an adequate quantity of organic matter. They do not thrive in alkaline soils. Even when planted in suitable soils they require good care, which includes paying special attention to their fertilization, cultivation, and the cover crops; most of this information has been published elsewhere. Although the trees may begin to bear in the second year they are usually 7 or 8 years old before producing what is considered a commercial crop of fruits.

In regard to the average yield of fruit or oil from an acre of tung trees of a given age, which is a question frequently asked, it is impossible to give an estimate of any value at this time because of the lack of adequate data. Not only is there much variation in the yield of the individual trees, but considerable variation also in the number per acre in the case of different plantings.

The so-called tung tree belt includes the southeastern portion of Georgia, the northern third of Florida, and a strip of land from 50 to 100

miles wide paralleling the Gulf of Mexico. This includes portions of Alabama, Louisiana, Mississippi, and Texas.

Attention is called to the following references:

"The Tung Oil Tree," Lord and Williamson, Gainesville, Fla.

"The Tung Oil Tree in Florida," W. Newell, *Univ. Fla. Agric. Exp. Sta., Bull.* **171.**

"China Wood Oil," W. M. Taylor, *U. S. Dept. Commerce, Misc. Series* **125.**

Am. Pt. and Var. Mfrs. Assoc. Circulars, Nos. **205, 241, 255** and **269,** H. A. Gardner.

"Illustrated Review: Questions and Answers on Tung Oil Production in America," 3rd Edition, 60 pp., June **1930,** American Tung Oil Corp., 2201 New York Ave., Washington, D. C.

"The Tung Oil Industry in the South," H. A. Gardner, *Ind. Eng. Chem.,* **24,** 687 (1932).

"Experiences in Tung Tree Culture," G. P. Hoffman, *Proc. Fla. State Hort.,* **1932,** 48.

"Variation in Tung Oil Tree," H. Mowry, *Fla. Agr. Exp. Sta. Bull.* No. 247 (1932).

"Varieties and Practices in the Tung Tree Groves," H. Mowry, *Proc. Fla. State Hort.,* **1932,** 5.

"Tung Oil," C. C. Concannon, Trade Promotion Series No. 133, U. S. Dept. Commerce (1932).

"A Bacterial Disease of the Tung Tree," L. McCulloch and J. B. Demaree, *J. Agric. Res.,* **45** 339 (1932).

"Tung Oil," E. S. Brooks, Bull. 1, Miss. State Dept. Agric. (1933), Jackson, Miss.

"L'Huile de Bois de Chine," Pierre Levy, 34 pp. (1934), Office National des Réchèrchés Scientifiques et Industrielles et Inventions, Bellevue, Seine et Oise, France. All phases of the industry are discussed.

"Tung Oil," L. Rowlands, *Chem. Industries,* **35,** 120 (1934). It discusses both agricultural and industrial possibilities in the United States.

"Zinc Sulphate for Tung Tree Groves," H. A. Gardner, Circ. 452 (1934), Nat'l. Pt., Var. and Lacquer Assoc.

"(British) Empire Production of Tung Oil," L. A. Jordan, *Oil Col. Trdes. J.,* **87,** 628 (1935).

"A Preliminary Report on Zinc Sulphate as a Corrective for Bronzing of Tung Trees," H. Mowry and A. F. Camp, Bull. 273, Fla. Agr. Exp. Sta. (1935).

"The Tung Oil Tree," W. Newell, H. Mowry and R. M. Barnette, Bull. 280, *Fla. Agr. Exp. Sta.* (1935), Gainesville, Florida. Includes a discussion of soils and use of fertilizers.

"Cultivation of Aleurites, Wood Oil Trees," J. Legros, *Monthly Bull. Agr. Sci. and Practice,* **26,** 129 to 160T, 183 to 197T, 237 to 251T (1935). Discusses botanical characters and areas of distribution of the five species, cultivation experiments in various countries, and results obtained up to 1935. Production of oil, export data, specifications, characteristics of oil and bibliography are given.

"The Tung Oil Tree in Texas," P. R. Johnson and S. H. Yarnell, Circ. 75 Texas Agr. Exp. Sta. (1935), College Station, Texas.

"The Tung Oil Tree in Georgia," Circ. 108, Ga. Agr. Exp. Sta. (1936), Experiment, Georgia.

"Culture of Tung Trees in Louisiana," Circ. 17, La. Agr. Exp. Sta. (1936), Baton Rouge, Louisiana.

"Experiments with Aleurites at Morocco," E. Miege, *Bull. Mat. Grasses Inst., Col. de Marseille,* **20,** 57 (1936).

"Diseases of Tung Trees in Louisiana," Bull. 282, La. Agr. Exp. Sta. (1937), Baton Rouge, La.

"Present State of Aleurites Cultivation in the British Possessions," J. Legros, *Monthly Bull. Agric. Sci. and Practice,* **28,** 282T, 311T (1937).

"Bibliography on Tung Tree and Tung Oil," K. Ho and H. Liu, pp. VII + 175, Gov't. Testing Bureau, Hankow, China (1937).

"Tung Oil Culture: Questions and Answers," H. A. Gardner and P. H. Butler, Special Circ., 112 pages, Nat'l Pt., Var. and Lacquer Assoc. (1937).

"Growing Tung Trees in South Mississippi," J. C. Robert and S. R. Greer, Miss. Agr. Exp. Sta. (1938), State College, Miss.

"Variations in China Wood Trees," J. A. Pickett and W. L. Brown, Circ. 115, Ga. Agr. Exp. Sta., (1938).

"Refractive Determination of Oil in Aleurites Seeds," D. Frahm and D. R. Koolhaas, *Rec. trav. chim.*, **57**, 395 (1938).

"Les Aleurites et L'Industrie de L'Huile de Bois de Chine," 255 pages, Intern'l. Inst. Agric., Rome (1938). This book discusses the botany, cultivation, soils, and the present state of cultivation in Africa, the Americas, Asia, and Oceania, and contains an extensive bibliography.

"Contribution à L'Étude des Huiles Seccatives d'Aleurites, Utilisées dans L'Industrie," P. Levy, 62 pp., Levallois-Perret: Société Industrielle d'Imprimare (1938).

"A Survey of Tung Groves in New Zealand," N. H. Taylor, J. K. Dixon, and L. Hodgson, Bull. 66, *Dept. Sci., Ind. Res.*, Wellington, N. Z. (1939).

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"The Tung Oil Trees (Aleurites) and the Tung Oil Industry Throughout the World," 237 pages, Intern'l. Inst. Agric., Rome (1939).

"The Analysis of Tung Fruit," R. S. McKinney and A. F. Freeman *Oil and Soap*, **16**, 151 (1939).

"A Rapid Method For the Determination of Oil in Tung Fruit," R. S. McKinney, *Oil, Pt. and Drug Reptr*, **140** (1941).

"The Moisture Content of Tung Fruit From Its Electrical Resistance," R. S. McKinney, *Oil and Soap*, **18**, 188 (1941).

"Dehydration of Tung Fruit," R. S. McKinney and A. F. Freeman, *Oil, Pt. and Drug Reptr.*, **140**, No. 6, 38 (1941).

"Tung Oil Extraction by a Solvent Process," A. F. Freeman and R. S. McKinney, *Oil, Pt. and Drug Reptr*, **140**, No. 5 (1941).

"Solvent Extraction of Tung Oil," W. G. Rose, A. F. Freeman and R. S. McKinney, *Ind. Eng. Chem.*, **34**, 612 (1942).

Tung trees have been introduced into Queensland and New South Wales, Australia, the North Auckland Peninsula, New Zealand, Argentina, Brazil, Paraguay, Burma, Ceylon, Malaya, Sukhunii and other districts of the Caucasus, U.S.S.R., bordering the Black Sea, Algeria, Morocco, Tunisia, Kenya, Madagascar, Rhodesia, Union of South Africa, Tanganyika and other African colonies, besides many other semi-tropical and tropical regions of the world. In tropical regions, tung tree *(A. fordii)* cultivation has been a failure, and to date none of them has a tung oil industry based on the cultivation of the tung *Aleurites montana*. There are indications that some of the subtropical regions mentioned will become important producers of tung oil.

Tung trees have been grown for a very long time in the southern part of Japan, but even now the quantity of oil produced is small and is not a factor in international commerce.

Tung Oil in China. The fruits in most regions are gathered before they have fully matured, either by hand picking or knocking them off with bamboo poles, which injures the trees. It would be preferable to allow the fruits to drop off, which they do soon after reaching maturity; this is the practice in the United States. The fruits are either heated in large iron pans over a fire and plunged into boiling water, or collected in heaps and allowed to ferment under a covering of straw or grass, until the seeds can be removed by picking them from the husks. The seeds are carried in baskets slung on bamboo poles to the nearest oil mills and sold. At the mills, the seeds are picked over, then the dirt is removed by a simple fanning mill or by pouring the seed from one basket to another in a drafty place. The cleaned seeds are roasted in large

wooden tubs with iron bottoms to dry them. In some regions, the seeds are dried in kilns or by exposure to the heat of the sun. These seeds give a much lighter-colored oil than those roasted. The dried seeds are crushed in a circular stone trough with a heavy stone roller, which is operated by human, buffalo, cow or donkey power. The crushed seeds are subjected to a steaming process in wooden vats until soft and are then mixed with sufficient straw to act as a binder. While still hot, the mixture is formed into round cakes by the aid of broad iron rings. The cakes are about four inches thick and from 15 to 18 inches in diameter, depending upon the size of the press. Before the cakes are put into the press, one or more of the iron bands is removed to allow them to be compressed. The press in most common use consists of a hollowed log of strong wood (held lengthwise by suitable supports resting on the ground) three feet or more in diameter and from 9 to 14 feet in length. The center of the log is hollowed out to a diameter of 15 to 18 inches through a slot cut seven inches wide. About one-fourth of the length of the log at each end of the cut is left solid so as to withstand the pressure. The cakes are slipped through the slot, then raised to a vertical position in the press. When the cakes are in position, discs of wood or stone, having the same diameter as the cakes, but provided with flanges which extend through the slot in the log, are placed at each end of the row of cakes. Pressure is exerted by driving wedges in against the discs with a battering ram, consisting of a log suspended by ropes from overhead. In some presses, provision is made for driving additional wedges other than those at the ends of the row of cakes. The oil drains through a small hole or holes in the bottom of the press, into a vat or tub below. The average yield of oil ranges from about 30 to 40 per cent of the weight of the kernels pressed. The press cake, which is readily removed from the press, after knocking out the wedges, owing to its strong purgative properties, is unsuitable for feeding stock and is chiefly used as a fertilizer.

After the oil is strained through coarse grass cloth, it is collected in covered bamboo baskets lined with many layers of waterproofed paper. These baskets, which hold from 120 to 380 pounds of oil, are carried to the rivers and placed on vessels for transportation to the distribution centers, of which Hankow is the most important. Also Hongkong and Shanghai are important export centers.

At these ports, the baskets of oil are carried to the godowns or storehouses, where the oil is decanted from the sediment, which is returned to the Chinese, who use it for various purposes. During the winter months, the oil solidifies in the baskets and the sediment is cut away from the clarified portion. The oil is separated into different grades, the highest grade being the oil lightest in color, and then tested for purity. The oil is exported in oak barrels or in tank ships. As the oil solidifies when chilled, storage tanks and ship tanks are provided with steam coils for melting the oil so that it can be removed.

Adulteration. Formerly, the tung oil exported from China, particularly during periods of high prices, was grossly adulterated with other

drying and non-drying oils. This practice, however, ceased directly after the establishment of the government testing laboratories at the exporting centers some years ago.

Uses of Tung Oil. The Chinese have used tung oil for many centuries for waterproofing wood, paper, and fabrics. At a very early period both the Chinese and Japanese discovered how to treat the oil so that upon "drying" it would give a clear, hard film. Even now, but very little raw tung oil is used either in the Orient or the Occident. Small quantities are added to the primary coat for cement surfaces and sometimes some is added to certain wall paints. Also cobalt, lead, and manganese tungate driers are made from the oil. After suitable treatment of the oil, it is used in the manufacture of paints, varnishes, enamels, lacquers, automobile brake linings, pressed fiber boards and tiles, linoleum, and printing ink.

Use of Tung Press Cake. The only practical use found as yet for the press cake is as a fertilizer material.

Characteristics of Tung Oil. The range of the characteristics of the oil are as follows: Sp. g. at 15.5° C. 0.939 to 0.943, at 25° C. 0.9341 to 0.9372; $N_D^{20°}$ 1.5163 to 1.5213, at 25° C. 1.5100 to 1.5200; Sap. V. 189 to 195; Iod. No. (Wijs) 157 to 172; Unsap. 0.4 to 0.8 per cent; Titer of fatty acids 37 to 38° C. Oil expressed from sound seed has an acid value from 0.2 to 0.7. Four samples of oil gave thiocyanogen values of 82.6, 82.9, 84 and 84.7.

Oils expressed from Florida (U. S. A.) tung nuts (*A. fordii*) at various times:

Numbers	1	2	3	4
Sp. g., 15.5° C.	0.9440	0.9410	0.9412	0.9394
$N_D^{25°}$	1.5175	1.5190	1.5188	1.5155
Acid V.	1.0	0.5	1.06	0.64
Iod. No. (Wijs)	161.0	166.0	166.1	165.0
Sap. V.	194.4	192.8	191.5	192.3
Unsap. (per cent)	....	....	....	....
Browne's heat test (Min.)	9⅝	10¾	11.	10.
Worstall's heat test (Min.)	5¾	6¼	5.5	7¾

Numbers	5	6	7
Sp. g., 15.5° C.	0.9408	0.9417	0.9410
$N_D^{25°}$	1.5181	....	1.5193
Acid V.	1.3	0.1	0.0
Iod. No. (Wijs)	165.8	170.*	166.6
Sap. V.	192.0	192.4	194.3
Unsap. (per cent)	0.52	0.23	....
Browne's heat test (Min.)	12.	9–10	9¼
Worstall's heat test (Min.)	7½	....	....

* Hübl method.

All these American oils were of light color and entirely free from foots.

Specification and Tests. The American Society for Testing Materials, after much study, has prepared the following specifications for raw tung oil.

	Maximum	Minimum
Sp. g., 15.5°/15.5° C.	0.943	0.940
Acid V. (alcohol-benzol)	8.0	....
Sap. V.	195.0	190.0
Unsap. (per cent)	.75	....
$N_D^{25°}$	1.5200	1.5165
Iodine No. (Wijs)	....	163.0
A. S. T. M. Heating Test (min.)	12.0	....

Color, not darker than a freshly prepared solution of 1.0 g. of $K_2Cr_2O_7$ in 100 ml. pure H_2SO_4 (sp. g. 1.84) or its equivalent in iron-cobalt solution or in Lovibond glasses.

Appearance.....clear and transparent at 65° C.

American Society for Testing Materials Quality Test. The test, a modification of the Worstall procedure, is made in the following manner: Weigh 150 grams of the oil to be tested in an ordinary agateware casserole, having a bottom diameter of 3 inches, and place it on a wide-flanged tripod having a 3-inch opening. The object of the flange is to prevent superheating of the sides of the casserole. Heat rapidly with a full Bunsen flame, stirring with a thermometer until the heat reaches 540° F. (282.2° C.). Turn down the flame and hold the heat as near 540° F. (282.2° C.) as possible, stirring with the thermometer until, on lifting the latter, the oil drops with a pronounced string, showing that polymerization has started. The time required after reaching 540° F. (282.2° C.) until the string is noted is the time of the heat test. For pure tung oils this will not exceed eight minutes. As soon as the oil strings, remove the lamp and the thermometer and stir with a stiff spatula until the oil is solid. After stringing, a pure tung oil will require not over 40 seconds more to become solid. When solid, allow to stand just one minute, then turn out upside down on a clean paper and cut with a clean spatula. Pure tung oil gives a gel that is dry, not adhering to the spatula when cut; that is, firm, crumbling under pressure of the spatula without sticking; and cut portions should crumble under pressure like dry bread crumbs. Adulterated tung oil gives a gel that is soft, sticky, and will not crumble.

Experience has shown that it is extremely important in making the quality test that the directions given above be closely followed in regard to every detail to avoid getting a gel which would result in classifying a pure tung oil as adulterated.

"China Wood Oil: Patents, Technology, and Bibliography," G. H. Stevens (845 Broad St., Newark, N. J.), a limited edition.

"Sampling of Tung Oil," *Chem. Age* (New York), **32**, 86 (1924).

"China Wood Oil," M. Toch, *J. Soc. Chem. Ind.*, **44**, 512T, 517T, 527T (1925).

"Drying of Chinese Lacquer Oil Varnishes," A. W. Hixson and Z. Z. Zee, *Pt., Oil Chem. Rev.*, **81**, 10 (1926).

"Adulteration of Wood Oil," *Chem. Met. Eng.*, **30**, 841 (1924).

"Recent Advances in Paint and Varnish Technology," *Oil. Col. Trds. J.*, **69**, 1238 (1926).

"Varnish for Preserve Cans," H. Serges, *Farben. Ztg.*, **32**, 695 (1927); *Chem. Abs.*, **21**, 1191 (1927).

"Chlorinated Rubber and Tung Oil Varnish," *Pt., Oil and Chem. Rev.*, **84** (Aug. 4), 10 (1927).

"U. S. China Wood Oil Importers' Trading Rules," *Oil, Pt. and Drug Reptr.*, **111**, No. 14, 21 (1927).

Am. Paint and Varnish Mfr's Assoc. Circulars, by H. A. Gardner, No. **264**, "Quick Drying Tung Oil Varnishes"; No. **267**, "Tung Oil in Lacquers for Exterior Wood Surfaces" No. **299**, "Observations on Painting Plaster and Cement"; No. **256**, by H. A. Gardner and H. C. Parks, "*Alpha* and *Beta* Elaeostearin Products from Tung Oil."

Composition of Tung Oil. Prior to 1936, investigators who examined tung oil from *Aleurites fordii* seed reported the following range of percentages of acids calculated as glycerides: Elaeostearic 76 to 82, oleic 10 to 16.4, and saturated acids 2.7 to 8.9. H. P. Kaufmann and J. Baltes [*Ber.*, **69**, 2676 (1936)] investigated two samples of oil which gave iodine numbers of 160.8 and 163.2, thiocyanogen values of 84 to 84.7, diene values of 68.0 and 70.0. They calculated from their analytical data that the mixed fatty acids from these oils contained the following percentages of constituents: Elaeostearic 74.5 and 76.7, linoleic 9.7 and 9.3, oleic 8.0 and 6.9, saturated acids 3.6 and 2.6 per cent. L. A. Jordon [*J. Soc. Chem. Ind.*, **53**, 1T (1934)] stated, however, that many unsuccessful attempts had been made trying to detect the presence in tung oil of an acid having two double bonds. The procedures used may possibly account for these negative results. McKinney and Jamieson [*Oil and Soap*, **15**, 30 (1938)] found but little linoleic acid in American tung oil. Their investigation of this oil indicated that it contained the following percentages of acids: Elaeostearic 86.3, linoleic 0.6, oleic 3.9, and saturated acids 4.4. They found that the α-elaeostearic acid, in contrast to the β-acid, reacted with maleic anhydride only to the extent of 86.6 per cent of the calculated quantity, and this use was not taken into consideration by previous investigators.

When tung oil is heated above 280° C. it has the unique property of solidifying to a jellylike mass. Several tests, based on this property, have been devised for testing the purity of the oil. The well-known Browne heat test [*Analyst*, **37**, 410 (1912)] will be described.

Apparatus—test tubes (15¾ × 1.6 cm.); corks to fit test tubes with a perforation which permits a glass rod 18 cm. long to be easily moved up and down; an 800-cc. beaker (15¾ × 10 cm.); a perforated cover for beaker to support 3 test tubes and thermometer. Method: In each of 2 test tubes, place 5 cc. of the oil to be tested and 5 cc. of the control sample in a third tube. Cork the tubes and insert the rods. Fill the beaker half full with cottonseed or soybean oil and suspend the thermometer 1.5 cm. from the bottom of the beaker. Heat the oil bath to 293° C. and suspend in it the 3 test tubes with the 5-cc. portions of oil, each 15 cm. above the bottom of beaker. Remove source of heat for about 45 seconds, then replace it and maintain oil bath as nearly as possible at 282° C. After 9 minutes, raise the glass rods at intervals of 15 seconds. Note time required for each sample to set firm. Pure tung oil sets firm in from 9 to 12 minutes. Samples of American tung oil frequently are firm in less than 10 minutes. Browne has shown that the presence of 10 per cent of soybean or other oil increases the time of setting 2.5 to

3 minutes. When the test is properly made it is possible to detect the presence of 5 per cent of foreign oil.

P. E. Jameson [*Analyst,* **45,** 328 (1920)] has shown that free fatty acids, when present in amounts of 2 per cent or more, increase the time of gelatinization, but after the removal of the free fatty acids the oils gave tests from 11.5 to 12 minutes instead of 13 to 14, as found with the untreated oils. The best procedure found for the removal of the acids was to mix 5 grams of dry calcium hydroxide with 100 grams of oil, stir thoroughly, then filter and apply the test to 5-cc. portions of the filtrate. A high-grade calcium hydroxide should be used.

Worstall's test, as modified by E. R. Bolton and K. A. Williams [*Analyst,* **51,** 335 (1927)], follows: Place 150 grams of the sample to be tested in a stout aluminum beaker (3 inches in diameter and 4 inches high) and heat so as to reach a temperature of 285° C. in approximately 4 minutes. During the heating, stir the oil vigorously with a thermometer. When the temperature is 285° C., start a stop-watch, continue the stirring, and note the time when polymerization begins, indicated by the failure of the oil to drop from the thermometer when raised. It is important to maintain the temperature as close as possible to 285° C. Pure tung oil gives a heat test in less than 8 minutes; those of fine quality usually give the test in 7 minutes or less. Bolton and Williams state that if a long-stem thermometer is used, a stem connection must be applied. A variation of 3° C. from standard temperature throughout the polymerization test will cause a difference of as much as one minute.

Bolton and Williams (*loc cit.*) have extended their modification of the Worstall test as follows: Cut from the center of the mass of polymerized oil about 2 grams, weigh, and transfer to a mortar which contains 3 grams of clean dry sand and 20 cc. of petroleum ether. Carefully incorporate the mixture in the mortar with a pestle until most of the petroleum ether has evaporated. Transfer the bulk of the mixture to an extractor, rinse the mortar thoroughly with small portions of petroleum ether, adding them to the extractor, and extract in the usual manner. After the extraction is completed, evaporate the solvent and weigh the residue, which, in the case of tung oil, amounts to about 28 ± 2 per cent. The authors examined many oils and found that no authentic tung oil gave over 30 per cent, provided that the polymerization had been actually made at about 285° C. Tung oil heated only to about 270° C. gave an extract of about 42 per cent. "In the case of adulterated oils the whole of the adulterant is obtained in the extract together with a small proportion of unpolymerized tung oil, except in the case of tung oil adulterated with linseed oil, which yields, after polymerization, approximately half the weight of the adulterant in the extract." It should be noted that the free fatty acids of tung oil do not polymerize to any extent, and when an oil contains much over 2 per cent of free fatty acids allowance must be made in computing the quantity of adulterant. Before the polymerization of the sample, the free fatty acids may be removed as already described under the Browne heat test.

A method proposed by J. N. Goldsmith [*J. Oil Col. Chem. Assoc.*, **9**, 342 (1926)] for the determination of tung oil alone or in mixtures is based upon the precipitation of the tung oil with nitrous acid. After purification of the precipitate with water, alcohol, and petroleum ether, it is dried in an atmosphere of inert gas and weighed. For details of method and results, the original must be consulted. The author has had no experience with this method.

Properties. Tung oil of good quality can be stored in full containers in the dark for several years without change, except a slight increase in acidity. Samples have been kept in the laboratory for about six years, without showing deterioration. Upon exposure to light, in the absence of air, the α-elaeostearin of the oil gradually changes to the β-glyceride, which separates as a white precipitate. The same change takes place more rapidly if a small percentage of sulfuric acid is dissolved in the oil. The purified β-elaeostearin melts at 61° to 62° C. Gardner and Parks (*U. S. Pt. Mfrs. Assoc. Circ.* **256**, 1925) have shown that "light-struck" oils give quite as satisfactory varnishes as those prepared from oils free from the β-glyceride. In view of several large shipments of the oil to the United States, which contained notable quantities of precipitated β-elaeostearin, Gardner (*Circ.* **270**, 1926) has suggested that the oil while in the steamers may have come in contact with some sulfur or pyrites remaining from a previous cargo.

Tung oil, on account of its laxative action, is not used for edible purposes. Recent experiments on rabbits and dogs by Dr. O. B. Hunter with the oil and the β-glyceride indicated that there was no evidence of toxic effect. When given in relatively large doses it had a mild laxative action without any irritating effect on the intestines.

A characteristic of tung oil is its high dispersive power, which at 40 is 0.0371, as compared with 0.0218 for linseed oil.

The gelatinization to a solid mass, when the oil is sufficiently heated, is due partly, if not entirely, to the polymerization of a portion of the glycerides present. Rhodes and Potts [*Chem. Met. Eng.*, **29**, 533 (1923)] found that in preventing gelatinization of the oil when heated, the substances with which they experimented stand in the following order: glycerin, oleic acid, rosin, ester gum, paracoumarone resin, and linseed oil. By the addition of about 6 per cent of glycerin, tung oil could be "bodied" without difficulty at 280° C. in the presence of 0.2 per cent of lead as linoleate. Rasquin [*Chem. Abs.*, **20**, 117 (1926)] produced a "stand oil" by heating tung oil mixed with decalin (decahydronaphthalene) and the resulting product gave a good film upon drying.

When tung oil of good quality is heated for a short time at about 200° C., it is noticeably bleached. M. Toch [*Oil, Paint, Drug Reptr.*, **107**, No. 17, 22 (1925)] states that the oil may be satisfactorily bleached by heating it to 120° C. for thirty minutes and agitating it with 5 per cent of fuller's earth or with 2½ per cent each of fuller's earth and bone char, but treatment with activated chars solidified the oil.

Eibner and Munzert (*Brit. Chem. Abs.*, **B**, **1927**, 707) state that

the gel formation essential to true drying proceeds more rapidly in tung oil films than in those of any other oil, because of the absence of any appreciable quantity of mixed glycerides, as well as of its strong tendency to gelatinize.

Rhodes and Ling [*Ind. Eng. Chem.*, **17**, 508 (1925)] have shown that raw tung oil, upon drying, absorbs 44 per cent of oxygen in a period of 500 hours, and during this time 36 per cent of volatile matter is given off. Their study indicated that the oxidation of this oil was an autocatalytic reaction, like that of drying linseed oil. They also found that when rosin is added to tung oil, the oxidation proceeds in two distinct stages: the first continues until 2.5 per cent of oxygen has been absorbed, then the more rapid second stage begins and continues to the completion of the oxidation. The oxidation is accelerated by the addition of cobalt, lead or manganese driers, but in the case of the cobalt drier, the oxidation of the oil or a mixture of oil and rosin proceeds without showing consecutive stages of reaction. When raw tung oil dries, the film is dull, opaque (frosted) and wrinkled. Fahrion's hypothesis, that the high viscosity of the oil and the resulting slow diffusion of oxygen into it accounts for the unequal volume changes in the top skin and under layer is quite generally accepted. The peculiar matted and webbed surface of the dried film was considered by Marcusson [*J. Soc. Chem. Ind.*, **42**, 838A (1923)] to be due to the formation of crystals of the β-elaeostearin; but microscopic examination failed to show any crystalline structure. Besides, this mat-like condition of the surface of the film is also obtained when the oil is allowed to dry in the dark, whereas the formation of β-elaeostearin requires the exposure of the oil to light. However, it is not to be inferred that dried raw tung films exposed to the light contain no β-elaeostearin. The addition of metallic driers, resinates, rosin, ester gum and linseed oil to the oil greatly reduces or eliminates these surface defects of the dried film. J. Marcusson [*J. Soc. Chem. Ind.*, **41**, 866A (1922)] states that the formation of β-elaeostearin causes the film of dried raw tung oil to be lacking in durability, but when the oil is heated to a high temperature with rosin or other ingredients in the manufacture of varnish, the tung oil is converted into polymerized products which no longer give the β-glyceride on exposure to light, but upon drying give an elastic and uniform film. However, Gardner and Parks (*loc. cit.*) found that good films were obtained in oils containing the β-glyceride; even a film from a benzol solution of the pure β-elaeostearin was hard and resistant to abrasion. The action of rosin or other substance in preventing the formation of a frosted film upon drying indicates that it may act as a solvent for the β-glyceride, when present, and it may also tend to prevent its formation.

In spite of the very numerous investigations which have been made, much remains to be discovered, particularly in connection with the changes which take place and the products found during the drying of tung oil.

Additional information will be found in the following references:

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"Drying of Fatty Oils," L. Auer, *Chem. Abs.*, **21**, 172 (1927).
"New Theory of Drying of Fatty Oils," A. V. Blom, *Chem. Abs.*, **21**, 172 (1927).
"Gas Coagulation Theory as Applied to the Drying of Fatty Oils," L. Auer, *Chem. Abs.*, **21**, 3475 (1927).
"Determination of Composition of Tung Oil by Means of Thiocyanogen Adsorption," H. P. Kaufmann, *Ber.*, **59**, 1390 (1926); *Analyst*, **51**, 473.
"China Wood Oil," M. Toch, *J. Soc. Chem. Ind.*, **44**, 512T, 517T, 527T (1925).
"The Drying Process of Chinese Wood Oil," W. Schmidt, *Chem. Abs.*, **18**, 2968 (1924).
"Chinese Wood Oil," A. Eibner, O. Merz and H. Munzert, *Chem. Abs.*, **18**, 3728 (1924).
"The Oxidation Processes in Drying Chinese Wood Oil," O. Merz, *Chem. Abs.*, **20**, 2255 (1926).
"Non-Identity of Elaeostearic Acid Tetrabromide from Tung Oil with Ordinary Linoleic Acid Tetrabromide," B. H. Nicolet, *J. Am. Chem. Soc.*, **43**, 938 (1921).
"The Chemistry of Drying Oils," R. S. Morrell and H. R. Wood (E. Benn, Lt., London, **1925**).
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In this connection, also consult Bauer and Rohrbach, *Chem. Umschau.*, **35**, 53 (1928); *J. Oil Col. Chem. Assoc.*, **9**, 299 (1928).
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"Tung Oil IV and V," A. Eibner and E. Rossman, *Brit. Chem. Abs.*—B. **1928**, 934.
"Some Observations on Cooking China Wood Oil," R. L. Houck, *Pt., Oil, Chem. Rev.*, **86**, No. 21, 10 (1928).
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"Constitution and Drying of Tung Oil," H. A. Gardner and G. G. Sward, *Pt., Oil and Chem. Rev.*, **88**, No. 22, 10 (1929).
"Determination of Tung Oil," J. Marcusson, *Farben Ztg.*, **35**, 1203 (1930); *Brit. Chem. Abs.*—B, **1930**, 467.
"Constitution and Drying of Tung Oil," H. A. Gardner and G. G. Sward, *Pt., Oil, Chem. Rev.*, **88**, No. 22, 10 (1929).
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"Chemical Studies on Tung Oil Seeds. II. Physical and Chemical Properties of Proteins Isolated from Seeds of *Aleurites fordii*," Peh-Wung Liu, *J. Agric. Chem. Soc. (Japan)*, **11**, 781 (1935); *Chem. Abs.*, **30**, 2409 (1936).

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"Nomograph for Iodine Value of Tung Oil," C. S. Wan and K. Ho, *Ind. Eng. Chem. Anal. Ed.*, **8**, 282 (1936).

"Diene Synthesis in the Field of Fats. II. Composition of China Wood Oil," H. P. Kaufmann and J. Baltes, *Berichte*, **69**, 2676 (1936).

"Polarization and Electric Moment of Tung Oil," T. Y. Hsii and C. T. Kivei, *J. Chinese Chem. Soc.*, **4**, 105 (1936); *Brit. Chem. Abs.*—**B 1936**, 1000.

"The Substitution of Tung Oil," J. R. Stewart, *Drugs, Oils and Paints*, **52**, 404 (1937).

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"The Drying Oils," A. E. Reineck, *Pt., Oil, Chem. Rev.*, **99**, No. 5, 9 (1937).

"Film-Forming Oils," W. V. Lee, *Oil Col. Trds. J.*, **91**, 833 (1937).

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"The Study of Drying Oil Problems by Experiments in Monolayers," G. Gee *J. Soc. Chem. Ind.*, **56**, 1132 (1937).

"Refractometric Determination of Oil in *Aleurites* Seeds," E. D. G. Frahm and D. R. Koolhaas, *Rec. trav. chim.*, **57**, 395 (1938).

"Dermatitic Properties of Tung Oil," M. W. Swaney, *Ind. Eng. Chem.*, **30**, 514 (1938). Gives 25 references.

"The Iodine Value of Tung Oil," J. D. von Mikush, *Oil and Soap*, **15**, 186 (1938).

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"The Thermal Polymerization of Drying Oils," C. P. A. Kappelmeir, *Chem. Ztg.*, **62**, 821, 843 (1938), *Chem. Abs.*, **33**, 1969 (1939).

"Reaction of Wijs Solution with Tung Oil," S. W. Wan and D. B. Hu, *J. Am. Chem. Soc.*, **61**, 2277 (1939).

Abrasin or Mu (Tung) Oil. This oil is obtained from the seeds of the tung tree *Aleurites montana*, which has been briefly described under tung oil. The *A. montana* is indigenous to China and Indo-China. In recent years, through the activities of the experiment stations of the Institute of Agronomic Research, a remarkable increase in the production of this oil in Indo-China has resulted. For many years there it has been planted as a "shade tree" on the coffee and tea plantations. As in the case of the *A. fordii*, experiments have been made and others are in progress to cultivate it in many tropical and subtropical regions of the world. At present, even in the more favorable subtropical regions, there is no important production of the oil outside of China and Indo-China.

The fruits contain from 35 to 46 per cent of the nuts. The kernels, which amount to from 55 to 64 per cent of the nuts, contain from 51 to 67 per cent of oil. The range of the characteristics of the oil is as follows: Sp. g. at 15.5° C. 0.9360 to 0.9421, at 25° C. 0.9321 to 0.9357; $N_D^{25°}$ 1.5130 to 1.5190, at 20° C. 1.5132 to 1.5190; Sap. V. 190.2 to 195; Iod. No. (Wijs) 156 to 167 (mostly 161 to 164); Unsap. 0.4 to 0.5 per cent. Usually the period of time for gelation by various heat tests is somewhat

longer than that for the *A. fordii* oil. The gelation period for samples of the oil heated to 282° C. range from about 13 to 18 minutes.

Attention is called to the following references:

"A Note on Tung Oil from *A. montana* and Specification Tests," L. A. Jordan, *J. Soc. Chem. Ind.*, **53**, 21T (1934).

"Cultivation of *Aleurites* in Indo-China," D. Deuss, *Récherchés et Inventions*, No. 249, 235 (1935).

"Abrasin (Mu) Oil. A Quick Drying Oil from *A. montana*," G. S. Sward, Circ. 491, Nat. Pt., Var., Lacquer Assoc., (1935).

"Wood Oil from *Aleurites Montana*," A. B. Boelman, *Landbouw (Landbonkundig Tijdschrift Voor Nederlandsch-Indie, Buitenzord, Java)*, **13**, 109 (1937).

"Relations between the Constants of Wood Oil," E. D. G. Frahm and D. R. Koolhaas, *Rec. trav. chim.*, **57**, 79 (1938); *Chem. Abs.*, **32**, 3174 (1938). It was found that only with fresh oils does a linear relation exist between the diene number and the refractive index. 75 samples of expressed *A. montana* oil (Java) were tested.

"Tung Oil in Indo-China," *Bull. Imp. Inst.*, **37**, 32 (1939).

Japanese Tung (Wood Oil). This oil is obtained from the seeds of the trèe *Aleurites cordata* of the *Euphorbiaceae*. It is native to Japan, being found throughout the island of Hondo. Fukui is the chief producing province. Both the cultivated and wild trees there do best on the mountain and hillsides. In general appearance and size this tree is similar to *Aleurites montana*. The fruit, which is similar and distinct from those of *A. fordii* and *A montana*, contains from 3 to 5 seeds. The seeds, which weigh about one gram, consist of 64 per cent of kernel and 36 of shell. Kernels having a moisture of 2.9 per cent contained 67.5 per cent of oil.

Although the oil contains much elaeostearic acid, as found by K. H. Bauer [*Chem. Umschau*, **32**, 3 (1925)], when heated it does not gelatinize in a short time as is the case with tung oil. However, when several drops of the oil are placed upon a 10 per cent chloroform solution of antimony trichloride, the oil solidifies at once, as does tung oil.

Characteristics of oil. Sp. g. at 15° C. 0.934 to 0.940; $N_D^{20°}$ 1.5020 to 1.5093; Iod. No. 148 to 160; Sap. V. 189 to 196; R.M.V. 0.3 to 0.4; Unsap. 0.4 to 0.8 per cent.

R. S. McKinney and G. S. Jamieson [*Oil and Soap*, **14**, 2 (1937)] investigated the oil which they expressed from a sizable sample of seeds received from the Yokohama Nursery Company, Yokohama, Japan. The characteristics of the oil were as follows: Sp. g. at 25°/25° C. 0.9313; $N_D^{25°}$ 1.5059; Sap. V. 190.2; Iod. No. (Rosenmund-Kuhnheim) 145.2; SCN V. 80.9; Acid V. 0.60; Unsap. 0.57 per cent; Sat. acids (Bertram) 6.18 per cent. Calculations (based upon the assumption that no linoleic acid was present) indicated that the oil contained 70.5 per cent of elaeostearic acid and 18.5 per cent of oleic acid. More recently, R. Yamasaki, K. Itihara, and K. Arisake [*J. Soc. Chem. Ind. (Japan)*, **43**, 154B (1940); *Chem. Abs.*, **34**, 6463 (1940)] reported that the oils examined by them gave iodine numbers (Wijs, 2 hrs.) of 154, 161, and 164, and diene values (Ellis-Jones) 50.3, 51.2, and 54.1. Using the average of these values for the 3 oils, they calculated the average quantity of elaeostearic acid to be 57.6 per cent.

In Japan, where production varies from 400,000 to 2,500,000 pounds

per year, the oil is used to waterproof paper and fabrics and in the manufacture of paints, varnishes, and other products.

For some years, the "All Union Selection Station of Humid-Subtropical Cultures" at Sukhumi, Transcaucasus (U.S.S.R.) has been studying the cultivation of the *cordata* and other *Aleurites* species. The characteristics of the *cordata* oils produced there are similar to those given by the Japanese oil. Also, cultivation of this tree has been studied in several other countries including the Belgian Congo [L. Adriens, *Congo,* **1**, 499 (1938)] where some study has been made of the oil from seed produced there.

Bagilumbang Oil. This oil, which is known also by the names of banucalag and soft lumbang, is obtained from the seeds of the tree, *Aleurites trisperma,* native to the Philippines. There, as well as in Malaya and some other tropical localities, the tree is being cultivated on a small scale. Unlike tung trees it appears to thrive in calcareous soils. The tree grows to a height of about 45 feet. The somewhat round angular fruit is about 2 inches in diameter and contains 3 seeds, which have brittle, hard shells about 0.25 inch thick. When the nuts dry, the kernels, unlike those of the lumbang nuts, shrink slightly from the shells; consequently, it is easy to crack the thin shells and extract the kernels. The kernels constitute about 60 per cent of the weight of the nuts and contain about 50 per cent of oil. The oil should be expressed within a few months after the nuts have fallen from the trees, otherwise an inferior oil will be obtained due to the deterioration of the kernels. As the press cake is poisonous, it is suitable only for use as a fertilizer.

Richmond and Rosario [*Philip. J. Sci.,* **2**, 439 (1907)] examined the oil and obtained the following characteristics: Sp. g. at 15° C. 0.9368; Sap. V. 200.3; Iod. No. (Hanus) 158.5; $N_D^{15°}$ 1.483. H. A. Gardner [the *U. S. Pt. Mfrs. Assoc. Circ.* **75**; *J. Soc. Chem. Ind.,* **37**, 215A (1918)] found the following: Sp. g. at 15° C. 0.9380; Sap. V. 190 to 194; Iod. No. 161 to 164.2; $N_D^{25°}$ 1.4929.

G. S. Jamieson and R. S. McKinney [*Oil and Soap,* **12**, 146 (1935)] examined the seeds; which were collected from an old tree growing at Homestead, Florida. They consisted of 63.3 per cent of kernel and 36.7 of shell. The kernels, which varied in weight from 4 to 5.3 grams, contained 59.94 per cent of oil and 3.95 of moisture. The characteristics of the solvent-extracted oil were as follows: $N_D^{25°}$ 1.4971; Sap. V. 196.0; Iod. No. (calculated) 187.0; SCN V. 69.9; Acid V. 0.87; Unsap. 0.5 per cent; Sat. acids (Bertram) 16.5 per cent; Unsat. acids 77.0 per cent. No gelation of the oil occurred when heated up to 310° C.

A small portion of the oil mixed with an equal volume of a 10 per cent chloroform solution of antimony trichloride solidified in about 2 hours, whereas American tung oil similarly treated solidified in one-half hour. A film of the oil on a glass slide, at ordinary temperature, solidified to a non-tacky condition within 36 hours. The film, which was rough and opaque, was similar to that formed on tung oil. H. A. Gardner [*Pt. Mfrs. Assoc. Circ. 75* (1919)] reported that a varnish

made with the oil gave a waterproof film. He concluded from his experiments that the properties of the oil made it desirable for use in the manufacture of paints and varnishes.

Jamieson and McKinney (*loc. cit.*) calculated from their analytical data that the oil from Florida seed contained the following percentages of acids as glycerides: Oleic 12.9, elaeostearic 67.1, and saturated acids 17.3. However, four years later E. D. Frahm and D. R. Koolhaas [*Rec. trav. chim.*, **58**, 277 (1939)] who examined a sample of the oil having similar characteristics from seed grown in Java, definitely showed that it contained a notable quantity of linoleic acid, and consequently less elaeostearic acid than that given above for the Florida oil. This oil gave the following characteristics: Sp. g. at 15/15° C. 0.9344; $N_D^{25°}$ 1.4980; Sap. V. 190.8; Iod. No. (Wijs) 133.1; Diene V. (Ellis and Jones) 43.2; R.M.V. 0.61; Acid V. 4.9; Unsap. 0.5 per cent; Sat. acids (Bertram) 17.0 per cent; Total acids 93.1 per cent.

The diene value indicated that this oil contained 47.3 per cent of elaeostearic acid. It was calculated that the oil contained the following percentages of acids as glycerides: Elaeostearic 49.4, linoleic 18.8, oleic 11.3, palmitic 9.5 and stearic 8.3.

More recently, Jamieson and W. G. Rose examined a sample of oil expressed from seeds grown in Puerto Rico. The oil gave the following characteristics: $N_D^{25°}$ 1.4942; Iod. No. (Wijs) 127.2; SCN V. 71.2; Diene V. (Ellis and Jones) 34.9; Sat. acids 18.0 per cent; Unsap. 0.51 per cent. Calculations which were based on an empirical diene value for α-elaeostearic acid of 89.5 gave the following percentages of acids in the oil: Elaeostearic 39.0, linoleic 19.9 and oleic 18.4. It will be observed that this oil contains much less elaeostearic acid and much more oleic acid than those previously examined.

Lumbang or Candlenut Oil. Lumbang or candlenut oil is obtained from the seeds of the tree *Aleurites moluccana,* which is found in Polynesia, India, and the Philippines, Java, Australia, and the Pacific Islands, including Hawaii. The tree has been introduced into the West Indies, Brazil, Florida, and elsewhere.

Trees growing in India and other regions which were classified as *A. triboba* have been found to be identical with those classified as *A. moluccana.*

The tree reaches a height of about 60 feet and has long, wide-spreading branches with large, irregularly lobed and entirely ovate leaves. The walnut-like ovoid fruits are about 2 inches in diameter and contain one or two seeds enclosed in hard tough shells, which have a rough and ridged exterior.

Formerly, the Hawaiians strung the nuts together on sticks and used them for lighting their houses; hence the name "candlenut."

The fruits are allowed to fall and lie on the ground until the outer portions have decayed; then the nuts are collected.

As the nuts are difficult to crack, it is customary in some localities to collect them in shallow pits and cover them with straw, which is set on fire. The heated nuts are sprinkled with cold water, which causes

the shells to crack. In other places the nuts are boiled for several hours with water, which effects the separation of the kernels from the shells, and then cracked by hand. During the boiling, the kernels change from white to brown and yield only dark-colored oil. R. H. Aquilar of the Philippine Bureau of Science heated the nuts to 95° C. for 3 or 4 hours, then plunged them into cold water, where they remained overnight. By the next morning the shell had broken so that the kernels were easily removed. From these kernels, oil of good quality was expressed. The native procedure, which yields the best oil, is to crack the sun-dried nuts by hand and pick out the kernels with a pointed instrument—a slow and tedious operation. The kernels are crushed and are usually pressed hot in primitive mills. Cold-pressing, however, yields a pale yellow oil, while the hot-pressed oil varies from yellow to brown. The press cake, owing to its strong purging effect, is used only as a fertilizer. In connection with native feasts, the Hawaiians use the roasted kernels, but even then, they can be eaten only in very small quantities. The kernels constitute about 30 per cent of the nut and contain from 55 to 65 per cent of oil. From 100 pounds of nuts it is said that about 17.5 pounds of oil is yielded by pressure.

Characteristics. Sp. g. at 15° C. 0.920 to 0.927; Sap. V. 190 to 193; Iod. No. (various methods) 140 to 164; N_D at 15° C. 1.4790, at 20° C. 1.4772 to 1.4783, at 25° C. 1.4770 to 1.4783, and at 40° C. 1.4696; Unsap. 0.9 per cent.

Composition. Jamieson and R. S. McKinney [*Oil and Soap,* **14,** 203 (1937)] expressed the kernels from 95 pounds of candlenuts from the Philippines in a Carver hydraulic press. The very pale-yellow oil gave the following characteristics: Sp. g. 25°/25° 0.9233; $N_D^{25°}$ 1.4749; Sap. V. 190.8; Iod. No. (Hanus) 151.7; SCN V. 97.1; Acid V. 1.15; Unsap. 0.30 per cent; Hexabromide V. (Steele and Washburn) 19.3, Sat. acids 8.39 per cent; Unsat. acids 86.61 per cent.

The oil was found to contain the following percentages of acids: Oleic 26.23, linoleic 39.62, linolenic 20.76, palmitic 4.38, stearic 3.93 and arachidic 0.08 per cent. The oil contains no elaeostearic acid.

A Brazilian sample of the oil known there as "iguape" was examined by Moacyr Silva [*Rev. chim. ind. (Rio de Janeiro),* **6,** 96 (1937)]. The kernels contained 60 per cent of oil. The oil gave the following characteristics: Sap. V. 192.1; Iod. No. 160.2; $N_D^{20°}$ 1.4731; M. Pt. fatty acids 20.6 °C.

Attention is called to the following references:

"Boletim de Informacoes—Nogueira de Iguape," M. Silva, Rio de Janeiro, 1936. 11 pages.

"Ceylon Candlenut Oil," R. Child, *Oil and Soap,* **18,** 224 (1941).

Properties and Uses. The oil is inedible, because of its laxative properties. West and de Leon [*Phil. J. Sci.,* **24,** 123 (1924)] made a comparison of the blowing of lumbang and linseed oils at 75° C. For the first 30 hours, lumbang oil absorbed oxygen more rapidly than linseed oil, but after 40 hours the two oils absorbed the same quantity of

oxygen. West and co-workers found that in drying powers, raw, boiled and blown lumbang oil compared favorably with linseed oil. West and Smith (*Bur. For. Bull.* **24**, Phil. Bur. Forestry) prepared paints, varnish, printing ink, soap, and a rubber substitute from the oil and reported that satisfactory products were obtained.

However, in view of the large percentage of oleic and the small percentage of linolenic glycerides in lumbang oil, as compared with linseed oil, it would not be expected that the drying powers of the former would be equal to those of linseed oil.

West and Gonzag [*Phil. J. Sci.*, **23**, 277 (1923)] conducted experiments on the hydrogenation of lumbang oil. By using 3 per cent of nickel catalyst, 7 hours' treatment gave a product which melted at 49° to 56° C.; after 15 hours, the melting point was 67° to 69° C.; and after 20 hours, the product melted at 67.5° to 71.5° C., and had an iodine number (Hübl) of 1.08.

In some countries the oil is used as a wood preservative, for making paints, varnish, and soap. In the Philippines, where the oil has been expressed for many years, it is used locally for making paints, for protecting the bottoms of dugouts and other small craft from marine borers, and as a burning oil.

Walnut Oil. This oil is obtained from the walnut kernels of the tree *Juglans regia* (the Persian walnut, which is commonly known as the English walnut). The walnut is extensively cultivated in Europe, China, United States, and elsewhere. The kernels contain from 60 to about 70 per cent of oil. The oil has been expressed commercially for many years in various European countries and more recently from the waste "meats" from the California shelling plants. The kernels from the mature nuts, which have been kept in a dry place for about 3 months after collection, are usually pressed cold in Europe; then the press cake is ground and pressed hot. The cold-pressed, pale-colored oil, which has a delicate pleasant taste, is largely used for edible purposes. The hot-pressed oil is employed in making paints and soap. From very early times, walnut oil has been used in the preparation of artists' "colors," as it is a good drying oil. The usual range of the characteristics is as follows: Sp. g. at 15° C. 0.925 to 0.927; $N_D^{40°}$ 1.469 to 1.471, at 15° C. 1.480; Sap. V. 189 to 197.3; Iod. No. 132 to 152 (usually above 140); Titer 14° to 16° C.; Sol. Pt. −12° to −16° C.

Jamieson and McKinney [*Oil and Fat Ind.*, **6**, No. 2, 21 (1929)] examined a sizable sample of California walnut oil expressed at the Pacific Nut Company's plant at Los Angeles. This oil had the following characteristics: Sp. g. at 25° C. 0.9235; $N_D^{25°}$ 1.4751; Sap. V. 194.5; Iod. No. (Hanus) 158.5, (Wijs) 161.7; Acid V. 5.1; Acetyl V. 6.1; R.M.V. 0.1; Pol. No. 0.2; Unsap. 0.5 per cent; Hexabromides 8.88 per cent; Sat. Acids 5.34 per cent; Unsat. 89.74 per cent.

The oil contained the following percentages of fatty acids: Oleic 16.9, linoleic 69.7, linolenic 3.1, myristic 0.01, palmitic 4.4, stearic 0.9, and arachidic acid 0.01 per cent. The high iodine value of the Cali-

fornia oil is noteworthy. In 1923, H. A. Gardner (*Am. Pt. and Var. Mfrs. Assoc. Circ.* **189**) examined a sample of oil from California which gave an iodine number of 154 by the Hanus method. This result, together with that determined by the authors, would indicate that California walnut oil is characterized by having an iodine number much higher than that commonly reported for European oil.

Black Walnut Oil. The kernels of the American black walnut, *Juglans nigra,* contain about 60 per cent of oil, for which the following characteristics have been reported: Sp. g. at 15° C. 0.9215 to 0.929; Sap. V. 191 to 195; Iod. No. 135 to 144.

Jamieson and R. S. McKinney [*Oil and Soap,* **13,** 202 (1936)] examined two samples of the oil expressed from the black walnut meat and shell particles which accumulate at the shelling plants. The first sample supplied by the Smalley Shelling Company at Sulphur Springs, Arkansas, was expressed by means of the Anderson oil expeller. The second sample obtained by a hydraulic press from shelling plant waste from Arkansas nuts was furnished by D. C. Ingraham, Berkeley, California. The characteristics of these two oils which were determined were as follows: Expeller oil $N_D^{25°}$ 1.4730; Sap. V. 193.5; Iod. No. (Hanus) 135.1; SCN V. 86.0; Unsap. 0.42 per cent; Sat. acids 5.53; Unsat. acids 88.14 per cent. Hydraulic oil $N_D^{25°}$ 1.4731; Sap. V. 191.5; Iod. No. (Hanus) 140.5; Sat. acids 5.24; Unsat. acids 8.96 per cent.

The expeller oil was found to contain the following percentages of acids: Oleic 34.1, linoleic 46.8, linolenic 7.2, myristic 0.43, palmitic 3.29, stearic 1.77 and lignoceric acid 0.04 per cent.

The oil could be used for either edible or technical purposes. It does not have as strong drying properties as that from the nuts of the *Juglans regia.*

As is well known, the shelled nuts are much in demand for eating as well as in making cakes, candy and ice-cream.

Butter Nut Oil. The kernels of the American butter nut *(Juglans cinera)* amount to about 15 per cent of the nut and contain about 58 per cent of oil. The following characteristics of the oil were determined: $N_D^{25°}$ 1.4764; Sap. V. 191.7; Iod. No. (Hanus) 162.7.

Japanese Walnut Oil. This oil is found in the kernels of the nut of the tree, *Juglans sieboldiana,* S. Ueno and Y. Nishikana [*J. Soc. Chem. Ind. (Japan),* **40,** 313 (1937); *Brit. Chem. Abs.*—B1937, 1366] examined a sample of oil with the following results: Sp. g. at 15° C. 0.9241; N_D 1.4770; Sap. V. 191.0; Iod. No. (Wijs) 149.7; SCN V. 88.4; Acid V. 1.4; Unsap. 0.55 per cent; Sat. acids 6.3 per cent. The insoluble mixed fatty acids contained the following percentages of individual acids: Oleic 22.7, linoleic 62.1, linolenic 8.6 and saturated acids 6.6.

Manchurian Walnut Oil. This oil is found in the nut kernels of the tree, *Juglans manschurica.* The kernels contain about 58 per cent of oil. Y. V. Branke and A. A. Komissarchuk [*Bull. Far Eastern Branch Academy of Science, U.S.S.R.,* No. 14, 85 (1935); *Chem. Abs.,* **30,** 2784 (1936)] examined the oil, with the following results: $N_D^{20°}$ 1.4790;

Sap. V. 188; Iod. No. 158.1; R.M.V. 0.98; Pol. No. 1.08; Unsap. 0.53 per cent; Hexabromides 7.52.

The mixed fatty acids contained the following percentages of constituents: Oleic 18.69, linoleic 76.27, linolenic 2.24, palmitic 2.9, and stearic 0.6.

It appears that the quantity of linolenic acid reported is based upon the amount of ether-insoluble bromides, and consequently is somewhat low.

Hickory Nut Oils. The kernels of the shellbark hickory (*Carya ovata*) constitute about 63 per cent of the nut, and those having a moisture content of 3.5 to 4 per cent contained from 64 to 70 per cent of oil. The characteristics found for the expressed oil by G. O. Peterson and E. H. S. Bailey [*J. Ind. Eng. Chem.*, **5**, 739 (1913)] were as follows: Sp. g. at 24° C. 0.9119; $N_D^{20°}$ 1.4699; Iod. No. 106.8; Sap. V. 189.6; R.M.V. 0.47, and insoluble fatty acids 95.7 per cent.

They also examined the oil expressed from the kernels of the swamp hickory, *Carya amara,* with the following results: $N_D^{20°}$ 1.4699; Iod. No. 105.2; Sap. V. 190.0; R.M.V. 0.48 and insoluble fatty acids 95.6 per cent.

These results indicate that these two oils are very much alike.

Oil from Seeds of Trichodesma Zeylanicum (Nat. Ord. Boraginaceae). The zeylanicum is a weed which grows in abundance in the Morogoro district, Tanganyika Territory, on waste land and old cotton fields. The Imperial Institute [*Bull. Imp. Inst.*, **24**, 443 (1926)], which examined the seed and oil, has reported the following information:

The small seeds, which have a brittle husk and a soft, cream-colored kernel, were found to contain 9.2 per cent of moisture and 28.7 of oil. The golden yellow oil, which was obtained by extraction with petroleum ether, gave the following characteristics: Sp. g. at 15°/15° C. 0.9288; $N_D^{40°}$ 1.4710; Sap. V. 192; Iod. No. (Hübl, 17 hrs.) 161.1; Unsap. 0.6 per cent; Acid V. 0.3; Titer 22°.

A film of oil on glass dried in 6 days; the resulting product was soft. The oil has a pleasant, nut-like taste and might be used for edible purposes. Although it is a drying oil, experiments would have to be made to ascertain for what uses it was best adapted as a paint or varnish oil. As the meal is bitter and contains a substance of alkaloidal nature, it is unsuitable for use as a feed.

Tall (Tallol) Oil. This so-called oil is obtained as a by-product derived from the waste liquors of the pinewood pulp mills. The waste liquor is concentrated by evaporation until the soaps separate. The soap curds are removed and acidified with sulfuric acid. The product which separates is the crude tall oil of commerce. This product was first recovered on a commercial scale some years ago in the Baltic countries of Europe, but recently it is being recovered in quantity in the United States.

It consists of a mixture of fatty and resin acids, sterols, higher alcohols and other constituents. Depending upon the source and factory procedure, the product varies much in composition. The fatty acids

vary from 20 to 60 per cent, the resin acids from 10 to 60, and the unsaponifiable constituents from as low as 5 to at times as high as 24 per cent. The range of the characteristics is as follows: Sp. g. at 15.5° C. 0.950 to 1.00; $N_D^{20°}$ 1.4958; Sap. V. 145 to 175; Iod. No. (Wijs) 120 to 188; Acid V. 145 to 179; Resin Acids No. 40 to 120; Moisture 0. to 3.0 per cent: Unsap. 6 to 20 per cent; ash 1.0 to 3.0 per cent; color, brown to black.

The crude oil is refined by distillation under diminished pressure with the aid of steam. The characteristics are as follows: Sp. g. at 15.5° 0.950 to 0.990; $N_D^{20°}$ 1.4760; Sap. V. 165 to 185; Iod. No. (Wijs) 100 to 150; Acid V. 165 to 185; Resin Acids No. 10 to 80; Unsap. 3.0 to 15%; Ash 0.0 to 0.2%; color, straw to brown. Tall oil when saponified yields a soft soap which is much used in Finland and Sweden. Up to 25 per cent of the usual fats can be substituted by tall oil in the manufacture of hard soap. It is used as a cutting oil as well as for making textile soaps, asphalt, tar and other emulsions, in the preparation of driers, sulfonated oil, and after esterification with glycerine as a drying oil. The pitch remaining from distillation of tall oil is said to be used in the manufacture of ink.

Attention is called to the following references:

"Tall Oil Fat Acids with Regard to Chemistry and Paint Technology," H. Nielson, *Fette u. Seifen*, **44**, 426 (1937).
"Fatty Acids from Pine Wood," J. A. Wallach, *Soap*, **13**, No. 3, 31 (1937).
"Purification of Tall Oil," H. Heller, *Chem. Ztg.*, **10**, 54 (1939).
"Fatty Acids from Pulp Mill Wastes," A. Pollak, *Oil and Soap*, **15**, 33 (1938).
"Rapid Methods for the Estimation of Rosin and Fatty Acids in Tall Oil," R. Hastings and A. Pollak, *Oil and Soap*, **16**, 101 (1939).
"Industrial Utilization of Tall Oil," A. Pollak, *Oil and Soap*, **17**, 87 (1940).
"Sulphonation of Tall Oil. Separation of Rosin and Fatty Acids," F. C. Vibrandt, P. E. Chapman and J. M. Crockin, *Ind. Eng. Chem.*, **33**, 197 (1941).

Cacahuananche Oil. The oil is obtained from the seed in the fruit of the *Licania arborea*, of the Rosaceae family, a native of Central America and Mexico. The single kernel which amounts to 43 per cent of the fruit contains about 69 per cent of oil. The characteristics of the oil expressed from Mexican fruits in our laboratory are as follows: $N_D^{25°}$ 1.5163; Sap. V. 187.3; Iod. No. (Wijs-1 hr.) 153.0; diene V. (Ellis-Jones) 60.9; carbonyl V. (Leithe) 121.4; Unsap. 0.5 per cent; acid V. 0.5; Sat. acids 11.1 per cent; Brown heat test 15.5 minutes. The percentage of the fatty acids in the oil are as follows: Licanic 70.3, linoleic, 7.3, oleic 5.2, elaeostearic 1.5, and saturated acids 11.1. Calculations from analytical data indicated 1.5 per cent of elaeostearic acid, but no confirmatory evidence of it could be obtained.

It should be noted that, as would be expected, the oil is similar to the Brazilian oiticica (*Licania rigida*) oil both in composition and drying properties. [cf. Mexican Oiticica Oil, H. A. Gardner, Circ. 654 (1943). Nat'l. Pt., Var. and Lacquer Assoc.]

Chapter V

The Fatty Acids

The saturated and unsaturated acids found in fats contain even numbers of carbon atoms. The saturated acids with few, if any, exceptions, have a straight-chain structure. The same is true of all the unsaturated acids except those of the chaulmoogric acid group, which have a cyclic structure.

Böhm has shown that tiglic acid ($C_5H_8O_2$) is not present as a glyceride in croton oil. According to Verkade and Coops [*Biochem. Z.*, **206**, 568 (1929)], the oil from *Datura stramonium* does not contain daturic acid ($C_{17}H_{34}O_2$), as repeatedly reported.

It should be noted that Hilditch and co-workers [*J. Soc. Chem. Ind.*, **46**, 462T and 467T (1927)] have definitely shown that hypogeic, rapic and chieranthic acids, reported as occurring in peanut, rape, and wallflower seed oils, respectively, are non-existent; consequently, they receive no further attention in this work.

In regard to the solubility data given under the individual acids, it should be understood that in the case of mixtures, the solubility of an acid is notably greater, because of the presence of the other acids in the solution. Acids of lower molecular weight than that of valeric are readily soluble in water. At 15° C., 100 cc. of water dissolves 3.5 grams of valeric acid, 0.882 gram of caproic acid, 0.079 gram of caprylic acid, and capric acid is much less soluble than caprylic acid. At 100° C., 100 cc. of water dissolves 0.250 gram of caprylic and 0.100 gram of capric acid. Acids above capric in this series are practically insoluble in water. Also, the boiling points which are given for various methyl and ethyl esters, are those reported in the literature, and it should be noted that these temperatures apply to a specific set of experimental conditions that cannot be described here. In fact, the boiling points, or more correctly, distillation temperatures vary somewhat, depending upon the height the vapors rise from the liquid esters to envelop the thermometer, the size of the flask in relation to the quantities of the ester, and the rate of heating. It is very difficult to determine accurately the boiling point of the higher fatty acid esters under diminished pressure.

For the determination of acids from formic to capric inclusive, attention is called to "Steam Distillation of Volatile Acids" by D. C. Dyer [*J. Biol. Chem.*, **28**, 445 (1917)]. For the identification of organic acids with the *para*-phenylphenacyl bromide, *see* Drake and Bromitsky [*J. Am. Chem. Soc.*, **52**, 3715 (1930)].

See Whitemore and Lauro [*Ind. Eng. Chem.*, **22**, 646 (1930)] for the preparation, properties, and uses of heavy-metal soaps made from pure fatty acids (lauric, palmitic, stearic, oleic and erucic acids).

Attention is called to the following references:

"Esterification Processes and Equipment," D. B. Keyes, *Ind. Eng. Chem.*, **24**, 1096 (1932).

"Para-Halogen-Phenacyl Esters of the Normal Fatty Acids," C. G. Moses and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 2101 (1932).

"Composition of Fatty Acid Mixtures. II. A Further Development of the Twitchell Mixed Melting Point Method for the Determination of Individual Saturated Fatty Acids," R N. Wenzel, *Ind. Eng. Chem., Anal. Ed.*, **6**, 1 (1934).

"A Comparative Study of Known Methods for the Determination of Solid Unsaturated Acids in the Presence of Saturated Acids," A. Lyntenberg and T. Dudkina, *Fettchem. Umschau*, **42**, 91 (1935); *Chem. Abs.*, **29**, 7681.

"The Behavior of Linolenic Acid, Linseed and China Wood Oils on Heating," K. Meinal, *Naturwiss.*, **23**, 721 (1935); *Chem. Abs.*, **30**, 2026 (1936).

"Fatty Acid Nitriles, Amides, and Ketones for Extreme-Pressure Lubricants," A. W. Ralston, *et al.*, *Nat. Petrol News*, **28**, No. 50, 59 (1936); *Brit. Chem. Abs.*, —**B193**, 753.

"Use of Thio-Benzyl Thiuronium Chloride for the Isolation and Identification of Organic Acids," J. J. Donleavy, *J. Am. Chem. Soc.*, **58**, 1004 (1936).

"A Method for the Production of Hydroxy Acids," A. W. Ralston and S. T. Bauer, *Oil and Soap*, **13**, 170 (1936); includes also the preparation of nitriles, their properties and uses.

"The Oxidation of Some Polyhydroxylic and Polyethylenic Higher Fatty Acids by Aqueous Alkaline Permanganate," T. G. Green and T. P. Hilditch, *J. Chem. Soc.*, **1937**, 764.

"On Phthalic-mono Per-Acid and Its Application as Oxidation Agent in Place of Benzoic Per-Acid," H. Böhm, *Berichte*, **70**, 379 (1937).

"Cellulose Esters and Ethers," *Chem. Trde. J.*, **100**, 7 (1937). Describes those of fatty acids of higher molecular weight.

"Preparation of Modified Resins by Use of Fatty Acid Derivatives," A. W. Ralston, *Oil and Soap*, **16**, 215 (1939).

"Methods of Analysis of Mixtures of Oleic, Linoleic, and Saturated Esters, and Their Application to Highly Purified Methyl Oleate and Methyl Linoleate," R. W. Riemenschneider and D. H. Wheeler, *Oil and Soap*, **16**, 219 (1939).

"Esters of Aliphatic Thio-Acids of High Molecular Weight," A. W. Ralston, E. W. Segelbrecht and S. T. Bauer, *J. Organic Chem.*, **4**, 502 (1939).

"The Preparation and Properties of High Molecular Weight Primary Amines," A. W. Ralston, *Oil and Soap*, **17**, 89 (1940).

"The Insecticidal Properties of Some Fatty Acid Derivatives," A. W. Ralston, J. P. Barrett and E. W. Hopkins, *Oil and Soap*, **18**, 11 (1941).

"New Fatty Acid Derivatives," A. W. Ralston, *Chem. Met. Eng.*, **48**, 126 (1941).

Acetic Acid CH_3CO_2H; Mol. Wt. 60.11; B. Pt. 118° C.; M. Pt. 16.6° C. The acid is reported to be present in several oils, but in all probability it is not in the form of the glyceride and not a normal constituent of the oils themselves.

***n*-Butyric Acid** $CH_3(CH_2)_2CO_2H$; Mol. Wt. 88.10; B. Pt. 163° C., Sol. Pt. −19° C.; M. Pt. −7° C.; methyl ester B. Pt. 102° C., and ethyl ester at 120° C. Acid is soluble in water, alcohol, ether, and is volatile with steam. It is a normal constituent of milk fat of cow, goat, sheep, etc., whereas human milk fat contains but very small quantities.

Caproic (*n*-Hexanoic) Acid $CH_3(CH_2)_4CO_2H$; Mol. Wt. 116.15; B. Pt. 202° C.; M. Pt. −8° C.; methyl ester B. Pt. 150° C. at 760 mm., 52° C. at 15 mm., and ethyl ester 167° C. at 760 mm. (Solubility of acid 0.09 in water.) M. Pt. of derivatives: amide 100° C., toluidide 75° C., naphthalide 112° C. Solubility of salts: *Lead* (M. Pt. 73° to 74° C.) 1.36 in ether at B. Pt.; *silver* 0.089 in water and 0.029 in 0.05*N silver nitrate*; *barium* 11 in water; *calcium* 4.5 in water; *zinc* 1 in water at 35° C. Volatile in steam.

Various esters, including the allyl, amyl and ethyl caproates, are used in the manufacture of flavorings and perfumes. The acid is used commercially also in connection with the making of certain synthetic pharmaceuticals and other products.

Caprylic (*n*-Octanoic) Acid $CH_3(CH_2)_6CO_2H$; Mol. Wt. 144.21; B. Pt. 236° C. (237.0 corr.); M. Pt. 16.5° C.; B. Pt. 124° C. at 10 mm., solubility in water 0.08 at 15° C.; 0.25 at 100° C.; volatile in steam; methyl ester B. Pt. 207.8° C. at 760 mm. Derivatives: Anhydride B. Pt. 280° to 290° C.; M. Pts.: amide 97° to 98° C., anilide 57° C., toluidide 67° C., naphthalide 95° C. Salts: Ammonium, M. Pt. 70° to 85° C., soluble in methyl and ethyl alcohol, but sparingly so in ether and chloroform. Lead salt, M. Pt. 83.5° to 84.5° C.; solubility in ether at 20° C. 0.09, at B. Pt. 0.55° C. This acid is almost insoluble in petroleum ether. Solubility of silver salt 0.018 in water, 1:005 in 0.1*N* silver nitrate; cadmium salt 0.1 in water; barium salt 0.61 in water.

Occurrence: Milk fats, coconut oil, and palm kernel oils.

Capric (*n*-Decanoic) Acid $CH_3(CH_2)_8CO_2H$; Mol. Wt. 172.26; B. Pt. 268° to 270° C. at 760 mm., 153° to 154° C. at 13 mm.; M. Pt. 31.3° C.; practically insoluble in water at ordinary temperatures, 0.1 in water at 100° C.; methyl ester, B. Pt. 223° C. at 760 mm. and 114° C. at 15 mm.; ethyl ester, B. Pt. 242° to 245° C. at 760 mm. M. Pts. of derivatives: Amide 108° C., anilide 61° C., toluidide 80° C., naphthalide 99° C., anhydride 24° C. Salts: Lead, solubility, 0.03 in ether at 20° C., 0.43 at B. Pt., 0.017 in petroleum ether at B. Pt. (40° to 60° C.); M. Pt. 100° C. Barium, calcium, and strontium salts, almost insoluble in water at ordinary temperatures, but slightly so in boiling water and somewhat more soluble in boiling alcohol. For the quantitative determination of fatty acids by steam distillation *see* D. C. Dyer, *Biol. Chem.*, **28**, 445 (1917).

Cf. W. Nelson and A. C. Bratton [*J. Am. Chem. Soc.*, **59**, 1424 (1937)]. Attention is called also to the paper by H. A. Schuette and H. A. Vogel [*Oil and Soap*, **16**, 209 (1939)] which gives solidification point curves for binary mixtures of capric, lauric, myristic and palmitic acids.

Occurrence: Elm seed oil contains about 50 and the California bay tree seed oil about 37 per cent of the acid. Coconut oil contains 9.5 to 11 and palm kernel oils of various kinds contain from 3 to 8 per cent of capric acid.

Uses: Capric as well as caprylic and caproic acids (the technical grade of which in each case contains about 90 per cent of the acid designated) are used for the preparation of various derivatives and other products, which include certain types of plasticizers, plastics, pharmaceuticals and synthetic perfumes. Certain esters are used in the manufacture of essences.

Lauric (*n*-Dodecanoic) Acid $CH_3(CH_2)_{10}CO_2H$; Mol. Wt. 200.31; B. Pt. at 760 mm. about 300° C., with slight decomposition, 176° C. at 15 mm.; M. Pt. 43.6° C.; somewhat volatile with steam; very slightly soluble in boiling water and insoluble in cold water; methyl ester

B. Pt. 141° C. at 15 mm., M. Pt. 0.5° C.; ethyl ester, B. Pt. 269° C. at 760 mm.; M. Pts. of derivatives: Amide 110° C., anilide 68° C., toluidide 81° to 82° C., naphthalide 100° C., anhydride 42° C., 2 methyl-5 isopropylanidide (cymidine) 82° to 83° C. [Hann and Jamieson, *J. Am. Chem. Soc.*, **50**, 1442 (1928)].

Solubility of salts: *Barium*, 0.008 in water at 15.3° C., 0.01 in alcohol at 16.5° C., 0.013 at 35° C., 0.084 in methyl alcohol at 15° C., 0.007 in ether at 25° C.; *calcium*, 0.004 in water at 15° C., and 0.055 at 100° C.; *lead*, M. Pt. 104° to 105° C., 0.010 in ether at 15° C., 0.021 at 35° C., 0.009 in alcohol at 25° C., 0.264 at 50° C., in methyl alcohol 0.061 at 15.5° C., 0.280 at 50° C.; insoluble in boiling petroleum ether; *lithium*, 0.154 in water at 16° C., 0.187 at 25° C., 0.280 at 50° C., in ether 0.011 at 16° C., in chloroform 0.006 at 15° C., in acetone 0.300 at 15° C., 0.430 at 35° C., in alcohol 0.403 at 20° C., 1.149 at 65° C., in methyl alcohol 3.16 at 15° C., 6.09 at 50° C.; *magnesium*, 0.010 in water at 15° C., 0.026 at 50° C., in alcohol 0.519 at 15° C., 0.591 at 25° C., 0.805 at 35° C., and 1.267 at 50° C., in ether 0.015 at 25° C., in acetone 0.117 at 15° C.; *silver*, insoluble in water at 15° C., practically so in alcohol and ether, in methyl alcohol 0.074 at 15° C. and 0.083 at 50° C.; *zinc*, 0.01 in water at 15° C. and 0.019 at 100° C., in alcohol 0.013 at 15° C. and 0.88 at 78° C.

Occurrence: Coconut oil, various palm kernel fats, myristica fats, etc.

The seed fats of *Actinodaphne hookeri, Litsaea sebifera* and *L. zeylanica*, which are found in India, contain 96, 96 and 85 per cent respectively of trilaurin S. V. Puntambekar [*Indian Forester*, **60**, 707 (1934)].

Uses: Commercial grades of lauric acid are used for making shampoos, shaving creams, and various derivatives including lauryl alcohol, which after being sulfonated and neutralized is used as a detergent. Lauryl rhodinate can be used as an insecticide for aphids, red spiders, etc. The mono- and di-glycerides serve as emulsifying and stabilizing agents for salad dressings and other fatty food preparations; they are used as well as diglycol laurate in the treatment of certain textiles and "light weight" leathers.

Myristic (*n*-Tetradecanoic) Acid $CH_3(CH_2)_{12}CO_2H$; Mol. Wt. 228.2; B. Pt. 250.5° C. at 100 mm. and 196.5 at 15 mm.; M. Pt. 54° C.; insoluble in cold or boiling water, soluble in organic solvents; methyl ester, M. Pt. 18° C., B. Pt. 167° to 168° C. at 15 mm.; ethyl ester, B. Pt. 295° C. at 760 mm. M. Pts. of derivatives: Amide 102° C., toluidide 93° C., naphthalide 105° C., anhydride 51.5° C., 2 methyl-5 isopropylanilide 88° to 89° C.

For melting points and heats of crystallization of myristic acid derivatives, *see* W. E. Gardner and J. E. Rushbrooke, *J. Chem. Soc.*, **1927**, 1351. *See* also "The Preparation of Myristic Acid from Nutmeg Butter and Fat," Verkade and Coops, *Chem. Abs.*, **21**, 3347 (1927).

Salts: *Ammonium*, insoluble in cold ether and chloroform, slightly soluble in alcohol; *barium*, 0.007 in water at 15.3° C.; 0.01 at 50° C., in alcohol, 0.009 at 16.5° C.; 0.011 at 25° C., and 0.04 at 50° C., in ether, 0.003 at 25° C., in methyl alcohol, 0.057 at 15° C., and 0.108 at 50° C.;

lithium, in water, 0.027 at 16.3° C., 0.036 at 25° C., and 0.062 at 50° C.; in alcohol, 0.194 at 20° C., 0.224 at 25.4° C., and 0.435 at 50° C., in ether, 0.013 at 15.8° C., and 0.004 at 25° C., in methyl alcohol, 1.346 at 15.2° C., 1.680 at 25° C., and 3.281 at 50° C., in acetone, 0.413 at 15° C., and 0.502 at 35° C., in chloroform, 0.004 at 15.2° C.; *lead,* in ether, 0.013 at 14.5° C., and 0.056 at 36° C., in alcohol, 0.056 at 15.5° C., 0.078 at 25° C., and 0.082 at 35° C., 0.101 in benzene at 15° C., 0.010 in ethyl acetate and 0.077 at 50° C., 0.021 in petroleum ether (40° to 60° C.) at 40° C.; *comagnesium,* 0.006 in water at 15° C., 0.007 at 20° C., and 0.014 at 50° C., 0.158 in alcohol at 15° C., 0.236 at 25° C., and 0.577 at 50° C., in ether, 0.010 at 25° C., in methyl alcohol, 0.571 at 15° C., and 0.763 at 25° C., *silver,* 0.007 at 35° and 50° C., 0.008 in alcohol at 25° and 50° C.

Occurrence: Myristica fats, coconut oil and palm kernel oils, milk fats.

Uses: Commercial grades of myristic acid are used for the preparation of esters (including the mono-, di- and triglycerides), myristyl alcohol, and other derivatives for use by cosmetic, detergent, leather and textile manufacturers.

Palmitic (*n*-Hexadecanoic) Acid $CH_3(CH_2)_{14}CO_2H$; Mol. Wt. 256.42; B. Pt. 215° C. at 15 mm.; M. Pt. 62.6° to 63° C.; insoluble in cold and boiling water, solubility in alcohol, *see* Hehner and Mitchell [*Analyst,* **21,** 323 (1896)], Falciola [*ibid.,* **36,** 23 (1911)], Twitchell [*Ind. Eng. Chem.,* **6,** 564 (1914)], and Einstein [*J. Soc. Chem. Ind.,* **39,** 663A (1920)]. The acid is very soluble in hot alcohol; methyl ester, M. Pt. 28° to 29° C., B. Pt. 196° C. at 15 mm.; ethyl ester, M. Pt. 24° C., B. Pt. 184.5° to 185° C. at 10 mm. M. Pts. of derivatives: 2-Methyl 5-isopropylanilide 90° to 99° C.; anhydride 63° to 64° C. For the separation of saturated and unsaturated acids by means of thallium salts, *see* D. Holde and co-workers [*J. Soc. Chem. Ind.,* **43, B-755** (1924); *Chem. Abs.,* **19,** 2032 (1925)].

Solubility of salts: *Ammonium,* 0.29 in ether at 13° C., and 0.20 in acetone at 13° C., in absolute alcohol, 0.70 at 10° C., 11.0 at 50° C.; *barium,* 0.004 in water at 15° C., 0.007 at 50° C., 0.01 in alcohol at 16.5° C., 0.001 in ether at 25° C., 0.045 in methyl alcohol at 15° C., and 0.088 at 50° C.; *calcium,* 0.003 in water and 0.010 in alcohol at 15° C.; *cerium* [Merrill, *J. Chem. Soc.,* **113,** 116 (1918)], insoluble in water, 0.01 in alcohol; *lead,* M. Pt. 112° to 113° C., in ether 0.01 at 15° C., in benzene 0.009 at 15° C., in alcohol 0.001 at 35° C., and 0.012 at 50° C., in methyl alcohol 0.05 at 15.5° C., and 0.093 at 50° C.; *lithium,* 0.01 in water at 18° C., 0.015 at 35° C., in alcohol 0.0196 at 20° C., 0.118 at 25.4° C., 0.248 at 50° C., and 0.39 at 65° C., in ether 0.007 at 15.5° and 25° C., in methyl alcohol 0.616 at 15.2° C., 0.771 at 25° C., and 1.652 at 50° C., in acetone 0.434 at 15° C., 0.508 at 25° C., and 0.537 at 35° C.; *magnesium,* in water 0.005 at 15° C., 0.009 at 50° C., in alcohol 0.034 at 15° C., 0.058 at 25° C., 0.151 at 50° C., in ether 0.004 at 25° C., in methyl alcohol 0.227 at 15° C., 0.336 at 25° C., and 0.500 at 51.5° C., in acetone 0.166 at 15° C., 0.160 at 25° C.; *silver,*

0.004 in water at 35° C., in alcohol 0.007 at 25° and 50° C., in methyl alcohol 0.06 at 15° and 50° C., in ether 0.009 at 15° C.; *thallium,* M. Pt. 115° to 117° C. (completely at 170° C.). It is insoluble in ether, soluble in hot alcohol and water.

Stearic (*n*-Octadecanoic) Acid $C_{18}H_{36}O_2 = CH_3(CH_2)_{16}COOH$; Mol. Wt. 284.47; M. Pt. 69.3° to 71° C.; B. Pt. 232° C. at 15 mm.; insoluble in cold and hot water; very soluble in hot alcohol; according to Falciola [*Analyst,* **36,** 23 (1911)], 100 grams of absolute alcohol retains 2.0 grams at 20° C. and 0.90 gram at 10° C., 75 per cent alcohol 0.15 gram at 10° C.; methyl ester, M. Pt. 38° to 39° C.; B. Pt. 214° to 215° C. at 15 mm.; ethyl ester, M. Pt. 36.7° C. Levene and Taylor [*J. Biol. Chem.,* **59,** 905 (1924)] state that ethyl stearate melts at 32.5° to 33.5° C. and boils at 152° C. under 18 mm. The pure acid melts at 70.5° to 71.5° C. M. Pts. of derivatives: Anhydride 71° C.; 2-methyl-5-isopropylanilide 93° to 94° C. Solubility of salts: *Lead* (M. Pt. 115.6° C.), 0.00 in alcohol at 25° C., and 0.004 at 50° C., in ether 0.007 at 14.5° C., in methyl alcohol 0.039 at 15° C., and 0.083 at 50° C., practically insoluble in petroleum ether at 20° C.; *ammonium,* at 15° C., 0.1 in ether and 0.08 in acetone; Falciola found that 100 grams of absolute alcohol at 10° C. retained 3 grams at 20.5° C. and at 50° C. 5.5 grams; *barium,* in alcohol 0.006 at 16.5° C., and 0.003 at 50° C., in ether 0.001 at 5° C., in methyl alcohol 0.042 at 15° C., and 0.077 at 50° C.; *calcium,* 0.004 in water at 15° C., insoluble in alcohol; *cerium,* insoluble in water, and 0.6 in ether at 15° C.; *lithium,* 0.010 in water at 35° C., in alcohol 0.072 at 20° C., and 0.200 at 50° C., in ether 0.011 at 15.8° C., in methyl alcohol 0.342 at 15° C., 0.439 at 25° C., and 1.057 at 50° C., in acetone 0.571 at 15° C., 0.706 at 25° C., and 0.663 at 35° C.; *magnesium,* 0.003 in water at 15° C., and 0.008 at 50° C., in alcohol 0.017 at 15° C., and 0.031 at 35° C., in ether 0.003, in methyl alcohol 0.084 at 15° C., 0.100 at 25° C., and 0.166 at 51.5° C., in acetone 0.191 at 25° C.; *silver,* 0.004 in water at 50° C., in alcohol 0.007 at 25° and 50° C., in ether 0.007 at 15° C.; *thallium,* M. Pt. 119° C.

Aluminum, calcium, magnesium and zinc stearates are all of commercial importance. These stearates are used in lubricating compounds, in waterproofing textiles, in certain printing inks and paints (as flatting agents in wall paints). Zinc stearate is also used in antiseptic powders and certain soaps.

Commercial stearic acid is prepared in large quantities and is graded according to its melting point. Depending upon the fat and method used in the preparation, this product contains more or less palmitic and unsaturated acids. It is graded as single-pressed (M. Pt. 125° to 126° F., Iod. No. 12 to 14), double-pressed (M. Pt. 129° to 130° F., Iod. No. 5 to 6) and triple-pressed (M. Pt. 130° to 131° F., Iod. No. less than 3). Another, known as "white block stearine," melts at 118° to 120° M. and is much softer in texture than other grades; it is made from "inferior oils." Depending upon the quality, these products are used in the manufacture of candles, cosmetics, buffing compounds, metal

and shoe polishes, and rubber compounding. The amide and toluidide are used in certain preparations for treatment of textiles.

It may be of some interest to note that the seed fats of the *Dipterocarpaceae, Guttiferae, Sapotaceae* and *Sterculiaceae* families contain large percentages of stearic acid.

Additional information will be found in the following references:

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"Use of Stearic Amide and Toluidide in Preparation for Use in the Textile Industry," *Chemicals*, **26**, No. 25, 19 (1927).

"Stearic Acid Standards," *Soap*, **3**, No. 2, 37 (1927); *Chem. Abs.*, **22**, 1245 (1928).

"Stearic Acid: A Rubber Compounding Material," *Chem. Markets*, **20**, 865 (1927).

"Nature, Manufacture and General Use of Stearic Acid," D. F. Cranor, *Ind. Eng. Chem.*, **21**, 719 (1929).

"Stearic and Oleic Acids as Rubber Compounding Ingredients," R. P. Dinsmore, *ibid.*, **21**, 722 (1929).

"Effect of Stearic Acid on Various Crude Rubbers," E. W. Fuller, *ibid.*, **21**, 723 (1929).

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"Separation of Palmitic and Stearic Acids by Fractional Precipitation of the Lithium Salts from 95 Per Cent Alcohol," *see* "Oil of Grape Seeds," E. André, *Compt. rend.*, **175**, 107 (1922).

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"Stearic Acid and Red Oil Specifications," *Oil and Fat Ind.*, **4**, 396 (1927).

"Molecular Orientation of Surfaces of Solids, II, The Work of Adhesion of Saturated Fatty Acids for Water," A. H. Nietz, *J. Phys. Chem.*, **32**, 620 (1928).

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"Manufacture of Aluminum Stearate," F. J. Licata, *Oil Col. Trds. J.*, **89**, 1970 (1936).

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"Dichlorostearates as Driers," W. Howlett and R. B. Waddell, *Ind. Eng. Chem.*, **33**, 629 (1941); gives 66 references.

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"Acid Soaps," H. Bennett, *Oil and Soap*, **9**, 68 (1932). Discusses use of diglycol stearate in paints and inks.

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"The Effect of Different Soaps on Lead Arsenate in Spray Mixtures," J. M. Ginsburg, *J. Agric. Res.*, **46**, 179 (1933).

"Methods of Making and Using Metallic Stearate in Varnish and Lacquer, P. H. Fawcett, *Pt., Oil., Chem. Rev.*, **96**, No. 3, 8 (1934).

"The Colloid Chemistry of Sugar-Fatty Acid Compounds," D. Schmaltz, *Kolloid Z.*, **71**, 234 (1935); *Chem. Abs.*, **29**, 7754 (1935).

Arachidic (Eicosanoic) Acid $C_{20}H_{40}O_2$; Mol. Wt. 312.5; M. Pt. 76 to 77° C.; ethyl ester, M. Pt. 41.5 to 42.5° C.; methyl ester M. Pt. 46.5 to 47.0° C.; nitrile, M. Pt. 49° C.; amide 109° C.; analide M. Pt. 96° C.; *p*-chlorphenacyl ester, M. Pt. 86° C.; *p*-bromphenacyl ester, M. Pt. 89° C.

According to F. Francis and S. H. Piper [*J. Am. Chem. Soc.*, **61**, 577 (1939)] the pure synthetic normal acid melts at 75.35° C., the ethyl ester at 40.15° C. and the methyl ester at 45.8° C.

Francis, Piper and T. Malkin [*Proc. Royal Soc., London*, **A128**, 214 (1930)] concluded from their investigations that the arachidic acid from peanut oil is not identical with the normal acid, as did Levene and Taylor [*J. Biol. Chem.*, **59**, 905 (1924)]. These latter investigators, by means of x-ray examination, showed that this arachidic acid fraction, regardless of how many times it was recrystallized, still contained small quantities of other closely related acids.

Besides peanut and tonka bean oils, many others of the *Leguminosae* contain arachidic acid, but in very much smaller proportions.

Large quantities of the *n*-eicosanoic acid have been found in kussum (macassar), pulsam, rambutan, and soap tree seed fats. All of these fats come from trees of the *Sapindaceae* family.

Behenic (*n*-Docosanoic) Acid $C_{22}H_{44}O_2$; Mol. Wt. 304.57; M. Pt. 81 to 82° C.; ethyl ester, M. Pt. 50° C.; methyl ester, M. Pt. 54° C.; amide, M. Pt. 111° C.; analide, M. Pt. 102° C. The acid was first found by A. Voelcker [*Liebig's Ann.*, **64**, 342 (1848)] in ben (moringa) seed oil. A sample of the oil which was examined by the writer [*Oil and Soap*, **16**, 173 (1939)] contained 6.5 per cent of the acid. D. R. Paranjpe [*J. Indian Chem. Soc.*, **18**, 768 (1931)] reported that the mixed fatty acids from the seed oil of *Parkia biglandulosa (Mimosaceae)* contained 7.9 per cent of this acid. It is found also in smaller quantities in peanut oil, and a few tenths of a per cent are found in the seed

oils of the *Cruciferae* plants. It can be obtained by the hydrogenation of erucic acid, a major constituent of mustard and rape seed oils.

For the synthesis of behenic and other acids of higher molecular weight see F. Francis, G. Collins and S. H. Piper [*Proc. Royal Soc., London,* **A158,** 691 (1937)].

Lignoceric (*n*-tetracosanoic) Acid $C_{24}H_{48}O_2$; Mol. Wt. 368.63; M. Pt. 84.1°; methyl ester, M. Pt. 57.8°; ethyl ester, M. Pt. 54.3° C. E. Jantzen and C. Tiedcke [*J. prakt. Chem. (2),* **127,** 277 (1930)] found that peanut oil contained this acid. According to S. M. Mudbidri, P. R. Ayyar and H. E. Watson [*J. Indian Inst. Sci.,* **A11,** 173 (1928); *Chem. Abs.,* **25,** 3034 (1931)] the fatty acids from the seed oil of the coral pea tree, *Adenanthera pavonina,* contain over 25 per cent of the acid.

F. Francis, S. H. Piper and T. Malkin [*Proc. Royal Soc., London,* **A128,** 214 (1930)] have shown by x-ray spectrum analysis that lignoceric acid from peanut oil and beechwood tar is identical with the synthetic acid.

Many seed oils contain small percentages of lignoceric acid. As isolated, it melts at 81° C. and even after many recrystallizations from alcohol or other solvents useful for this purpose, no higher melting point is obtained. It has been shown that this product contains, besides lignoceric acid, small proportions of other closely related acids. [*Cf.* A. C. Chibnal, S. H. Piper and E. F. Williams, *Biochem. J.,* **30,** 100 (1936)].

Cerotic (*n*-Hexacosanoic) Acid $C_{26}H_{52}O_2$; Mol. Wt. 396.68; M. Pt. 87.7° C.; methyl ester, M. Pt. 62.9° C.; ethyl ester, M. Pt. 59.95° C.; amide, M. Pt. 109° C. The lead and magnesium salts are insoluble in alcohol, ether and water; the potassium and sodium salts are insoluble in benzene, ether and petroleum ether. The acid is soluble in boiling ethyl and methyl alcohols, glacial acetic acids and other organic solvents. The acid is a constituent of beeswax and various vegetable waxes. Very small percentages have been found in various seed fats.

A wide range (78 to 85° C.) of melting points of the acid from natural sources has been reported by various observers. This is due to the presence of varying quantities of closely related acids; the separation of which from cerotic acid is extremely difficult. [F. Francis, S. H. Piper and T. Malkin, *Proc. Royal Soc., London,* **A128,** 214 (1930); A. C. Chibnal, *et al., Biochem. J.,* **28,** 2189 (1934)].

Montanic (*n*-Octacosanoic) Acid $C_{28}H_{56}O_2$; Mol. Wt. 424.73; M. Pt. 90.9° C.; ethyl ester, M. Pt. 64.6° C.; methyl ester, 66.7° C. [F. Francis and S. H. Piper, *J. Am. Chem. Soc.,* **61,** 577 (1939)].

The acid isolated from montan wax melts at about 86° C. X-ray examination showed the presence of small percentages of several other closely related acids.

Melissic (*n*-Triacontanoic) Acid $C_{30}H_{60}O_2$; Mol. Wt. 452.98; M. Pt. 93.6° C.; methyl ester, 70.8° C.; ethyl ester, 68.3° C. The lead salt is insoluble in alcohol and ether at ordinary temperatures. It is a constituent of beeswax and many waxes of vegetable origin. As

ordinarily separated from waxes, it melts from 88 to 89° C. due to the presence of small proportions of other closely related acids which are not removed by repeated crystallization.

Other Acids

Pelargonic (Nonyl, Nonoic) Acid $C_9H_{18}O_2 = CH_3(CH_2)_7COOH$; Mol. Wt. 158.25; M. Pt. 12° C. It is soluble in alcohol, ether, and slightly so in water. The barium salt has but little solubility in cold alcohol and ether. This acid is obtained as an oxidation product of oleic acid.

Azelaic Acid $C_9H_{16}O_4 = (CH_2)_7 . (COOH)_2$; Mol. Wt. 188.38; M. Pt. 106° C.; 100 grams of water at 15° C. dissolves 0.212 gram; 100 grams of ether at 15° C. dissolves 2.680 grams. The acid is obtained as an oxidation product of oleic acid.

Suberic Acid $C_8H_{14}O_4 = (CH_2)_6 . (COOH)_2$; Mol. Wt. 174.43; M. Pt. 140° C.; 100 grams of water at 20° C. dissolves 0.169 gram; 100 grams of ether at 15° C. dissolves 0.809 gram. The acid is an oxidation product of oleic acid.

Sebacic Acid $C_{10}H_{18}O_4 = (CH_2)_8 . (COOH)_2$. Mol. Wt. 202.24; M. Pt. 133°–4° C.; 100 grams of water at 20° C. dissolves 0.10 gram, at 50° C., 0.22 gram of acid. It is soluble in alcohol and ether.

The acid is made by heating sodium ricinoleate with sodium hydroxide (Beilstein, Vol. II, 718). It can be used as a softening agent for rubber, and is used in the manufacture of the synthetic fiber nylon.

Unsaturated Fatty Acids

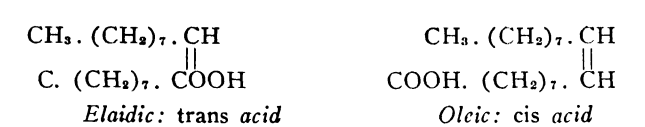
Tiglic Acid $C_5H_8O_2$; Mol. Wt. 100–122; M. Pt. 64.5° C.; B. Pt. 198.5° C., ethyl ester, B. Pt. 156° C.; gives dibromide. Böhm [*Chem. Umschau*, **33**, 36 (1926)] states that this acid is not present as a glyceride in croton oil, but is a constituent of the resin in the oil.

Oleic (9:10-Octadecenoic) Acid $C_{18}H_{34}O_2 = CH_3 . (CH_2)_7 . CH:CH.(CH_2)_7 . COOH$; Mol. Wt. 282.4; Iod. No. 89.89; SCN Value 89.88; M. Pts. 13.2° and 16.3° C.; B. Pt. 153° C. at 1 mm. and 232°–3° C. at 15 mm. pressure; dibromide, M. Pt. 29° C.; ethyl or methyl esters, B. Pt. about 150° C. at 3 mm. The final product of hydrogenation is stearic acid. Oxidation with hydrogen peroxides gives a dihydroxy acid melting at 95° C., and alkaline permanganate at low temperatures forms another which melts at 132° C. (Under selected conditions, 80 per cent of the oleic acid present is converted into dihydroxystearic acid.) For the determination of oleic acid as dihydroxystearic acid, *see* the A. Lapworth and E. N. Mottram [*J. Chem. Soc.*, **127**, 1628 (1925)] method. At higher temperatures, permanganate oxidation of oleic acid produces azelic and oxalic acids, and some other substances. In a hot acetone solution, permanganate ruptures oleic acid at the double bond, giving azelaic and nonoic acids.

The treatment of oleic acid with nitrous acid converts part of it into

the geometric isomer *elaidic* acid which melts at 44° C. H. N. Griffiths and T. P. Hilditch (*J. Chem. Soc.*, **1932**, 2315) have shown that by this means 66 per cent of the oleic acid can be changed to elaidic acid.

A. Müller and G. Shearer [*J. Chem. Soc.*, **123**, 3156 (1923)] have shown by x-ray examination that elaidic acid is the *trans* (geometric) isomer of oleic acid. Their formulas are as follows:



Elaidic: trans *acid* — *Oleic:* cis *acid*

Iso-oleic acids and their formation will be discussed later.

The isolation of oleic acid from fats in a pure condition is extremely difficult. Those interested should consult the "Preparation and Properties of Highly Purified Methyl Oleate" by D. H. Wheeler and R. W. Riemenschneider [*Oil and Soap*, **16**, 207 (1939)] who describe the acid obtained from the ester.

C. R. Noller and R. A. Bannerot [*J. Am. Chem. Soc.*, **56**, 1563, (1934)], using 9-chloro-nonyl chloride as a starting point, synthesized oleic acid and obtained a mixture which consisted of 37 per cent of oleic and 67 of elaidic acids.

Commercial oleic acid, which is commonly known as "Red Oil," always contains more or less saturated acids (chiefly palmitic and stearic) and small percentages of linoleic acid. It is used for making emulsions and wetting agents, textile soaps, and oleates of aluminum, copper, lead and other metals which are used for various purposes. Aluminum oleate, known in the trade as "pulp oil" serves as a "thickener" of certain types of lubricants. Nickel and tin oleates are added to lubricants to prevent the formation of sludge under service conditions [W. J. Mardles, Tech. Publ'n. International Tin Res. & Devel. Council C. No. 2 (1934); *Brit. Chem. Abs.*, **B1934**, 997)]. It is also used to retard oxidation of textile oils [*Oil Col. Trds. J.*, **99**, 337 (1936)]. E. Sinkinson and S. D. Michaelson [Am. Inst. Min'g. Met. Engrs. Publication No. 733 (1936); *Chem. Abs.*, **30**, 8536 (1936)] discuss the use of the acid as a flotation agent for the separation of Californian magnesite from other minerals. As a preservative of fish nets, copper oleate is very effective [*Chem. Trde. J.*, **86**, 439 (1930)]. W. E. Fleming and F. E. Baker [*J. Agric. Res.*, **49**, 39 (1934)] discuss the advantage and disadvantage of the addition of one per cent of lead oleate to lead arsenate insecticide.

Salts: Lead oleate is very soluble in alcohol, ether and petroleum ether. The lead salts of elaidic and iso-oleic acids are sparingly soluble in these solvents (see lead-salt alcohol and ether methods for the separation of saturated and unsaturated acids). *Lithium oleate:* In absolute alcohol, 0.91 at 18° C. and 1.01 at 25° C., soluble in hot alcohol, in water 0.067 at 18° C. and 13.0 at 25° C. It is insoluble in ether and benzene. *Magnesium oleate:* In water, 0.022 at 15° C., in 90 per cent alcohol, 8.60 at 25° C. *Barium oleate:* Insoluble in water and nearly

so in alcohol. It dissolves in moist boiling benzene, but upon cooling, practically all the salt separates in a crystalline form. *Cereous oleate* is completely soluble in ether. *Potassium oleate:* 100 cc. of water at 15° C. dissolves about 25 grams, 100 grams of 95 per cent alcohol dissolves 41.2 grams. *Sodium oleate:* M. Pt. 232 to 235° C.; at 15° C. 100 cc. of water dissolves about 10 grams.

Salts of Elaidic Acid: The barium, lead, and silver salts are insoluble in water and have but little solubility in alcohol (100 cc. dissolve 0.01 gram of lead salt), ether or benzene at ordinary temperatures.

Iso-oleic Acids. Oleic acid (or its glycerides) when partially hydrogenated, distilled at atmospheric pressure or heated with sulfuric acid (owing to a partial migration of the double bond along with some stereoisomeric changes) is converted into the so-called iso-oleic acids. This mixture of isomeric acids, depending upon the method of formation and the experimental conditions, probably varies considerably in comparison. Their lead salts are characterized by having little solubility in either alcohol or ether at ordinary temperatures.

Additional information will be found in the following references:

"Ozonides of Oleic Acid," Harries and Thume, *Analyst*, **31**, 412 (1906).

"The Action of Halogens on Oleic Acid," Morgan and Dinogradoff, *ibid.*, **39**, 311 (1914).

"Catalytic Reduction of Oleic Acid by Hydrogen and Nickel," Shaw, *J. Soc. Chem. Ind.*, **33**, 771 (1914).

"Properties of the Oleates of Some Heavy Metals," Albuquerque, *J. Chem. Soc.*, **118**, 216 (1920).

"The Formation of Solid Iso-oleic Acids by Hydrogenation of Ordinary Liquid Oleic Acid," C. W. Moore, *J. Soc. Chem. Ind.*, **38**, 320T (1919).

"Relation of Oleic Acid to Elaidic Acid," B. H. Nicolet, *J. Am. Chem. Soc.*, **43**, 2122 (1921).

"The Catalytic Decomposition of Oleic Acid," Mailhe, *J. Soc. Chem. Ind.*, **41**, 334A (1922).

"Hydroxystearic Acid and Some of Its Derivatives," Radcliffe and Gibson, *Chem. Abs.*, **17**, 2104 (1923); *J. Soc. Chem. Ind.*, **42**, 150A (1923).

"Isomerism in Fatty Oils and Its Technical Significance," E. Eibner, *Chem. Umschau*, **29**, 309 (1923).

"Oleic Alcohol and Its Composition," Toyama, *J. Soc. Chem. Ind.*, **43**, B-223 (1924).

"Formation of Iso-unsaturated Solid Acids During Hydrogenation of Fatty Oils," Schi-ichi Nemo, *Chem. Abs.*, **20**, 834 (1926).

"Method for the Determination of the Hydrogenation Number of Unsaturated Compounds," A. Grün and W. Halden, *Chem. Absts.*, **18**, 912 (1924).

"A New Method of Ascertaining the Position of the Ethylenic Linkage in Acids of the Oleic Series," E. F. Armstrong and T. P. Hilditch, *J. Soc. Chem. Ind.*, **44**, 43T (1925); *cf. ibid*, 180T.

"The Preparation and Properties of Purified Oleic Acid and Some of Its Salts," Lapworth, Pearson and Mottram, *Biochem. J.*, **19**, 7 (1925).

"Oxidation of Unsaturated Fatty Acids with Hydrogen Peroxide and Benzoyl Peroxide," K. H. Bauer and K. Kutscher, *Chem. Umschau*, **32**, 57 (1925).

"Determination of Oleic Acid as Di-hydroxystearic Acid," A. Lapworth and E. N. Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

"Di-bromides of Oleic Acid, Elaidic Acid and the Purification of Oleic Acid," D. Holde and A. Gorgas, *Brit. Chem. Abs.*,—B, **1927**, 83. *Chem. Abs.*, **21**, 732 (1927). The purified oleic acid gave an iodine number of 89 to 95 and boiled under 0.6 mm. pressure at 200° C. The dibromide melted at 28.5° to 29° C. and the elaidic dibromide melted at 29° to 30° C. These authors confirmed Nicolet (*loc. cit.*) in that the addition and removal of bromine causes no *cis-trans* isometrization.

"The Isomerism of the Di-hydroxy Stearic Acids Produced by Oxidation of

Acids of the Oleic Series and Elaidic Series," T. P. Hilditch, *J. Chem. Soc.*, **1926**, 1928.

"The Synthesis of 9-10-11-12- and 13-Hydroxystearic Acids," C. S. Tomecks with R. Adams, *J. Am. Chem. Soc.*, **49**, 522 (1927).

"Determination of Oleic Acid and Elaidic Acids in Presence of Each Other," J. P. K. Van Steur, *Analyst*, **52**, 608 (1927).

"Catalytic Decomposition of Oleic Acid," B. M. Marks and H. C. Howard, *Ind. Chemist*, **4**, 386 (1928).

"Cadmium Oleate, A New Impregnating Medium," H. J. Braun, *Brit. Chem. Absts.*—B, **1930**, 65.

"The Spontaneous Ignition of Commercial Oleic Acid," P. Erasmus, *Allgem. Öl Fettzeit*, **27**, 309, 345, 367, 408 (1930); *Chem. Abs.*, **25**, 2583 (1925).

"Autoxidation of the Fatty Acids. I. Oxygen Uptake of Elaidic, Oleic and Stearic Acids," G. W. Ellis, *Biochem. J.*, **26**, 791 (1932); states that at ordinary temperatures oleic and elaidic acids do not absorb oxygen gas except in negligible amounts.

"Phenacyl Esters of the Oleic Acid Series," W. Kimura, *J. Soc. Chem. Ind., Japan* (Suppl. Bdg), **35**, 221 (1932); *Chem. Abs.*, **26**, 4583 (1932).

"Notes on a Semi-Quantitative Modification of the Elaidin Test," H. N. Griffiths and T. P. Hilditch, *Analyst*, **59**, 312 (1934).

"Preparation of Pure Elaidic Acid and the Elaidination Reaction," A. Lyntenberg, *Fettchem. Umschau*, **42**, 89 (1935).

"The Elaidinization of Oleic Acid and the *Cis-trans* Isomerism," *Oil Col. Trds. J.*, **94**, 1227 (1938); gives 25 references.

"The Isomeric Structure of the C_{18} Unsaturated Acids From Their Raman and Infra Red Spectra," J. W. McCutcheon, M. F. Crawford and H. L. Welsh, *Oil and Soap*, **18**, 9 (1941).

Petroselinic (6:7-Octadecenoic) Acid $C_{18}H_{34}O_2 = CH_3 . (CH_2)_4 . CH:CH.(CH_2)_{10} . COOH$; Mol. Wt. 282.4; Iod. No. 89.89; M. Pt. 30° C.; lead salt has little solubility in cold alcohol or ether; oxidation with per-acetic acid gives a 6:7-dihydroxy-stearic acid, M. Pt. 114° C. and with alkaline permanganate, an isomer, M. Pt. 122° C., is obtained. Treatment with nitrous acid produces about 60 per cent of *trans* 6:7-octadecenoic acid, M. Pt. 53° C. [H. N. Griffiths and T. P. Hilditch, *J. Chem. Soc.*, **2315** (1932)].

This acid is a major component of the seed fats of the *Araliaceae* and *Umbelliferae*. It is a constituent of one and possibly more seed fats of the *Simarubaceae*.

Linoleic (9:10-, 12:13-Octadecadienoic) Acid $C_{18}H_{32}O_2 = CH_3 . (CH_2)_4 . CH : CH . CH_2 . CH : CH . (CH_2)_7 . COOH$; Mol. Wt. 280.4; Iod. No. 181.06; M. Pt. −6.5° C.; tetrabromide, M. Pt. 114° to 115° C.; lead salt is readily soluble in alcohol and ether; salts of barium, calcium, copper, and zinc are soluble in ether and hot alcohol. Catalytic hydrogenation of the acid gives stearic acid as the final product. Oxidation of the acid by a dilute solution of alkaline permanganate gives two sativic (tetrahydroxystearic) acids, one melting at 174° C. and the other at 163.5° C. Those reported as melting between 153 and 157° C. by previous investigators are now known to be eutectic mixtures of the two already mentioned.

Bromination of the acid at about 0° C. produces two tetrabromides. The one known as the α melts at 114 to 115° C. and the other, known as the β, is a liquid at ordinary temperatures. Riemenschneider, Wheeler, and Sando [*J. Biol. Chem.*, **127**, 391 (1939)], from their investigation of linoleic acid from cottonseed oil and that regenerated from the α and β

tetrabromides, have concluded that the natural and regenerated linoleic acids have but one geometrical configuration. For details and bibliography, the original paper should be consulted.

Attention is called also to a paper on the constitution of the linoleic acid of seed fats by T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.*, **58**, 233 (1939).

Ammonium linoleate has been suggested for use in the preparation of "soluble" oils (in place of sulfonated oils) for making polishes, textile softeners and agricultural sprays. Calcium linoleate is used as an emulsifying agent and stabilizer for flat paints, fillers, and enamels. Linoleates of lead and other metals are used as "driers" for paints, varnishes, etc.

Tariric Acid $C_{18}H_{32}O_2$; Mol. Wt. 280.25; M. Pt. 50.5° C.; dibromide, M. Pt. 33° C.; tetrabromide, M. Pt. 125° C.; 100 grams of alcohol at 15° C. dissolves 2.48 grams of acid. Armand [*Compt. rend.*, **114**, 79 (1892)] isolated the acid from tariric seed fat and determined its composition, and later (*ibid.*, **123**, 1000) showed that it could be reduced to stearic acid. Grimme [*Chem. Rev. Fett. Harz. Ind.*, **19**, 51 (1912)] also found the acid in the fats of several of the species of *Picramnia*. Oxidation of the acid in the cold with permanganate gave a dihydroxy-acid which melted at 98° C. More extensive oxidation gave adipic acid ($C_6H_{10}O_4$, M. Pt. 149° C.) and lauric acid (M. Pt. 43.5° C.). Direct bromination of the acid gave the tetrabromide, whereas in cold chloroform solution only the dibromide was obtained. Armand [*Compt. rend.*, **124**, 473 (1902)], from his investigation, concluded that the acid had a triple bond between the twelfth and thirteenth carbons.

A. Steger and J. van Loon [*Rec. trav. chim.*, **52**, 593 (1933)] have showed that it is a 6:7-octadecenoic acid, $CH_3 . (CH_2)_{10} . C . C : (CH_2)_4 COOH$. The dibromide prepared by them melted at 33.3° C. They found that the seed fat of *Picramnia sow* contained almost 95 per cent of this acid.

Linolenic Acid $C_{18}H_{30}O_2$ is $\Delta^{9:10,\ 12:13,\ 15:16}$-octadecatrienoic acid [$CH_3 . CH_2 . CH:CH . CH_2 . CH:CH . CH_2CH:CH . (CH_2)_7 . COOH$]. Mol. Wt. 278.42; Iod. No. 273.5; M. Pt. −12.8° C.; B. Pt. 157 to 158° C. at 0.002 mm. pressure; methyl ester, B. Pt. 207° C. at 14 mm.; ethyl ester 132° C.; lead salt readily soluble in alcohol and ether. As in the case of linoleic acid, two isomers appear to occur together in linseed, perilla, candlenut and various other oils. The so-called *alpha* acid yields the ether-insoluble hexabromide, whereas the hexabromide of the other isomer is very soluble [E. Erdman and F. Bedford, *Ber.*, **42**, 1324 (1909)]. When the ether-insoluble hexabromide is reduced with zinc powder and again brominated in an ether solution, only part of the linolenic acid present is obtained as crystalline hexabromide, which is due to the transformation of some of the linolenic acid into an isomeric form, the hexabromide of which is soluble in ether.

The oxidation of the acid with alkaline permanganate yields two

hexahydroxystearic acids known as linusic, M. Pt. 203° C. to 205° C., and isolinusic, M. Pt. 173 to 175° C. These acids are insoluble in ether, sparingly so in cold alcohol, and soluble in hot water. Of these two, the isolinusic acid is the one most soluble in hot water.

The final product, upon hydrogenation of linolenic acid, is stearic acid.

Attention is called to the following references:

"New Hexabromide Method for Linseed Oils," Steele and Washburn, *Ind. Eng. Chem.*, **12**, 52 (1920).

"Linolenic and Hexabromstearic Acid and Some Derivatives," S. Coffey, *J. Chem. Soc. Trans.*, **119**, 1306 (1921).

"Bromine Derivatives of Linolenic Acid," W. Kimura, *Chem. Abs.*, **23**, 2261 (1929).

"Thiocyanate Determination of Fats Containing Linolenic Acid," H. P. Kaufmann and M. Keller, *Z. angew. Chem.*, **42**, 70, 73 (1929).

"Qualitative Test for Linolenic Acid; Its Value and Limitations," G. J. Martin, *J. Am. Chem. Soc.*, **58**, 364 (1936).

"Spectroscopic Changes in Acids," T. Moore, *Biochem. J.*, **31**, 138 (1937); describes how a solid unsaturated acid which melts at 77° C. and gives no ether-insoluble hexabromide is formed by prolonged boiling of linseed oil fatty acids with alcoholic potash.

An Isolinolenic Acid. This acid was discovered in the seed oil of the night candle plant, *Oenothera biennis* of the *Oenotheraceae* by A. Heiduschka and K. Lüft [*Arch. Pharm.*, **257**, 33 (1919)]. A. Eibner, L. Widenmeyer and E. Schild [*Chem. Umschau*, **34**, 312 (1927)] determined it to be $\Delta^{6:7,\ 9:10,\ 12:13}$-octadecatrienoic acid [$CH_3 . (CH_2)_4 . CH : CH . CH_2 . CH : CH . CH_2 . CH : CH . (CH)_4 . COOH$]. Its hexabromide melts at 169° C. Oxidation by alkaline permanganate gives a hexahydroxystearic acid which melts at 245° C.

Attention is called to the following references:

"Linolenic Acid and Its Isomers," J. W. McCutcheon, *Canadian J. Res.*, **18**, 231 (1940).

"The Geometric Isomerism of the Linolenic Acids. Elaido-linolenic Acid," J. P. Kass, J. Nichols and G. O. Burr, *J. Am. Chem. Soc.*, **63**, 1060 (1941).

"Studies on Chemistry of Fatty Acids. VII. The Multiple Nature of the Linoleic and Linolenic Acids Prepared by the Bromination-Debromination Procedure," N. L. Mathews, W. R. Brode and J. B. Brown, *J. Am. Chem. Soc.*, **63**, 1064 (1941).

Ricinoleic Acid $C_{18}H_{34}O_3$; Mol. Wt. 298.27; M. Pt. 4° to 5° C.; Acetyl V. 165; Iod. No. 85.1; Neut. V. 188.3; $[\alpha]_D$ 6.25° to 7.5° in acetone solution; lead salt is readily soluble in ether, but is almost insoluble in petroleum ether; barium, calcium and magnesium salts are soluble in hot alcohol, but not much so in the cold solvent; the methyl ester distills at 245° C. under 10 mm. pressure, whereas the acid undergoes decomposition. A dilute alkali permanganate solution in the cold produces two isomeric trihydroxystearic acids, $C_{18}H_{33}O_2(CH)_3$, which melt at 110 to 111° C. and 140 to 142° C., respectively. Treatment with nitrous acid gives ricinelaidic acid, M. Pt. 52° to 54° C. The acid also forms a dibromide.

Alkyl ricinoleates can be used as general plasticizers, emulsifying and wetting agents, as well as in the manufacture of pyroxylins.

References are as follows:

"Separation of Ricinoleic Acid from Castor Oil," K. Inokuchi, *Mat. grasses*, **18**, 7671 (1926).

"Investigation of Ricinoleic Acid," A. Grün, *J. Soc. Chem. Ind.*, **26**, 57 (1907). The acid, to the extent of over 40 per cent, is reported to be present in the oil from ivory wood seed, *Chem. Abs.*, **24**, 3668 (1930).

According to Margaillon, [*Compt. rend.*, **192**, 373 (1931)] the seed oil of *Wrightia annamensis* contains a large quantity of an isomeric ricinoleic acid.

"The Preparation of Pure Sodium Ricinoleate," H. O. Halvorson, *Proc. Soc. Expl. Biol. Med.*, **22**, 553 (1925).

"The Production of Pure Glycerides of Ricinoleic Acid," P. Panjutin and M. Rapoport, *Chem. Umschau*, **37**, 130 (1930).

"The Purification of Sodium Ricinoleate," T. H. Rider, *J. Am. Chem. Soc.*, **53**, 4130 (1931).

"Castor Oil. IV. Physical Properties of Pure Ricinoleic Acid," E. André and C. Vernier, *Ann. Official Nat. com'l. liquids*, **6**, 110 (1931).

"Ricinoleates of α-Phenylamine and L-ephedrine," E. André and C. Vernier, *Compt. rend.*, **194**, 469 (1932).

"Preparation of Pure Fatty Acids from Fats; In Particular from Castor Oil," M. Jakes and J. Hökl, *Chem. Listy*, **32**, 1522 (1938); *Brit. Chem. Abs.*, **B1938**, 401.

"Studies on the Chemistry of the Fatty Acids. V. The Preparation of Methyl Ricinoleate and Ricinoleic Acid by Fractional Crystallization Procedures," J. B. Brown and N. D. Green, *Am. Chem. J.*, **62**, 738 (1940).

"Occurrence of an Isomer of Ricinoleic Acid in the Fatty Oil from Seeds of *Vernonia anthelmintica*," N. L. Vidyarthi and M. V. Mallya, *J. Indian Chem. Soc.*, **16**, 479 (1939); *Analyst*, **65**, 186 (1940).

Erucic Acid $CH_3 . (CH_2)_7CH : CH . (CH_2)_{11}CO_2H = (C_{22}H_{42}O_2)$; Mol. Wt. 338.56; Iod. No. 75.0; M. Pt. 33° to 34° C.; B. Pt. 264° C. at 15 mm.; methyl ester, B. Pt. 221° to 222° C. at 5 mm.; dibromide, M. Pt. 46° to 47° C. It has properties similar to oleic acid, but the lead salt has only a slight solubility in cold ether and cold alcohol. Catalytic reduction by hydrogen gives behenic acid. Fusion with caustic potash gives arachidic and acetic acids. Treatment of the bromide with alcoholic potash gives behenolic acid (M. Pt. 57.5° C.). Oxidation with permanganate gives dihydroxybehenic acid. Treatment with nitrous acid or sulfur dioxide under pressure transforms the acid into a geometrical isomer called brassidic acid.

Rape, mustard and other seed oils of the *Cruciferae* contain erucic acid. For its preparation see K. Täufel and C. Bauschinger, *Ztschr. angew. Chem.*, **41**, 157 (1928), *Oil Col. Trds. J.*, **75**, 1184 (1929). For the detection of the acid see [H. P. Kaufmann and H. Fiedler, *Fette u. Seifen*, **45**, 465 (1938); *Chem. Abs.*, **33**, 419 (1939)].

Brassidic Acid $C_{22}H_{42}O_2$; Mol. Wt. 338.56; Iod. No. 75.03; M. Pt. 65° C.; B. Pt. 265° C. at 15 mm.; ethyl ester M. Pt. 30.5° C.; anhydride, M. Pt. 64° C. Lead salt has little solubility in alcohol or ether. This acid is formed by the action of nitrous acid on erucic acid.

Cetoleic Acid $C_{22}H_{42}O_2$; described by Y. Toyama [*Chem. Abs.*, **22**, 575 (1928)], is an isomer of erucic acid and is of common occurrence in marine animal and fish oils. This acid was formerly considered to be erucic acid.

Hydnocarpic Acid $C_{16}H_{28}O_2=\begin{matrix}CH{=}CH\\ \\ CH_2{-}CH_2\end{matrix}\!>CH(CH_2)_{10}COOH.$

Mol. Wt. 252.38; M. Pt. 60.5° C.; Iod. No. 100.61; $[\alpha]_D^{25°}$ 69.3. Ethyl ester, B. Pt. at 10 mm. 200° C. $[\alpha]_D^{25°}$ 61.94; $N_D^{25°}$ 1.4578. These values were determined by H. I. Cole and H. Cardoso [*J. Am. Chem. Soc.*, **59,** 963 (1937)]. The lead salt is sparingly soluble in ether. Catalytic reduction gives dihydrohydnocarpic acid melting at 63 to 64° C. For synthesis of the acid, see Noller and Adams [*J. Am. Chem. Soc.*, **48,** 1080 (1928)].

Hydnocarpic acid was found in hydnocarpus oil by Power and Barrowcliffe [*J. Chem. Soc.*, **87,** 884 (1905)], who showed that it had a cyclic structure. The structure given was determined by Shriner and Adams [*J. Am. Chem. Soc.*, **47,** 2727 (1925)].

Chaulmoogric Acid $C_{18}H_{32}O_2=\begin{matrix}CH{=}CH\\ \\ CH_2{-}CH_2\end{matrix}\!>CH(CH_2)_{12}COOH.$

Mol. Wt. 280.43; M. Pt. 68.5° C.; Iod. No. 90.51; $[\alpha]_D^{25°}$ 60.3; Ethyl ester, B. Pt. at 10 mm. 222° C.; $[\alpha]_D^{25°}$ 55.42; $N_D^{25°}$ 1.4592. These values were determined by Cole and Cardoso [*J. Am. Chem. Soc.*, **59,** 963 (1937)]. The lead salt is sparingly soluble in ether. Catalytic reduction gives dihydrochaulmoogric acid, M. Pt. 71.2° C. Chaulmoogric acid boils at 247 to 248° C. under 20 mm. pressure.

Power and Gornall [*J. Chem. Soc.*, **86,** 853 (1904)] discovered this cyclic acid in chaulmoogric and hydnocarpus oils. Shriner and Adams [*J. Am. Chem. Soc.*, **47,** 2727 (1925)] showed that the acid has the structure as given above. Stanley and Adams synthesized it from hydnocarpic acid [*J. Am. Chem. Soc.*, **51,** 1515 (1929)]. Chaulmoogryl-aminophenols have been described by Dr. Santos and A. P. West [*Chem. Abs.*, **23,** 4678 (1929)], and capryl, allyl, phenyl, ortho-, meta- and para-cresols by Herrera, Batteke, and West [*Phil. J. Sci.*, **31,** 161 (1926)]. For the manufacture of esters see *Chem. Abs.*, **17,** 612 (1923)]. G. A. Perkins [*Phil. J. Sci.*, **24,** 621 (1924)] describes methods for the preparation of sizable quantities of ethyl, propyl, heptyl, and any esters of the mixed acids from the chaulmoogra oil.

The preparation of substituted amines and amides is described by J. H. Payne, R. Wrenshall and K. Van H. Duker [*J. Am. Chem. Soc.*, **56,** 2126 (1934)]. Crotyl, oleinyl, and other unsaturated esters of chaulmoogra acids are described by K. Burchkies [*Ber.*, **71,** 233, 1855 (1938)].

Gorlic Acid $C_{18}H_{30}O_2=\begin{matrix}CH{=}CH\\ \\ CH_2{-}CH_2\end{matrix}\!>CH(CH_2)_5CH:CH(CH_2)_4COOH.$

Mol. Wt. 278.42; $[\alpha]_D^{25°}$ 60.7°; M. Pt. 6° C.; Iod. No. 182.34. At 10 mm. pressure, the acid distills at 232.5° C. and the ethyl ester at 214° C. These values were determined by H. I. Cole and H. T. Cardoso [*J. Am. Chem. Soc.*, **60,** 612 (1938)]. André and Jonatto [*Bull. soc. chim.*, **43,**

347 (1928)] isolated the acid from gorli seed oil, but evidence of such an acid was found previously in chaulmoogra oil by Dean and Wrenshall [*Chem. Abs.*, **19**, 2476 (1925)].

Alepric Acid $C_{14}H_{24}O_2$; Mol. Wt. 224.33; M. Pt. 48° C.; $[\alpha]_D^{24°}$ 80°; Iod. No. 113.15. This acid was isolated also from *H. wightiana* seed oil by Cole and Cardoso (see Aleprylic Acid). It gave a $[\alpha]_D^{25°}$ 77.2° which indicated that the preparation contained 96.4 per cent of the acid.

Aleprylic Acid $C_{12}H_{20}O_2$; Mol. Wt. 196.28; M. Pt. 32° C.; $[\alpha]_D^{25°}$ 90.78; Iod. No. 129.32.

This acid was discovered as a minor constituent of the oil from the seed of *Hydnocarpus wightiana* and described by H. I. Cole and H. T. Cardoso [*J. Am. Chem. Soc.*, **61**, 234 (1939)].

Elaeostearic ($^{9:10,\ 11:12,\ 13:14}$**-Octadecatrienoic) Acid** $C_{18}H_{30}O_2 = CH_3.(CH_2)_3.(CH{:}CH)_3.(CH_2)_7COOH$; Mol. Wt. 278.42: M. Pt. α-acid 48 to 49° C. and β-acid 71° C.; Iod. No. 273.5 (and for two double bonds 182.35); lead salts sparingly soluble in alcohol and ether. Exposure to light or treatment with traces of iodine or sulfur and warming changes the α-acid into the β-isomer. Bromination in the usual manner gives a tetrabromide, M. P. 115° C.; but with the aid of ultraviolet light, the hexabromide is formed. Hydrogenation of the acids reduces them to stearic acid as the final product. The α- and β-acids give additional products when heated with maleic anhydride (Diels-Alder reaction) which melt respectively at 62.5 and 77° C. [R. S. Morrell and H. Samuels, *J. Chem. Soc.*, **1932**, 2251].

The Wijs iodine number method, as ordinarily conducted, gives values accounting for halogen reacting with but two double bonds, whereas the Hanus reagent gives notably higher results, indicating some reaction with the third double bond during a reaction period of 30 minutes.

Besides tung oil and several other *Aleurites* spec. (*Euphorbiaceae*), elaeostearic acid has been found to be a constituent of seed oils of one or more species of the *Rosaceae* and *curcurbitaceae*.

Attention is called also to the following references:

"Determination of the Constitution of Tung Oil Fatty Acids by Spectroscopic Methods," by W. Manecke and F. Volbert, *Farben. Ztg.*, **32**, 2887 (1927); *J. Soc. Chem. Ind.*, **46**, B-821 (1927).

"Chinese Wood Oil. III. Constitution of Elaeostearic Acid," A. Eibner and E. Rossmann, *Chem. Abs.*, **22**, 4839 (1928).

"Structure of α-Elaeostearic Acid," J. Böeseken, *Analyst*, **53**, 54 (1928).

"The Catalytic Reduction of α- and β-Elaeostearic Acids under the Influence of Nickel," J. Böeseken, J. Van Kumpen and P. L. Blanken, *Chem. Abs.*, **24**, 2985 (1930).

"Unsaturated Acids and Thiocyanogen," H. P. Kaufmann, *Seifensieder Ztg.*, **55**, 297 (1928). One thiocyanogen radical combines with elaeostearic, oleic, petroselinic, ricinoleic, erucic, and linoleic acids.

"On Knowledge of Elaeostearic Acids," E. Rossmann, *Chem. Umschau*, **39**, 220 (1932).

"The Doubly Conjugated System in the Glycerides of α- and β-Elaeostearic Acids," R. S. Morrell, S. Marks, and H. Samuels, *J. Soc. Chem. Ind.*, **52**, 130T (1933).

"Preparation of Pure Elaeostearic Acids from China Wood Oil," A. W. Thomas and J. C. Thomson, *J. Am. Chem. Soc.*, **56**, 898 (1934).

"Reactions in Monolayers of Drying Oils. I. The Oxidation of the Maleic Anhydride Compounds of β-Elaeostearic Acid," G. G. and C. R. Rideal, *Proc. Roy. Soc., London*, **A153**, 116 (1935).

"Drying Oils and Related Compounds," R. S. Morrell and W. R. Davis, *Trans. Faraday Soc.*, **32**, 209 (1936); *Chem. Abs.*, **30**, 277 (1936); deals in part with reaction of elaeostearic acid and maleic anhydride.

"Thermal Polymerization of Ethyl Elaeostearate, 9:11 and 9:12-Ethyl Linoleate," J. S. Brod, W. G. France, and W. L. Evans, *Ind. Eng. Chem.*, **31**, 114 (1939).

Licanic Acid $C_{18}H_{28}O_3$; Mol. Wt. 292.45; α-acid melts at 74–5° C. and the β-acid at 99.5° C.; Iod. No. 260.4 (and 173.6 for two double bonds).

W. B. Brown and E. H. Farmer [*Biochem. J.*, **29**, 631 (1935)] have shown that the α-acid is 4 keto $\Delta^{9:10,\ 11:12,\ 13:14}$-octadecatrienoic acid $CH_3.(CH_2)_3.(CH:CH)_3.(CH_2)_3.CO(CH_2)_2COOH$. These investigators [*J. Chem. Soc.*, **1935**, 1630] prepared the semicarbazones of the α- and β-acids. The α-acid semicarbazone which melted 110–111° C., upon being boiled a very short time in alcohol, was changed to a substance melting at 127° C.; the nature of this is not known. The β-acid semicarbazone melts at 138° C. The α-acid, a major constituent of oiticica oil, is readily changed into the β- (or iso-licanic) form by irradiation in the presence of a trace of iodine or sulfur.

Tetradecenoic (Myristoleic) Acid $C_{14}H_{26}O_2$; Mol. Wt. 226.35; Iod. No. 112.14. Catalytic reduction yields myristic acid.

Although the 9:10-acid is the one commonly found in fish, land and marine animal fats [Hilditch and Houlbroke, *Analyst*, **53**, 246 (1928)], the 5:6- [Tsujimoto, *J. Soc. Chem. Ind., Japan*, **9**, 102 (1926)] and the 7:8-acids have been found in whale oils.

Hilditch and Jasperson [*J. Soc. Chem. Ind.*, **57**, 84 (1938)] have found that the acid is a minor constituent of several vegetable oils. It is probably the 9:10-acid, but its identity remains to be determined. A. Atherton and M. L. Meara [*J. Soc. Chem. Ind.*, **58**, 353 (1939)] reported that the mixed fatty acids from the seed fat of *Pycnanthus kombo* (*Myristica angolensis*) contained 23.4 per cent of this acid.

Hexadecenoic (Palmitoleic) Acid $C_{16}H_{30}O_2$; Mol. Wt. 254.40; Iod. No. 99.78; methyl ester, B. Pt. 140° C. at 5 mm. Catalytic reduction gives palmitic acid and alkaline permanganate oxidation yields a dihydroxy acid which melts at 124.5° C.

This 9:10-hexadecenoic acid, which is one of the major constituents (15 or more per cent) of marine animal oils, has been also named zoömatic and physitoleic acid. T. P. Hilditch [*Rec. trav. chim.*, **57**, 503 (1938)], in his paper on the distribution of this acid in natural fats, suggests that its systematic name hexadecene-9-oic acid be now used, and that the older names be discarded.

Although widely distributed, the acid is most abundant in fats of aquatic fauna, algae and diatoms. It is a minor constituent of various seed and fruit oils as shown by T. P. Hilditch and H. Jasperson [*J. Soc. Chem. Ind.*, **57**, 84T (1938)]. Also H. Fiedler [*Fette u. Seifen*, **46**,

453 (1939)] discusses the occurrence of this acid in natural fats, citing 24 references.

Parinaric Acid $C_{18}H_{28}O_2$; Mol. Wt. 276.40; M. Pt. 83 to 83.5° C.; Iod. No. 367.35. E. H. Farmer and E. Sunderland [*J. Chem. Soc.*, **1935**, 759] investigated this acid and suggested that it was a tetraene acid having the structure $CH_3 . CH_2(CH : CH)_4 . (CH_2)_7COOH$; this was confirmed by H. P. Kaufmann, J. Baltes and S. Funke [*Fette u. Seifen*, **45**, 302 (1938)]. This acid is a major constituent of the seed oil of *Parimarium laurinum (Rosaceae)*.

Punicic Acid $C_{18}H_{30}O_2$; Mol. Wt. 278.4; M. Pt. 44° C.; Iod. No. 273.5. It is a constituent of pomegranate (*Punica granatum* of the *Punicaceae*) seed oil. Y. Toyama and T. Tsuchiya [*J. Soc. Chem. Ind. Japan*, **38**, 182B (1935); *Chem. Abs.*, **29**, 5294 (1935)] isolated the acid and found that it was an isomer of elaeostearic acid. This was confirmed by E. H. Farmer and F. A. van der Heuvel [*J. Chem. Soc.*, **1936**, 1809]. It is not so readily oxidized when exposed to air as is α-elaeostearic acid. These investigators could not get the acid to react with maleic anhydride, which indicated that it did not contain conjugated double bonds. Exposure of a xylene solution of the acid, to which a very small quantity of sulfur had been added, to ultraviolet light changed it to β-elaeostearic acid. Hydrogenation of the acid converted it into stearic acid. Absorption spectra measurements were also made; these showed that the acid was not α- or β-elaeostearic acid or a mixture of them. For other details, the original reference should be consulted.

Hydroxy Acids

Dihydroxystearic Acids $C_{18}H_{36}O_4$; Mol. Wt. 316.47; Acetyl V. 280.5. The acid obtained by the oxidation of ordinary oleic acid in an alkaline solution with permanganate [*cf.* Lapworth and Mottram, *J. Chem. Soc.*, **127**, 1628 and 1987 (1925)] melts at 141 to 143° C., but others report melting points from 131 to 137° C. It is insoluble in water, sparingly so in ether, and soluble in hot alcohol. The corresponding dihydroxy acid obtained by the oxidation of elaidic acid melts at 99 to 100° C.; that from petroselinic acid at 122° C. The dihydroxy acid, which is present to the extent of one per cent in castor oil, melts at 141 to 142° C. Tomecks and Adams [*J. Am. Chem. Soc.*, **49**, 522 (1927)] synthesized a number of hydroxystearic acids; Radcliffe and Gilson prepared derivatives [*J. Soc. Chem. Ind.*, **42**, 150A (1923)].

Trihydroxystearic Acids $C_{18}H_{36}O_5$; Mol. Wt. 332.47; Acetyl V. 367.4. Oxidation of ricinoleic acid in an alkaline solution in the cold by a dilute permanganate solution gives hydroxy acids that melt at 110 to 111° C. and 140 to 142° C. The lower-melting-point acid is readily soluble in ether and benzene; the other is soluble in boiling water, but sparingly so in alcohol and ether.

Tetrahydroxystearic (Sativic) Acids $C_{18}H_{36}O_6$; Mol. Wt. 348.47; Acetyl V. 444.8. Two sativic acids are obtained by the oxidation of linoleic acid in the usual manner with permanganate in the presence of

alkali. They dissolve readily in hot alcohol or glacial acetic acid and have a slight solubility in boiling water. They are insoluble in cold water, ether, and are but little soluble in many other organic solvents. One of the acids melts at 174° C. and the other at 163.5° C.

Hexahydroxystearic (Linusic) Acids $C_{18}H_{36}O_8$; Mol. Wt. 380.47; Acetyl V. 532.5. The permanganic oxidation of linolenic acid in alkaline solution yields a linusic acid which melts at 203.5° C. It is very soluble in water, more so than the sativic acids, sparingly soluble in alcohol, and insoluble in ether. The second or isolinusic acid, obtained along with the first, melts at 173° to 175° C. It is readily soluble in hot water, hot alcohol, and insoluble in chloroform, ether, etc. The preparation of hydroxy acids from unsaturated acids is described by Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th Ed., Vol. 1, pp. 574–9.

Alcohols

Although (wax-free) vegetable fats themselves contain no alcohols such as are found in animal and vegetable waxes, those obtained by catalytic reduction under high pressures from various fatty acids have in recent years become of industrial importance. In view of these developments, the following references may be of interest:

"Fatty Alcohol Sulfonation Products," M. Briscoe, *J. Soc. Dyers*, **1932**, 127; *Oil Col. Trds. J.*, **81**, 1484 (1932).

"The Place of Sulfonated Fatty Alcohols in Industry," M. Briscoe, *Chem. Markets*, **30**, 238 (1932).

"The Catalytic Hydrogenation of Esters to Alcohols," K. Folkers and H. Adkins, *J. Am. Chem. Soc.*, **53**, 1095 (1931); **54**, 1145 (1932).

"Sulfonated Higher Alcohols," D. H. Killefer, *Ind. Eng. Chem.*, **25**, 138 (1933).

"Determination of Fatty Alcohols in Their Sulfonated Products," K. Lindner, A. Russe, and A. Beyer, *Fettchem. Umschau*, **40**, 93 (1933); *Chem. Abs.*, **27**, 3838 (1933).

"The Analysis of Aliphatic Alcohol Sulfonates," H. Jahn, *Chem. Ztg.*, **57**, 383 (1933); *Chem. Abs.*, **27**, 3839 (1933).

"Sulfated Fatty Alcohols," C. A. Tyler, *Soap*, **10**, No. 4, 21 (1934); discusses their uses.

"Cetyl Alcohol—Universal Cosmetic Base," J. Kalish, *Drug Cosmetic Ind.*, **37**, 595 (1935).

"Fatty Alcohols and Their Derivatives," A. H. Prevost, *Chem. Ind.*, **41**, 477 (1937).

"Preparation of Higher Alcohols by Hydrogenation of Copper Salts," S. Ueno, *J. Soc. Chem. Ind. Japan* (Sppl. B.), **62**, (1938); *Oil Col. Trds. J.*, **93**, 1675 (1938).

Glycerin (Glycerol) $C_3H_8O_3 = CH_2OH \cdot CHOH \cdot CH_2OH$; Mol. Wt. 92.09; M. Pt. 20° C.; B. Pt. 290° C. at 760 mm. 210° C. at 50 mm., 182° C. at 20 mm. and 155° C. at 5 mm. Pure glycerin, upon distillation at ordinary pressure, undergoes but slight decomposition. In the presence of even small quantities of salts of various kinds, decomposition occurs during distillation with the formation of acrolein, water and polyglycerides.

Glycerin was discovered by K. W. Scheele in 1779, but its present name is due to Chevreul. Several chemists, including Berthelot, found that it was a trihydric alcohol.

Glycerin is a clear, colorless, hydroscopic, thick liquid with a slight

but characteristic odor, and it has a sweet taste. Although soluble in all proportions in alcohol and water, it has very little solubility in the fats and oils, and is practically insoluble in benzene, chloroform, anhydrous ether and petroleum ether. However, it is soluble in a mixture consisting of 2 volumes of absolute alcohol and 1 volume of ether (or chloroform), and this mixture of solvents may be used to separate glycerin from gums, gelatin, sugars, and many salts. Glycerin itself is a good solvent for many salts and other substances. It occurs chiefly in combination with fatty acids, the esters of which are known as glycerides. Fats, which for one reason or another have undergone extensive hydrolysis, rarely contain any detectable quantities of glycerin. Occasionally, it has been found in highly acid palm oil. It is apparent that glycerin is rapidly converted into other substances, and with very few exceptions, directly after the hydrolysis of the glycerides. In some cases, and under certain conditions, the hydrolysis, at least in part, proceeds by stages, with the result that diglycerides (and perhaps monoglycerides) are formed and remain without further change for long periods of time. Although the author has isolated diglycerides in some cases, he has never been able to find any evidence of the presence of monoglycerides. Glycerin is found uncombined in fermented sugar solutions. This fact was discovered by Pasteur in 1873.

The modern manufacture of glycerin is a highly specialized industry and a description of the equipment and methods employed is consequently outside the scope of this volume. Attention is directed to the comprehensive monograph of the American Chemical Society entitled "Glycerol and the Glycols," by J. W. Lawrie (Reinhold Publishing Corp., New York, 1928), in regard to the various methods of glycerin manufacture, specifications, uses, methods of examination, and much other pertinent information.

The chief source of glycerin is still the spent lyes of the soapmakers. These are concentrated and freed as completely as possible from salts, etc., and the glycerin is distilled from them under a high vacuum with the aid of superheated steam. Depending upon the demand, more or less of this product is redistilled under diminished pressure and decolorized, if necessary, by treatment with bleaching carbon.

The still residues or "foots" contain salts, more or less glycerin and polymerized glycerin, and other non-volatile substances. The undistilled glycerin and polymers generally amount to about 25 per cent of the foots. For additional information, "The Composition of the Residue on Distillation of Crude Glycerin," by E. Lewis [*J. Soc. Chem. Ind.*, **41**, 91T (1922)] may be consulted. Also attention is called to the following references:

"Refining of Salt Crude Glycerin," W. E. Sanger, *Chem. Met. Eng.*, **27**, 827 (1922); "Recovery of Glycerin from Spent Soap Lyes," Sanger, *ibid.*, p. 1211.

"The Manufacture and Uses of Glycerin," Anon., *J. Soc. Chem. Ind.*, **43**, 586 (1924).

"Glycerol Distillation, II, Wood Glycerol Refining Plant," E. T. Webb, *Chem. Abs.*, **20**, 3583 (1926).

"Glycerin and Its Substitutes," Drake and Lewis, *J. Soc. Chem. Ind.*, **47**, 1073 (1928).
"Viscosity of Glycerin Solutions," Z. V. Cocks, *J. Soc. Chem. Ind.*, **48**, 279T (1929).
"New Applications of Glycerin," G. Leffingwell and M. A. Lesser, *Chem. Ind.*, **42**, 395 (1938).
"Glycerin Distillation," O. H. Wurster, *Oil and Soap*, **15**, 292 (1938).
"Synthesis of Glycerides with the Aid of Trityl Compounds and Application of This New Method," P. E. Verdake, *Fette u. Seifen*, **45**, 457 (1938).
"Unusual Uses of Glycerin," *Chem. Ind.*, **44**, 293 (1939).
"Fat Splitting and Glycerol Manufacture," R. Heublyum, *Mfg., Perfumer*, **3**, 214 (1938); *Chem. Abs.*, **33**, 1939 (1939).
"Synthetic Glycerin: Can It Be Produced Competitively?" H. A. Levey, *Chem. Ind.* **44**, 143 (1939).
"Use of Glycerin in New Chemical Specialties," G. Leffingwell and M. A. Lesser, *Chem. Ind.*, **57**, 57 (1940).
"Synthetic Glycerin From Alcohol," E. C. Williams, *et al.*, *Chem. Met. Eng.*, **47**, 834 (1940).
"Glycerin: Some Observations on Its Recovery and Refining in Modern Soap Plant Practice," J. W. McCutcheon, *Soap*, **17**, No. 11, 24 (1941).
"Glycerin Derivatives: Their Properties and Uses," R. N. du Puis, C. W. Lenth and J. B. Segur, *Oil and Soap*, **18**, 31 (1941).
"Glycerin: Its Compounds and Uses," B. Leavitt, *Chem. Ind.*, **50**, No. 1, 34 (1942).
"Glycerin Recovery," W. J. Govan, Jr., *Oil and Soap*, **19**, 79 (1942).

The polymer diglycerin, known as "D" glycerin, is prepared and used in the manufacture of low-freezing dynamite. It is made by heating glycerin to about 260° C. under slightly reduced pressure for several hours with 0.2 per cent of sodium bicarbonate. Bashford (U. S. Patent 1,467,299, 1923) heats glycerin with 0.5 per cent of zinc chloride for 5 hours at 200° to 250° C., under reduced pressure. Hilbert (U. S. Patent 1,126,467, 1915) heats glycerin with 0.05 per cent of iodine for 2 hours at 210° C., while the mixture is constantly agitated. The diglycerin is purified by distillation. It boils at 257 to 260° C. at 30 mm.

Since about 1916, "fermentation" glycerin has at times been produced in considerable quantities, particularly in Germany during World War I. In order to increase the yield, various salts, including sodium sulfite carbonate, and phosphate, ammonium and potassium salts are added to the diluted molasses or other sugar solution before the fermentation is started. In most cases, the yield of glycerin amounts to about 8 or 10 per cent (although some have claimed considerably higher yields) of the weight of sugar taken. Cocking and Lilly (Brit. Patent 164,034) used a mixture of bisulfite and sulfate and claimed that as high as 45 per cent of the sugar can be converted into glycerin (*cf. Chem. Age*, **1922**, 30, 429). During the fermentation, alcohol and acetaldehyde are also produced. Those interested will find additional information in the following references:

Neuberg, *Biochem. Zeit.*, **89**, 365 (1918).
"Fermentation Glycerin," Connstein and Ludicke, *J. Soc. Chem. Ind.*, **38**, 391A (1918).
"Production of Glycerin from Molasses," Long, *J. Soc. Chem. Ind.*, **38**, 175 (1918). Also see *Chem. Trade J.*, **81**, 327 (1927), and *J. Soc. Chem. Ind.*, **39**, 608A (1919) for patented methods.

Glycerin is sold under the following grades: Crude glycerin, distilled or dynamite glycerin, and chemically pure glycerin (glycerol), and

various specifications are in use covering each of the grades. Crude glycerin includes the following: saponification glycerin, distillation glycerin, and soap lye or soap glycerin.

Uses. Glycerin is used in the manufacture of dynamite, tobacco, soft drinks, cosmetics, pharmaceutical preparations, certain kinds of leather, polishes, inks, artificial resins, ester gum, stable foams, and for many other purposes, including the drying of illuminating gas [*Oil Fat Ind.*, **6**, No. 8, 31 (1929)]. *See* "Preparation, Properties, and Uses of Glycerol Derivatives," A. Fairbourne and others, *J. Soc. Chem. Ind.*, **49**, Part I, p. 1021; Part II, p. 1069 (1930).

Trimethyleneglycol $CH_2OH \cdot CH_2 \cdot CH_2OH$; Mol. Wt. 76.06; B. Pt. 210 to 211° C.; one of the products formed when some of the glycerides of fats are decomposed, and obtained along with glycerin. During the distillation of glycerin, it occurs in the lower-boiling fraction; consequently this is not suitable for the manufacture of nitroglycerin.

Tests. When glycerin is heated with acid potassium sulfate, acrolein is evolved, which is easily detected by its pungent odor. For the detection of small quantities of glycerin, it is preferable to conduct the test in a hard glass test tube using a quantity of acid sulfate about double the weight of the sample to be tested. If the fumes are conducted into an ammoniacal solution of silver nitrate, the formation of a silver mirror indicates glycerin in the sample tested. Other tests have been proposed, but they are not specific for glycerin.

Determination of Glycerin. Methods have been described based upon weighing the separated glycerin, but it should be noted that it is slightly volatile at 100° C. Glycerin is lost during the concentration of aqueous solutions containing 70 per cent or more and also by the evaporation of alcoholic solutions in the ordinary manner on a steam bath. In either case, the quantity of glycerin lost by volatilization varies considerably and depends upon the extent of exposed surface of the liquid, and the shape and the material of the apparatus used. This loss is much reduced when the evaporation is made in small flasks in a place free from drafts. Of the numerous procedures that have been proposed for the determination of glycerin, the acetin and Hehner dichromate methods are those in most common use. The acetin method originated by Benedict and Cantor [*J. Soc. Chem. Ind.*, *7*, 696 (1888)] is based on converting the glycerin by acetic anhydride into the tri-acetate and from the quantity of caustic soda or potash required for its saponification, the quantity of glycerin present in the sample is calculated. Under "Methods of Analysis" will be found the procedure of the International Committee for the examination of crude glycerin.

For the determination of glycerin in aqueous solution use is frequently made of the specific gravity and the refractive index, for which tables of data covering a wide range of concentrations have been prepared and repeatedly published. Sachs and Riemer [*Chem. Abs.*, **21**, 3759 (1927)] and others have shown that practically identical results are obtainable by these methods. However, O. Berth (*Brit. Chem. Abs.* B**1928**, 717)

found that the acetin method, as ordinarily conducted, gives results from 0.2 to 0.3 per cent too high, and that they are due to the carbonate present in the alkali used; he has indicated how this can be avoided.

Fachini and Somazzi [*Chem. Trade J.*, **73**, 127 and 702 (1923)] use the dichromate method, but with the modification which includes the determination of the carbon dioxide formed according to the reaction $3C_3H_8O_3 + 7K_2CR_2O_7 + 28H_2SO_4 = 9CO_2 + 7CR_2(SO_4)_3 + 7K_2SO_4 + 40H_2O$. By their procedure, glycerin and trimethylene glycol are determined.

Flaschenträger (*Brit. Chem. Abs.*, B**1929**, 896) has developed a micro-method by which it is claimed that the glycerin can be determined in a 20-mg. sample of fat. It is based upon the method of Zeisel and Fanto, which depends upon the conversion of all of the glycerin by hydriodic acid into isopropyl iodide, and the determination of the iodine in this compound.

Methods by C. A. Rojahn [*J. Soc. Chem. Ind.*, **39**, 314A (1920)] and Cocks and Solnay [*J. Soc. Chem. Ind.*, **41**, 17T and 32T (1922)] have been proposed for the determination of trimethylene glycol ($CH_2OH—CH_2—CH_2OH$) present in crude and distilled glycerin. Other references are G. Smith [*J. Text. Inst.*, **17**, 187T (1926)] and O. Berth, *Oil Col. Trds. J.*, **76**, 493 (1929).

A close approximation of the percentage of glycerin in a fat can be calculated from the saponification value of the glycerides (neutral oil) by multiplying it for the factor 0.054664.

Glycerides. Triglycerides are the normal constituents of the fats, but as previously mentioned, under certain unknown conditions, small quantities of diglycerides (and possibly monoglycerides) are formed by the partial hydrolysis of the triglycerides. Formerly, it was believed that the fats consisted of simple triglycerides, such as palmitin, olein, etc., but later investigations have shown that the majority of the fats are composed almost entirely of mixed triglycerides, of which dipalmitoolein and palmitodistearin are examples.

A number of mixed triglycerides have been isolated from various fats. Some of these as well as many mono- and diglycerides, have been synthesized. Owing to the possibility of the shifting of the acyl groups from one position to another in the molecule as shown by Fischer, Bergmann and others, considerable doubt exists in regard to the structure of quite a number of the glycerides reported in the literature prior to 1920. In the synthesis of glycerides it is important to use only methods by which it is possible to combine and maintain each acyl group in a known position. Of course, no such precautions are necessary in preparing the so-called simple triglycerides.

For the preparations of simple glycerides, the method proposed by T. L. Garner [*J. Soc. Chem Ind.*, **47**, 279T (1928)] is suggested. It is based on heating equivalent quantities of the fatty acid and glycerin in an atmosphere of carbon dioxide, at a temperature of 200° C. for 6 hours, during which time the esterification flask is rotated. The yield of glyceride is reported as being almost theoretical. For convenience,

the three positions for esterification in the glycerin molecule have been designated in the following formula:

$$\begin{array}{l}(\alpha)\ CH_2OH\\ \quad\ |\\ (\beta)\ CHOH\\ \quad\ |\\ (\gamma)\ \text{or}\ (\alpha)\ CH_2OH\end{array}$$

Using acetone-glycerin as a starting point, Fischer and Bergmann prepared several monoglycerides [*Ber.*, **53**, 1589 (1920)], and these have been confirmed by later works of Bergmann and others using 2-phenyl-5-hydroxymethyloxazolidine. Those interested, should consult Bergmann [*Z. Physiol. Chem.*, **137**, 27 (1924)], Bergmann and Sabetay [*ibid.*, **137**, 47 (1924)] for details of these syntheses. By means of this zolidine derivative and some other substances mentioned by them, it is possible also to prepare di- and mixed triglycerides, in which the positions of the acyl groups are known.

Particular attention is directed to the extensive investigations of Averill, Roche and King [*J. Am. Chem. Soc.*, **51**, 866 (1929)] on the preparation and melting points of glycerides of known constitution. They used the later Fischer methods for the synthesis of symmetrical and unsymmetrical mixed glycerides, and prepared the compounds given in the table.

Glycerides	Melting Points ° C.	Previously Recorded Range of Melting Points ° C.
α-Monopalmitin	77.0	58.0 to 78.0
α-Monomyristin	67.3	68.0
α-Monocaprin	51.4	...
α-Monolaurin	63.0	52.0 to 63.0
α-Monostearin	81.1	61.0 to 82.0
α,α′-Dilaurin	56.6	55.0 to 57.0
α,α′-Distearin	79.1	74.0 to 79.0
α,α′-Dipalmitin	69.5	69.0 to 70.0
α,α′-Dimyristin	63.8 to 64.4	61.0 to 63.0
β-Trilaurin	45.6	45.0 to 46.4
β-Stearo-α,α′-dilaurin	50.9	37.5
α-Stearo-α,β-dilaurin	45.4	46.0
β-Lauro-α,α′-Dimyristin	49.2 to 49.5	46.5
α-Lauro-α′,β-dimyristin	48.5	45.0
β-Palmito-α,α′-dimyristin	59.8 to 60.0	...
α-Palmito-α,β-dimyristin	53.0	...
β-Stearo-α,α′-dipalmitin	64.8	59.0 to 63.3
α-Stearo-α′,β-dipalmitin	62.6	60.0 to 63.5
β-Aceto-α,α′-dipalmitin	54.0	49.0
α-Aceto-α′,β-dipalmitin	51.2	67.0
β-Capro-α,α′-dipalmitin	66.0	...
α-Capro-α′,β-dipalmitin	60.0	...
β-Lauro-α,α′-dipalmitin	63.5 to 4.0	...
α-Lauro-α′,β-dipalmitin	54.5	...
β-Myristo-α,α′-dipalmitin.	58.5 to 9.0	...
α-Myristo-α,β-dipalmitin	55.5	...
β-Aceto-α,α′-distearin	62.7	56.0 to 64.0

It will be observed that the symmetrical isomer in each case had a higher melting point than that of the unsymmetrical isomer. In quite a number of cases, the previously recorded melting points given for an

individual glyceride cover a wide range, and many are not in agreement with those found by these investigators. These differences are largely due to the methods employed for the synthesis.

Attention is also called to the following references:

"Glycerides and Fatty Acids," A. Heiduschka and H. Schuster, *J. Prakt. Chem.*, **120**, 145 (1928).

"Mechanism of Organic Reactions. I. The Wandering of Acyl Groups in Glycerol Esters," H. Hibbert and N. Carter, *J. Am. Chem. Soc.*, **51**, 1601 (1929).

"The Partial Esterification of Polyhydric Alcohols. Part 10. The Discovery of the First True β-Glyceride," A. Fairbourne, *J. Chem. Soc.*, **1930**, 369.

"The Physical Properties of Pure Triglycerides," R. B. Joglekar and H. E. Watson, *J. Soc. Chem. Ind.*, **47**, 365T (1928).

"Synthetic Glycerides. III. Mixed Triglycerides of the Distearin Series," J. N. Roehe and C. G. King, *J. Am. Chem. Soc.*, **54**, 705 (1932).

"The Component Glycerides of Partially Hydrogenated Fats. Part 1. The Alterations in Glyceride Structure Produced During Progressive Hydrogenation of Olive and Cottonseed Oils," T. P. Hilditch and E. C. Jones, *J. Chem. Soc.*, **1932**, 805.

"An Examination of Certain Azelo Glycerides Obtained During the Oxidation of Some Synthetic and Natural Glycerides," T. P. Hilditch and S. A. Saletore, *J. Soc. Chem. Ind.*, **52**, 101T (1933).

"Synthetic Glycerides. IV. Mixed Triglycerides of the Dilaurin Series," O. E. McElroy and C. G. King, *J. Am. Chem. Soc.*, **56**, 1191 (1934).

"Regularities in the Glyceride Structure of some Technically Important Vegetable Fats and Oils," T. P. Hilditch and E. C. Jones, *J. Soc. Chem. Ind.*, **53**, 14T (1934); *Cf. C.* Collin and Hilditch, *Biochem. J.*, **23**, 1273 (1929).

"A Note on the Rate of Formation of Fully Saturated Glycerides During Hydrogenation of Different Natural Fats," T. P. Hilditch and H. Paul, *J. Soc. Chem. Ind.*, **54**, 336T (1935).

"Experiments on the Direct Esterification of Higher Fatty Acids with Glycerol and Ethylene Glycol," T. P. Hilditch and J. G. Rigg, *J. Chem. Soc.*, **1935**, 1774.

"An X-Ray and Thermal Examination of the Glycerides. VII. Unsymmetrical Mixed Triglycerides," G. R. Carter and T. Malkin, *J. Chem. Soc.*, **1939**, 1518 (Also see pages 103, 577 and 1141).

"An X-Ray and Thermal Examination of the Glycerides. Part II." T. Malkin and M. R. Shurbagy, *J. Chem. Soc.*, **1936**, 1628.

"Recent Advances in the Drying Oil Field, with Special References to Glycerol Esters of Drying Oils," C. W. A. Mundy, *J. Oil Col. Chem. Assoc.*, **21**, 96 (1938).

"Mono and Di-Glycerides: Their Use in Food Manufacture," *Food Mfgr.*, **15**, 187 (1940).

"The Chemical Synthesis of Glycerides," F. A. Norris, *Oil and Soap*, **17**, 257 (1940). Gives a list of 146 patent and literature references.

"Composition and Structural Characteristics of Glycerides in Relation to Classification and Environment," H. E. Longenecker, *Chem. Rev.*, **29**, 201 (1941); 273 references.

Space is not available for listing the numerous references to the works of Grün, Bömer, Garner and others on the synthesis of various glycerides, but quite a number of these will be found under the references which have been given.

Sterols

Sterols, which are polycyclic hydroaromatic secondary alcohols, occur both free and in the form of esters wherever the phenomenon of life exists, and they play important roles in life processes about which comparatively little is known. They have been divided into three general groups. The zoösterols comprise those of animal origin; the phytosterols, those from phanerogamus plants; and the mycosterols, those from kryptogamus (particularly the fungi) plants.

Both the saturated and the unsaturated sterols occur in nature, but the latter, for the most part, are present in much larger quantities. The unsaturated sterols contain one, two, or three double bonds. All the sterols show optical activity, those which are unsaturated being levorotatory.

The glucosides of the phytosterols which are present in plants (bark, leaves, seeds, etc.) are known as phytosterolines; quite a number of these have been isolated from various sources and investigated.

The attention of those interested in the structure and chemistry of the sterols is called to "Sterols and Related Compounds," by E. Friedman, Cambridge, 1937 (Chemical Publishing Co., Brooklyn) and to "The Chemistry of Natural Products Related to Phenanthrene," by L. F. Fieser (Reinhold Publishing Corp., New York, 1937).

In the examination of fats and oils, the sterols will be found in the unsaponifiable fraction which also contains hydrocarbons, and in many cases, higher fatty alcohols. Most fats and oils contain only a few tenths of a per cent of sterols and the refined products contain even less.

Tests. Sterols give a white precipitate when the alcoholic solution is heated with an alcoholic solution of the glucoside digitonin ($C_{55}H_{49}O_{28}$). The precipitate is insoluble in water, acetone, ether, and very sparingly soluble in cold alcohol. Sterol esters are not precipitated by digitonin. Steuart [*Analyst,* **48**, 155 (1923)] recommends that the unsaponifiable matter from 50 grams of fat be dissolved in 50 cc. of 95 per cent alcohol and the addition of 50 cc. of 90 per cent alcohol containing 0.5 to 1 gram of digitonin. After the solution has stood about 16 hours, the precipitate may be collected in a Gooch crucible, washed with 95 per cent alcohol, then with ether, dried at about 110° C., and weighed, if desired. The sterols can be obtained from this compound by boiling with an excess of acetic anhydride (5 to 6 cc.) for a half hour, pouring the mixture into 75 cc. of water, and collecting the precipitate, after the esters have solidified, on a filter. The precipitate and filter are thoroughly washed with water, dried, and the acetates extracted from the digitonin by means of ether, *cf.* Lifschutz [*J. Chem. Soc.*, **114**, 179 (1918)]. Zuicker [*Pharm. Weekblad,* **54**, 101 (1917)] separated cholesterol in the form of a double compound with lithium chloride. The fat is dissolved in pyridine, and to this solution is added a saturated pyridine solution of lithium chloride. The double compound melts at 140° C. and is decomposed by boiling water. It is probable that similar compounds would be obtained with other sterols.

The characteristic color test for sterols, known as Liebermann's reaction, is made as follows: A small quantity of the sterol or unsaponifiable matter separated from a fat is dissolved in 2 cc. of acetic anhydride; when sulfuric acid (3 to 5 drops) is added, a violet pink color is developed. The Burchard modification, which is more commonly used, is based on dissolving the samples to be tested in 2 cc. of chloroform, 20 drops of acetic anhydride and 2 drops of sulfuric acid. The violet-reddish color soon changes to blue or green. On account of the colors given by resins, care should be taken that none of these substances is present

when the sterol tests are made. Many color reactions have been proposed for detecting sterols, among which may be mentioned those of G. S. Whitly [*Biochem.* J., **17**, 5 (1922)].

In regard to the identification of sterols by the melting points of their acetates, and in particular those obtained in the usual manner from the unsaponifiable matter from mixtures of fats and oils, attention of those interested is especially called to the investigation of Steuart [*Analyst*, **48**, 155 (1923)]. He concluded that this test definitely indicates whether the sample is purely of animal or vegetable origin, but that the detection of animal fat in admixture with vegetable fat or oils by this means is far from definite in many cases.

Cholesterol. $C_{27}H_{46}O$; Mol. Wt. 386.64; M. Pt. 148.5° C.; $[\alpha]_D^{15°}$-29.92° (ether solution); acetate, M. Pt. 114° C.; palmitate, M. Pt. 78.80° C.; stearate, M. Pt. 82° C.; oleate, M. Pt. 41-46° C.; dibromide, M. Pt. 109-111 and 123-24° C. With digitonin, it forms an addition product ($C_{27}H_{46}O.\ C_{55}H_{92}O_{29}$) which has but little solubility in alcohol at ordinary temperatures and even less in acetone, benzene and ether. From anhydrous solvents cholesterol crystallizes in fine, needle-shaped prisms and from 95 per cent alcohol, in flat monoclinic prisms which contain a molecule of water of crystallization. It is insoluble in water, sparingly so in cold alcohol, but readily soluble in hot alcohol, ether, chloroform, and other organic solvents. The dibromide is sparingly soluble in a mixture of ether and glacial acetic acid. [A. Windaus *Analyst*, **31**, 411 (1906)] and this offers a means for its separation from phytosterols, the bromides of which are reported to be soluble in this mixture of solvents.

It gives color tests with the Liebermann-Burchard, the Salkowski, the Rosenheim, and other reagents. Color tests cannot be used to distinguish cholesterol in the presence of phytosterols. On exposure to air and light it gradually undergoes some changes causing the melting point to become lower and also notably decreasing the solubility in ether.

Although various other sterols of animal origin have been isolated and studied, there appears to be no occasion for discussing them in this book.

Attention is called to some of the more recent references:

"Synthesis of Cholesterol in the Animal Body," H. J. Charmon, *Biochem. J.*, **19**, 424 (1925).

"A Critical Study of the Methods of Estimating Cholesterol and Its Esters," J. A. Gardner and F. W. Fox, *Biochem. J.*, **18**, 1058 (1924).

"Gravimetric Micro Cholesterol Determination," T. Tominaga, *Chem. Abs.*, **19**, 3101 (1925).

"Studies on the Cholesterol Content of Normal Human Plasma," J. A. Gardner and H. Gainsborough, *Biochem. J.*, **21**, 130 and 141 (1927).

"Determination of Cholesterol in Small Amounts in Blood," *S. M. Long, J. Biol. Chem.*, **76**, 361 (1928).

"The Allophanates of Certain Sterols and for Vitamin A," M. Tange and E. V. McCollum, *J. Biol. Chem.*, **76**, 445 (1928).

"Water-Soluble Cholesterol Esters," R. Schonheimer and F. Brensch, *Z. physiol. Chem.*, **211**, 19 (1932).

"Determination of Cholesterol by Chromic Oxidation," F. Kayser and C. Mathieu, *Bull. Soc. Chim.*, **6**, 715 (1939).

Phytosterols. The plant sterols which were isolated were for many years believed to be individual substances, but later investigations have shown that they are mixtures of two or more sterols, even though their melting points remain unchanged after repeated recrystallizations. The separation of an individual sterol in a pure condition is extremely difficult. R. J. Anderson and co-workers have called attention to the importance of determining the optical rotation in connection with the identification of the sterols. [*Cf.* Anderson, *et al., J. Am. Chem. Soc.*, **48**, 2976, 2987 (1924); *J. Biol. Chem.*, **71**, 389 (1927)].

Attention is called to the following references:

"Colour Reactions of Sterols with Nitric Acid," O. Rosenheim and R. K. Callow, *Biochem. J.*, **25**, 748 (1931).

"Phytosterols of Seeds and Fruits," P. Manceau and Bige, *Compt. rend. soc. biol.*, **107**, 635 (1931); *Chem. Abs.*, **26**, 2765 (1932).

"The Ring-System of Sterols and Bile Acids," O. Rosenheim and H. King, *J. Soc. Chem. Ind.*, **51**, 464 (1932).

"Carbon Skeleton of the Sterols," J. D. Bernal, *J. Soc. Chem. Ind.*, **51**, 466 (1932).

"Recent Developments in the Chemistry of the Sterols and Related Compounds," *J. Soc. Chem. Ind.*, **55**, 129 (1936).

"Fat Metabolism in Plants with Special Reference to Sterols," P. L. MacLachlan, *J. Biol. Chem.*, **113**, 197 (1936).

"Biochemistry of the Sterol Group: Sex Hormone Group," A. Butenandt, *J. Soc. Chem. Ind.*, **55**, 990 (1936).

"The Separation of Sterols by the Chromatographic Adsorption Method," K. Ladenburg, E. Fernholz, and E. S. Wallis, *J. Organic Chem.*, **3**, 294 (1938).

Sitosterol. $C_{29}H_{50}O$; Mol. Wt. 414.69; M. Pt. 140-141° C.; $[\alpha]_D^{20°}$ −36.6°; acetate, M. Pt. 130°-131° C.; benzoate, M. Pt. 145.5° C.; dibromide, M. Pt. 98° C. As ordinarily obtained, it melts at 137-138° C. and gives $[\alpha]_D^{20°}$ about −34°. The acetate melts at about 127° C. For many years prior to 1932, the formula for sitosterol was given as $C_{27}H_{46}O$. Those interested in the structure of sitosterols are referred to the investigations of Ruzicka and Eichenberger [*Helv. chim. acta*, **18**, 430 (1935)].

The sitosterols which have been isolated are as follows: α sitosterol, M. Pt. 135-136° C.; $[\alpha]_D^{20°}$ −13.45°; β sitosterol; M. Pt. 139-140° C.; $[\alpha]_D^{20°}$ −36.11°; acetate, M. Pt. 127-128° C., $[\alpha]_D^{20°}$ −39°; γ sitosterol, M. Pt. 143-144° C., $[\alpha]_D^{20°}$ −42.43°; acetate, M. Pt. 143-144° C., $[\alpha]_D^{20°}$ −46.09°.

Dihydrositosterol. $C_{29}H_{52}O$; Mol. Wt. 416.7; M. Pt. 144° C.; $[\alpha]_D^{18°}$ + 28°; acetate, M. Pt. 141° C., $[\alpha]_D^{18°}$ + 12.72°. It does not give the Liebermann-Burchard color test. Although this sterol is found in small proportions in various fats and oils, none to date has been obtained from either cottonseed or linseed oils.

Brassicasterol. $C_{28}H_{46}O$; Mol. Wt. 398.65; M. Pt. 148° C.; in chloroform $[\alpha]_D^{18°}$ −64.5°; acetate, M. Pt. 157°-158° C.; benzoate, M. Pt. 169° C. (fuses at 167°, giving a turbid liquid); tetrabromide acetate, Decomp. Pt. 209° C. It contains two double bonds. From alcohol, it crystallizes in thin hexagonal prisms which contain a molecule of water. It gives the sterol tests and forms a difficultly soluble addition product with digitonin.

Windaus and Welch [*Berichte,* **42,** 612 (1909)] describe the isolation and purification of the sterol from the unsaponifiable constituents of rape seed oil.

Stigmasterol. $C_{29}H_{48}O$; Mol. Wt. 412.67; M. Pt. 170° C.; in chloroform $[\alpha]_D^{20°}$ −51.0°; acetate, M. Pt. 144-145° C.; $[\alpha]_D^{20°}$ −45.0°; benzoate, M. Pt. 160° C.; palmitate, M. Pt. 99° C.; stearate, M. Pt. 101° C.; tetrabrom acetate, Decomp. Pt. 205° C. It contains two double bonds. From a mixture of alcohol and chloroform, it crystallizes with a half molecule of water. It gives the sterol color tests and forms a difficultly soluble digitonin addition product ($C_{29}H_{48}O$. $C_{56}H_{92}O_{29}$).

Calabar (*Physostigma venenosum*) bean fat, according to Windaus and Hauth [*Berichte,* **39,** 4378 (1906)], contains about one per cent of this sterol, which is found also in coconut, corn, rape and other oils.

Ergosterol. $C_{28}H_{44}O$; Mol. Wt. 396.63; $[\alpha]_D^{20°}$ −132° in chloroform; acetate, M. Pt. 173° C.; benzoate, M. Pt. 168° C.; palmitate, M. Pt. 107-108° C.

It was discovered in ergot oil by G. Tanret [*Comp. rend.,* **108,** 98 (1889)] and prior to the investigations of A. Windaus and A. Luttringhaus [*Berichte,* **65,** 1006 (1932)] the formula was given as $C_{27}H_{42}O$.

It occurs in considerable quantities in the unsaponifiable fractions of ergot oil and yeast, and in smaller amounts in fats of both animal and vegetable origin. It contains three double bonds. From alcohol, it separates with a molecule of water in the form of small, leaf-like crystals. From a mixture of ether and glacial acetic acid, hydroscopic needle-like prisms are obtained without water of crystallization. When crystallized from a mixture of one volume of ether and three of acetone, well-formed, elongated, six-sided prisms are obtained.

C. E. Bills and E. M. Honeywell [*J. Biol. Chem.,* **80,** 15 (1928)] have shown that the melting point determination is of no significance as an indication of purity because it varies widely on account of its being exceedingly sensitive to slight differences in moisture content. The melting point is reported to vary from 168 to 183° C. Being extremely sensitive to light, upon exposure it decomposes rapidly and becomes yellow. However, it can be kept without decomposition for a long time in the dark at 0° C. Ergosterol gives characteristic absorption bands in the ultraviolet at 260, 269, 281, and 293 μ, the maximum being at 281 μ. The Rosenheim test, which is made by adding to a chloroform solution of the sterol 9 parts of trichloracetic acid and 1 part of water, gives a red color which turns to a clear blue. As little as .01 mg. of the sterol gives a positive test. The Liebermann-Burchard reaction gives a red color which changes to green, then blue. A red color is obtained by adding antimony trichloride to a chloroform solution of the sterol. A number of other color reactions have been described.

Irradiation (using wave-lengths from 250 to 300 μ) changes some of the ergosterol into calciferol ($C_{27}H_{43}O$) which has antirachitic activity. Calciferol melts at 115-116° C. and gives a dinitrobenzoate, melting at 147° C. H. Steenbock *et al.* [*J. Biol. Chem.,* **97,** 249 (1932)] and Waddell [*J. Biol. Chem.,* **105,** 711 (1934)] have shown that calciferol is not

identical with vitamin D, as formerly believed.

Windaus, Inhoffen, and von Reichel [*Liebig's Ann.*, **510**, 248 (1934)] as well as O. Rosenheim and H. King [*J. Soc. Chem. Ind.*, **53**, 196 (1934)] discuss the constitution of ergosterol.

For additional information, the references given and those which follow should be consulted.

Hess and Weinstock, *J. Biol. Chem.*, **63**, 297 and 305 (1925).
Heilbron, Kamon and Morton, *Biochem. J.*, **21**, 1279 (1927).
F. Wokes, *Biochem. J.*, **22**, 830 (1928).
"A Specific Color Reaction for Ergosterol," Rosenheim, *Biochem. J.*, **23**, 47 (1929).
"Irradiated Ergosterol for Dressing Ulcers," C. J. Bond, *J. Soc. Chem. Ind.*, **47**, 418 (1928).
"Ergosterol of Yeast," F. Rundel and A. Detzel, *Chem. Abs.*, **24**, 624 (1930).
"Reactions of Isoergosterol," Heilbron and Spring, *J. Chem. Soc.*, **1929**, 2807.
"Heat of Combustion of Ergosterol and Cholesterol," Bills, Cox and Steel, *J. Biol. Chem.*, **84**, 655 (1929).
"Recent Progress in the Chemical Study of the Vitamins," J. C. Drummond, *J. Soc. Chem. Ind.*, **49**, 1T (1930).
"A Specific Colour Reaction for Ergosterol," O. Rosenheim, *Biochem. J.*, **23**, 47 (1929).
"Some New Esters of Ergosterol," H. Emerson and F. W. Heyl, *J. Am. Chem. Soc.*, **52**, 2015 (1930).
"The Purification of Ergosterol," R. K. Callow, *Biochem. J.*, **25**, 79 (1931).
"Ergosterol," E. L. Smith, S. G. Stevenson, and A. L. Bacharach, *Analyst*, **58**, 605 (1933).
"Salts of Ergosteryl Sulphate: Preparation and Antirachitic Activity on Irradiation in Aqueous Medium," S. Natelson, A. E. Sobel, and B. Kramer, *J. Biol. Chem.*, **105**, 761 (1934).

Dihydroergosterol $C_{28}H_{46}O$; Mol. Wt. 398.65; M. Pt. 174° C.; $[\alpha]_D^{14°}$ −20.1° in chloroform. It contains two double bonds and gives a positive Liebermann-Burchard test, but no tests with either Rosenheim or Tortelli-Jaffe methods. It occurs both in ergot and yeast. This sterol can be obtained by the catalytic hydrogenation of ergosterol.

Zymosterol $C_{27}H_{44}O$; Mol. Wt. 384.62; M. Pt. 108-109° C.; $[\alpha]_D^{20°}$ + 49.5; acetate, M. Pt. 115° C.; $[\alpha]_D^{20°}$ + 33.5°. When crystallized from a mixture of glacial acetic acid and methyl alcohol, it contains a half molecule of water and melts at 107° C. With antimony trichloride, it gives a blue, then a violet color, showing a greenish fluorescence, and a positive Liebermann-Burchard test. This sterol is found in small quantities in yeast fat.

Other sterols isolated from yeast fat are as follows: Ascosterol $C_{27}H_{46}O$; M. Pt. 141-142° C.; $[\alpha]_D^{20°}$ + 45.0; benzoate, M. Pt. 130° 131° C.; $[\alpha]_D^{24°}$ + 37.0°; faecosterol, $C_{27}H_{46}O$; M. Pt. 161-163° C.; $[\alpha]_D^{25°}$ + 42.1; acetate; M. Pt. 159-161° C.; benzoate, M. Pt. 144-146° C., $[\alpha]_D^{20°}$ + 35.4°; neosterol $C_{27}H_{44}O$; M. Pt. 164-165°; $[\alpha]_D^{20°}$ 105°; acetate, M. Pt. 173-174° C.; benzoate, M. Pt. 173-175° C.; $[\alpha]_D^{24°}$ −50.6°.

Phytosterolines. Glucosides of phytosterols are found in the bark, leaves, seeds and other parts of plants [Power and Salway, *J. Chem. Soc.*, **103**, T399 (1913)]. Salway [*ibid.*, **103**, 1022 (1913)] synthesized the glucosides of cholesterol and sitosterol. The sitosterol glucoside pre-

pared by Salway melted with decomposition at 295 to 300° C., the tetra-acetyl derivative at 166 to 167° C., and the benzoate at 198° C. The naturally-occurring glucosides from various sources decomposed from about 260 to 298° C. (some of which may be stigmasterol glucosides). They are insoluble in water and sparingly soluble in hot alcohol, ether, chloroform or benzene, but dissolve readily in pyridine. They can be recrystallized from mixtures of pyridine and alcohol.

Jamieson [*Oil and Fat Ind.*, **3**, 153 (1926)] isolated a phytosteroline from crude cottonseed oil. The purified substance, by repeated recrystallization from alcohol when heated gradually, became brown from 250° C. and melted with decomposition at about 275 to 276° C. An elementary analysis agreed with the formula $C_{27}H_{45}O \cdot C_6H_{11}O_5$. The acetate crystallized from alcohol in the form of pearly flat prisms that melted at 166 to 167° C. The glucoside gives an intense Liebermann-Burchard color reaction. It has, when pure, but little solubility in alcohol or other solvents such as ether, chloroform, benzene, etc. These glucosides can be resolved into phytosterol and glucose by heating them with aqueous hydrochloric acid and amyl alcohol. (The stigmasteroline compound has the formula $C_{30}H_{49}O \cdot C_6H_{11}O_5$.)

Hydrocarbons

Most vegetable fats contain very small quantities of hydrocarbons. They are found along with the sterols in the unsaponifiable fraction.

K. Täufel, H. Thaler, and H. Schreyegg [*Fettchem. Umschau*, **43**, 26 (1936)] found that squalene ($C_{30}H_{50}$) amounted to 16.3% of the unsaponifiable fraction of yeast fat. K. Täufel, H. Heinish and W. Heiman [*Biochem Z.*, **303**, 324 (1940)] found that the unsaponifiable fractions of olive and wheat-germ oils contained squalene, whereas none could be detected in those of coconut, cottonseed, rape, and soybean oils.

Illipene, $C_{32}H_{56}$, from the seed fat from *Madhucca latifolia*, has been shown by K. H. Bauer and G. Umbach [*Berichte*, **65**, 859 (1932)] to be identical with carotene from Shea butter. J. Nakamiya [*Sci. Papers, Inst. Phys. Chem. Res.*, **28**, 16 (1935); *Chem. Abs.*, **30**, 315 (1936)] found gadusene, $C_{18}H_{32}$, an unsaturated hydrocarbon, in the unsaponifiable fraction of rice, soybean, and fishliver oils.

H. Marcelet [*Compt. rend.*, **202**, 867 (1936)] identified seven hydrocarbons in the condensate obtained by the deodorizing of refined olive oil. T. Thorbjarnarson and J. C. Drummond [*Analyst*, **60**, 23 (1935)] found that the hydrocarbon content of the unsaponifiable matter from olive oils from various countries ranged from 31 to 64 per cent, and concluded that the highly unsaturated hydrocarbon present was squalene.

Many fats contain carotenes, $C_{40}H_{56}$. Palm (pulp) oils contain notable quantities of this pigment which accounts for their intense color.

Phosphatides

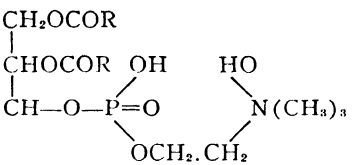
The several groups of these substances which are associated with the fats of animals and plants are also known as lipoids, lipins, lipids and

phosphalipins. B. Rewald [*Chem. Abs.*, 22, 3178 (1928)] considers the name "lipoid" preferable to the others.

No attempt will be made to discuss the various groups of these phosphatides, but some information will be given in regard to lecithin and cephalin, both of which are minor constituents of vegetable fats. Those desiring additional information are referred to the last edition of Maclean "Lecithin and Allied Substances" (Monograph Series on Bio-Chemistry, Longmans, Green and Co., London).

Lecithins are glycerides which contain 2 fatty acid radicals and phosphoric acid to which the base choline is attached. Cephalins are similar, but contain aminoethyl alcohol in place of choline. It should be noted that the purest lecithin yet obtained is believed to be a mixture of at least two substances (lecithins), and the same is true of cephalin. The fatty acids present may be either saturated or unsaturated. Those commonly present in vegetable fat phosphatides are palmitic, stearic, oleic and linoleic acids.

The following formula, in which R equals a fatty acid radical, shows the structure of one of these lecithins:



Lecithins are readily soluble in alcohol, benzene, ether and chloroform, but practically insoluble in acetone, ethyl acetate, and other similar esters. They form characteristic double salts with gold, platinum, and cadmium chlorides. Upon heating with acids or bases, they are readily decomposed into glyceryl phosphoric acid, choline, free fatty acids, and even free phosphoric acid. Apparently, from the limited investigations that have been made, refining an oil with caustic soda removes a considerable proportion of the phosphatides originally present.

The quantity of glyceryl phosphatides in an oil can be approximately calculated by multiplying the percentage of phosphorus pentoxide found by analysis, by the factor 11.37.

It has been repeatedly stated that "lecithin" can be precipitated almost entirely from oils by the addition of a sufficient quantity of acetone or ethyl acetate. Many experiments have been made covering a very wide range of conditions and it has been found that little, and often none, of the phosphatides present are precipitated.

The following references may be of interest:

"Determination of Lecithin," W. R. Bloor, *J. Biol. Chem.*, 23, 317 (1915); E. J. Baumann, *ibid.*, 59, 667 (1924).

"Glycerophosphates of Plant Seeds," A. Nemec, *Biochem. Zeit.*, 138, 198 (1923).

"Structure and Significance of the Phosphatides," Levene and Rolf, *Physiol. Rev.*, 1, 327 (1921); *Chem. Abs.*, 17, 114 (1923).

"Packer Furnishes Cephalin (for surgical use)," *Meat and Livestock Digest*, 6, No. 2, 2 (1925).

"Plant Phosphatides: Lecithin and Cephalin of the Soy Bean," Levene and Rolf, *J. Biol. Chem.*, **62**, 759 (1925); **68**, 285 (1926).
"The Preparation and Purification of Lecithin," Levene and Rolf, *J. Biol. Chem.*, **72**, 587 (1927).
"Synthesis of Lecithins," Grün and Lumpächer, *Berichte*, **60**, 147 (1927); *Chem. Abs.*, **21**, 1659 (1927).
"Soybean Lecithins (and cephalins)," B. Suzuki and co-workers, *Imp. Acad. Japan Proc.*, **6**, 262, 341 (1930); **7**, 226 (1931).
"Detection of Added Lecithin in Chocolate Products," W. O. Winkler and J. W. Sale, *J. Assoc. Off. Agric. Chem.*, **14**, 537 (1931).
"Distinction between Lecithin Preparations of Animal and Vegetable Origin," F. E. Nottbohm and F. Mayer, *Chem. Ztg.*, **56**, 881 (1932); *Analyst*, **58**, 43 (1933).
"Lecithin," J. Eichberg, *Drug Cosmetic Ind.*, **30**, 427 (1932).
"Changes in the Properties of Soap by Adding Lecithin," E. L. Lederer, *Seifensieder Ztg.*, **60**, 919 (1933).
"Lecithin in Medicine," Anon., *Drug Cosmetic Ind.*, **34**, 459 (1934).
"The Preparation of Crude Phosphatides from Soybean Oil., G. E. Halliday and H. R. Kraybill, *Cotton Oil Press*, **19**, No. 5, 13 (1935).
"The Physiology of the Plant Phosphatides, V." Grafe, *Beitr. Biol. Pflanz*, **23**, 336 (1935); *Chem. Abs.*, **30**, 7146 (1936).
"The Chemistry of Phosphatides and Their Utilization in Industry," E. B. Working, *Oil and Soap*, **13**, 261 (1936).
"Phosphatides as Commercial Products," B. Rewald, *Chem. Ind.*, **41**, 253 (1937).
"The Component Fatty Acids of the Phosphatides of Soya Beans and Rape Seeds," T. P. Hilditch and W. H. Pedelty, *Biochem J.*, **31**, 196 (1934).
"Soybean Phosphatides and Their Uses: A Review," G. A. Wieshahn, *Oil and Soap*, **14**, 119 (1937); contains 64 references.
"The Synthesis of Phosphatides," I. Kabashima, *Berichte*, **71**, 76 (1938).
"On the Determination of Phosphatides," A. Schramme, *Fette u. Seifen*, **46**, 635 (1939).
"Lecithin: Its Manufacture and Use in the Fat and Oil Industry," J. Eichberg, *Oil and Soap*, **16**, 51 (1939).

Inosite Phosphates (Phytins) $C_6H_{18}O_{24}P_6$ or $C_6H_6O_6[PO(OH)_2]_6$. Phosphoric acid ester of hexahydroxycyclohexane is a constituent of many, if not all, seeds and is probably present in the form of salts (magnesium, etc.). Very small quantities of this substance were isolated from a sample of crude cottonseed oil that was entirely free from press foots. It may also be a minor constituent of some other crude oils. When hydrolyzed under pressure with dilute sulfuric acid, inosite melting at 223° C. was obtained. Some seeds contain the enzyme phytase, which under certain conditions breaks down the hexaphosphates into the tri- and mono-compounds. Some of the references to the extensive studies of R. J. Anderson are as follows:

J. Biol. Chem., **12**, 97 and 471 (1912); "Cotton Seed," *ibid.*, **12**, 311 (1912); **17**, 141 (1914); *ibid.*, **18**, 441 and 425 (1914); **20**, 463 (1915); **44**, 429 (1920).
"The Phytin Content of Foodstuffs," Averill and King, *J. Am. Chem. Soc.*, **48**, 724 (1926). "Inosite Phosphates," G. Locatelli, *Chem. Abs.*, **23**, 4769 (1929); *Brit. Chem. Abs.*, **B1928**, 464.
"Estimation of Phytin Phosphorus," R. S. Harris and L. M. Mosher, *Ind. Eng. Chem., Anal. Ed.*, **6**, 320 (1934).
"Inositol Phosphoric Acid Compounds," S. Otolski, *Przemsyl. Chem.*, **18**, 519 (1934); a review which deals with the substances isolated from various vegetable products.
"Phytin in Human Nutrition," R. A. McCane and Elsie M. Widdowson, *Biochem. J.*, **29**, 2694 (1935).
"The Determination of Phytic Acid," L. Young, *Biochem. J.*, **30**, 252 (1936); discusses a colorimetric method.

Chapter VI

Methods

The Laboratory Extraction of Oils and Fats. The following procedures may be used for the preparation of samples in quantities sufficient for examination or experimental purposes.

Solvent Extraction. Seeds, decorticated kernels, or other oil-bearing products should be ground to a fine meal. Samples of a kilo or less are placed in a stout flask of suitable size and mixed thoroughly with an equal volume or slightly more of petroleum ether. After standing a half hour or longer the mixture is filtered on a Büchner funnel using only enough suction to withdraw the solvent through the meal and filter. The meal is washed with several small portions of solvent. With samples larger than a kilo, the extraction can conveniently be made in a glass percolator of the usual form. The meal is supported on a thin mat of absorbent cotton. A quantity of solvent is added so as to cover the meal completely to a depth of 4 or 5 inches. When the solvent has passed through the meal, it is returned to the percolator, and this treatment is repeated 3 or 4 times. In a similar manner the meal is treated with two more fresh portions of solvent. It is important to conduct the extraction in a room where there are no flames or sparking motors or other operating electrical equipment, in order to avoid the possibility of fire or explosions. The solvent containing the oil is distilled by means of a steam bath, until no more can be removed. The residual solvent with the oil is best removed under diminished pressure using a capillary tube in the usual manner. In the case of drying oils, the capillary tube should be connected with a supply of carbon dioxide to prevent oxidation during the heating. Precautions should be taken to use equipment which will not collapse under the reduced pressure. A pressure from 8 to 15 mm. will be found satisfactory. It is usually necessary to heat the oil to about 120 ° C. before all the solvent can be removed. In cases where the petroleum ether solution of the oil is turbid, which may be caused by fine particles of meal, moisture or both, it is preferable to dehydrate the solution with anhydrous sodium sulfate and filter before attempting to distill the solvent. In such cases it is sometimes necessary to use a filter aid, such as a powdered diatomaceous earth, in order to clarify the solution completely. An efficient, sizable oil extractor such as the one described by L. A. Munroe and D. C. Birmingham [*Ind. Eng. Chem.*, **20**, 425 (1928)] can be employed to advantage.

Fruits such as the olive and avocado should be partially but rapidly dehydrated after crushing or slicing, before attempting to extract the oil, in order to avoid troublesome emulsions. The dehydration is per-

formed in an oven heated to 70° C., in which the air has been replaced by nitrogen or carbon dioxide.

Expression of Oils and Fats. For the expression of oil from seeds a laboratory hydraulic press is required which will give a pressure of at least 3000 lbs. per square inch. A number of small, hand-operated hydraulic presses of various capacities and designs are manufactured for this purpose. Water should not be used in the tank and pressure cylinder of the press. A good grade of lubricating oil such as that used for automobile motors is satisfactory. The seed or kernels previously crushed or ground to a meal should be firmly packed in the cage of the press in such a manner that when pressure is applied it will be equally distributed in all directions. Failure to pay attention to this important detail will result in a poor yield of oil. When the cage is properly charged and in position, the pressure should be applied slowly, particularly after the oil begins to run, and from this point gradually increased until the maximum pressure is reached. As the oil drains from the press, the pressure will drop; consequently it will be necessary to restore the pressure several times before it can be maintained for any length of time. Usually, with the smaller presses, it is necessary to maintain the pressure several hours or longer in order to get a reasonable yield of oil. After pressing, the oil should be filtered, and kept in stoppered bottles or glass carboys. When the pressing is completed, the equipment should always be thoroughly cleaned without delay; otherwise it will be very difficult to clean it properly later. In most cases, the press can be cleaned with hot soapy water and thorough rubbing with a cloth or brush. Sometimes, it is first necessary to wash the cage several times with gasoline. After a final rinsing with clean hot water, wipe the cage dry with a clean cloth to prevent rusting.

Oil Samples. Samples of the oils to be tested should always be placed in clean, dry containers provided with clean corks. Oil on the neck of the container should always be removed before inserting the cork. When it is necessary to keep samples for some time, they should be stored in a cool, dark place. They can be kept much longer if placed in cold storage at 2° to 10° C. At no time should they be allowed to stand in bottles in direct sunlight, as under this condition they quickly deteriorate.

In all cases, the samples should be properly labeled, including the date the oil was expressed or extracted by solvents. As soon as the sample is obtained, the acid value should be determined, and again later at stated intervals, each time recording the date upon which the test was made. This will give an indication of the stability.

Sampling. The following directions for taking samples of commercial fats and oils have been adopted by the American Chemical Society's Committee on Analysis of Chemical Fats and Oils, *Ind. Eng. Chem.*, **18**, 1346 (1926):

1. *Sampling While Loading Tank Cars.*—Sample shall be taken at discharge of pipe where it enters tank-car dome. The total sample taken shall not be less than 50 pounds (23 kg.) and shall be a composite of small samples of about one pound

(450 grams) each, taken at regular intervals during the entire loading period. When the material flows freely and is not liable to clog, a sample may be taken continuously through a pet cock attached at a suitable point on the discharge line or pump, the pet cock to be ¼ inch size or larger and to be kept flowing continuously during the pumping period and so regulated as to produce a sample of not less than 50 pounds (23 kg.) to represent the tank car.

The sample thus obtained shall be thoroughly mixed and uniform, 3-pound (1.3-kg.) portions placed in air-tight 3-pound metal containers. At least three such samples shall be put up, one for the buyer, one for the seller, and the third to be sent to the reference chemist in case of dispute. All samples are to be promptly and correctly labeled and sealed.

2. *Sampling from Tank Car on Track.*

(a) *When contents are solid.*—Live steam must not be turned into tank cars or coils before samples are drawn, as there is no certain way of knowing when coils are free from leaks. If water is present under the solid material, this must be noted and estimated separately.

The sample is taken by means of a large tryer about 2 inches (5 cm.) across and about one and one-half times the depth of the car in length. Several tryerfuls are taken vertically and obliquely towards the end of the car until 50 pounds are accumulated, when the sample is softened, mixed, and handled as under (1). In case the contents of the tank car have become very hard, as in winter weather, so that it is impossible to insert the tryer, and it becomes necessary to soften them by means of the closed steam coils (in nearly all tank cars the closed steam coil leaks) or by means of open steam in order to draw a proper sample, suitable arrangements must be made between buyer and seller for the sampling of the car after it is sufficiently softened, due consideration being given to the possible presence of water in the material as received and also to the possible addition of water during the steaming. The Committee knows of no satisfactory direct method for sampling a hard-frozen tank car of tallow.

(b) *When contents are liquid.*—The sample taken is to be a 50-pound composite made up of numerous small samples taken from the top, bottom and intermediate points by means of a bottle or small metal container with removable stopper or top. This device attached to a suitable pole is lowered to the various desired depths, when the stopper or top is removed and the container allowed to fill. The 50-pound sample thus obtained is handled as under (1).

In place of the device described above, any sampler capable of taking a sample from the top, bottom, and center, or from a section through car, may be used.

(c) *When contents are in semi-solid condition, or when stearin has separated from liquid portions.*—In this case a combination of (a) and (b) may be used or, by agreement of the parties, the whole may be melted and procedure (b) followed.

(d) If strata of sediment, emulsion, water, or combination of these are present, they are to be taken off layer by layer and separately weighed and sampled.

Barrels, Tierces, Casks, Drums and Other Packages.

All packages shall be sampled, unless by special agreement the parties arrange to sample a lesser number; but in any case not less than 10 per cent of the total number shall be sampled. The total sample taken shall be at least 20 pounds (9 kg.) in weight for each 100 barrels, or equivalent.

1. *Barrels, Tierces and Casks.*

(a) *When contents are solid.*—The small samples shall be taken by a tryer through the bunghole or through a special hole bored in the head or side for the purpose with a 1-inch (25 mm.) or larger auger. Care should be taken to avoid and eliminate all borings and chips from the sample. The tryer is inserted in such a way as to reach the head of the barrel, tierce or cask. The large sample is softened, mixed and handled according to tank cars (1).

(b) *When contents are liquid.*—A glass tube with constricted lower end is inserted slowly and allowed to fill with the liquid, when the upper end is closed and the tube withdrawn, the contents being allowed to drain into the sample container. After the entire sample is taken, it is thoroughly mixed and handled according to tank cars (1).

(c) *When contents are semi-solid.*—The tryer or a glass tube with larger outlet is used, depending on the degree of fluidity.

(d) *Very hard materials such as natural and artificial stearins.*—By preference the barrels are stripped and samples obtained by breaking up contents of at least 10 per cent of the packages. This procedure is to be followed also in the case of cakes shipped in sacks. When shipped in the form of small pieces in sacks they can

be sampled by grab sampling and quartering. The final procedure is as outlined under tank cars (1).

2. *Drums.*—Samples are to be taken through the bunghole as under (1). The tryer or tube should be sufficiently long to reach to the ends of the drum.

3. *Other Packages.*—Tubs, pails, and other small packages not mentioned above are to be sampled by tryer or tube (depending on fluidity) as outlined above, the tryer or tube being inserted diagonally whenever possible.

4. *Mixed Lots and Packages.*—When lots of tallow or other fats are received in packages of various shapes and sizes, and especially when the fat itself is of variable composition, the procedure must be left to the judgment of the sampler. If variable, the contents of each package should be mixed as thoroughly as possible and the amount of the individual samples taken made proportional to the size of the packages.

Sample.—The sample must be representative, weigh at least 3 pounds (1.3 kg.) and be taken in accordance with the directions as given. It must be kept in an air-tight container in a dark, cool place.

In the case of fats, soften the sample by means of gentle heat, taking care not to melt it. When sufficiently softened, mix thoroughly with a mechanical egg beater or other equally effective mechanical mixer and weigh portions for analysis.

Determination of Moisture and Volatile Matter by Hot Plate Method. Weigh 5- to 20-gram portions of the sample into a beaker or casserole and heat on a heavy asbestos board over a burner or hot plate, taking care that the temperature of the sample does not at any time go above 130° C. During the heating rotate the vessel gently by hand to avoid spattering by the too-rapid evolution of moisture. The approach of the end point may be judged by the absence of rising bubbles of steam and by the absence of foam at the last. The heating, however, should momentarily be carrried on to incipient smoking, but not beyond this point. Cool and weigh. For oven and distillation methods, the American Chemical Society Committee's report [*Ind. Eng. Chem.*, **18,** 1346 (1926)], as well as N. T. Joyner and S. J. Rini [*Oil and Soap,* **16,** 233 (1939)], should be consulted.

The method described is applicable to all the ordinary fats and oils, including emulsions such as butter and margarines and "high acid" coconut oil, but it is not applicable to certain abnormal samples such as naphtha-extraction greases which contain, in addition to moisture, solvents of fairly high boiling point, which are volatilized with difficulty.

Determination of Oil in Oleaginous Products. Many types of extraction apparatus have been devised for the quantitative extraction of oil, but with very few exceptions they are both fragile and costly. The following efficient method, requiring only simple, strong apparatus, was adopted by the American Oil Chemists' Society in 1919 [*Cotton Oil Press,* **3,** No. 3, 91 (1919)].

Reagent. Petroleum ether boiling under 70° C. and leaving no residue upon evaporation.

Apparatus. Electric hot plate with low, medium, and high heat regulator or steam bath; condensers, block tin or glass; 50 cc. or other suitable-sized Pyrex extraction flasks (wide mouth 100- to 125-cc. flasks are preferable); 15-cm. filter papers such as Arthur Thomas Company's No. 27,766, American-made or equal quality; extraction tubes of the straight Butt type of tough, well-annealed glass with walls about 2 mm.

thick. The wide part of the tube is to be 28 mm. inside diameter and 150 mm. long; the low narrow portion is to be 10 mm. inside diameter, and 75 mm. long with the end ground to a point; sound corks to fit extraction flasks and large end of extraction tube. Cut holes in the corks to fit the condenser snugly and the restricted end of the extraction tube by which the extraction flask is attached. The apparatus is to be set up vertically and so adjusted that the extraction flask rests on the hot plate or steam bath.

Place about 35 cc. of the petroleum ether in the extraction flask which is attached to the extraction tube, and boil the solvent for two hours to remove all the extractive matter from the cork connections.

Method. Weigh accurately 2 to 5 grams (depending upon the oil content) of the finely ground sample without previous drying and transfer it to one of the 15-cm. filter papers. Roll the paper tightly about the sample, folding in both ends. Then roll this in a second paper, leaving one end of the roll open for the top. By folding in the bottom end of the roll tightly and closely, the roll will retain its shape before and after extraction. Insert the roll into the extraction tube and attach it to the condenser through which cold water is circulated. To a weighed extraction flask add 35 cc. of petroleum ether, and connect it with the extraction tube. The heat should be regulated so that the condensed solvent drips at the rate of 150 drops per minute. It is important that the extraction tube be so adjusted that the condensed solvent drips from the condenser on to the center of the top of the roll. Products which contain 10 per cent or less of oil are usually completely extracted in about two hours. Other products which contain more oil, after two hours' extraction, should be removed, air-dried and reground (if necessary, the sample may be mixed with 2 grams of clean sand to facilitate grinding), then placed in paper previously used to hold sample, and extracted again for two hours or longer until the remaining oil is all extracted. If there is any doubt in regard to the completeness of the extraction, cool the extraction flask and disconnect it, then attach another extraction flask containing 35 cc. of petroleum ether and continue the extraction. If this solvent upon evaporation leaves a weighable residue of oil, the extraction must be continued.

Carefully evaporate the solvent so as to lose no oil and dry the flask and residue for one or two hours in an oven heated to about 110° or 115° C.; remove vapors of solvent, and weigh. Heat again another hour, cool and weigh. If a constant weight is not obtained, repeat the heating. In the case of drying oils, the heating should be made in an atmosphere of carbon dioxide or other inert gas, to prevent the oxidation of the oil.

As seeds and nuts which contain over 40 per cent of oil cannot be ground without a loss of a portion of the oil, the following procedure has been devised: Weigh 2 grams of small seeds or large seeds, or nuts which have been cut into pieces the size of a pea, and place them in a previously extracted dry canvas bag ($3\frac{1}{2} \times 1\frac{3}{4}$ inches). On top of the sample place a half inch layer of extracted absorbent cotton. Hold the

bag on a smooth hard surface and crush the sample somewhat with a mallet. After extracting as directed above for two hours, remove the bag and crush the sample further. Repeat the extraction and crushing of the sample at least twice more, or until no more oil can be extracted. After the extraction is completed, remove the sample and preserve the bag for future extractions. Evaporate the solvent and determine the percentage of oil as previously directed.

Specific Gravity. The specific gravity of both fats and oils is best determined by means of the pycnometer in the following manner:

If necessary, carefully clean a 25 or 30 cc. pycnometer by filling it with a saturated solution of chromic acid and strong sulfuric acid. Let it stand for 3 or 4 hours, then empty, and rinse six times with water. Fill it with recently boiled water previously cooled at 20° C., holding the pycnometer in an inclined position so that the water will not splash or form bubbles. Insert the stopper and immerse the entire bulb in a constant-temperature water bath at 25° C. At the end of 30 minutes, adjust the level of the water to the proper point and place the perforated cap on the capillary tube. Remove the pycnometer from the bath; wipe dry with a clean cloth or towel, allow it to stand for half an hour, then weigh. Empty the pycnometer, rinse several times with small quantities of alcohol and twice with ether. Completely remove the ether and any remaining moisture. When the pycnometer has reached room temperature, weigh it. To ascertain the weight of the contained water at 25° C. subtract the weight of the pycnometer from its weight when filled.

To determine the specific gravity of an oil at 25°/25° C. cool, if necessary, the same to 20° C. and fill the dry pycnometer, being careful to avoid the formation of bubbles. Insert the stopper and place the pycnometer in the water bath at 25° C. for 30 minutes. Adjust the level of the oil and place the perforated cap over the capillary opening. Remove the pycnometer from the bath, wipe dry and weigh in same manner (at room temperature) as previously directed. Divide the weight of the oil by the weight of the water previously obtained and report the specific gravity at 25°/25° C.

The temperature correction for the specific gravity of oils when taken at other than the standard temperature may be calculated so as to give the approximate specific gravity at 25° C. as follows:

$G = G' + 0.0007\ (T - 25°\text{ C.})$.

G = specific gravity at 25° C.

G' = specific gravity at $\frac{T°\text{ C.}}{25°\text{ C.}}$

T = temperature at which specific gravity was determined.

0.0007 = mean correction for each degree centigrade.

To determine the specific gravity of fats not liquid at 25° C., follow the directions given for oils, but using a water bath kept at 40° C. (in a

few cases, 60° C. may be necessary). State the specific gravity at 40°/25° C. or 60°/25° C.

Comments. Only pycnometers made of glass with a very low coefficient of expansion should be employed.

For many years it was customary to determine the specific gravity of oils at 15°/4° C. or 15°/15°, but 25° C. has been found much more convenient for oils and low-melting fats.

Index of Refraction. The index of refraction is the degree of deflection caused in a ray of light in passing from one transparent medium into another. This property, which is possessed by fats and oils, is sometimes helpful in connection with their identification or testing their purity. The refractive index is most conveniently determined in the direct reading Abbé Refractometer with temperature-controlled prisms. The temperature is controlled by circulating water from a water bath around the prisms. The readings for oils may be made at 20° to 25° C. and for fats at 40° C. unless they have a higher melting point, when a temperature of 60° C. or higher may be employed.

Determination. Place the instrument in such a position that daylight or artificial light can readily be obtained for illumination of the refractometer prisms. Circulate water through the instrument at the desired constant temperature. Open the prisms by means of the head screw and place a few drops of oil or melted fat on about the center of the low prism. Bring the prisms together and fasten with head screw. Allow the instrument to stand for a few minutes so that the temperature of the sample and the prisms will be the same before adjusting and reading the instrument.

The method of measurement is based upon the observation of the position of the border line of total refraction in relation to the faces of the flint glass prisms. Bring this border line into the field of vision of the telescope by rotating the double prism by means of the alidade in the following manner: Hold the sector firmly, move the alidade forward or backward until the field of vision is divided into a light and dark portion. The line dividing these portions is the border line. This usually will not be a sharp line but a band of color. Eliminate the colors by slowly turning the screw head of the compensator until a sharp line is obtained. Then adjust this border line so that it falls on the point of intersection of the cross hairs. Read the refractive index of the substance on the scale of the sector. Check the accuracy of the instrument with the means provided. Also it may be standardized with water at 20° C. which has a refractive index at this temperature of 1.3330. Any correction found should be applied to all the readings.

The index of refraction varies with the specific gravity and in the same direction. As the temperature rises, the index of refraction falls. The indices of refraction which have been made at other temperatures can be reduced to the standard temperatures 20°, 25°, or 40° by the following formula:

$R = R' + 0.00038\ (T' - T)$
R = the reading reduced to temperature T
R' = the reading at temperature T'
T' = the temperature at which R' was read
T = the standard temperature
0.00038 = correction in scale divisions for one degree centigrade.

When only a Zeiss-Butyro Refractometer is available the readings obtained with this instrument can be calculated into refractive indices by substituting for 0.00038 in the above formula, 0.55 in the case of fats or 0.58 in the case of the oils which have the higher index of refraction.

A large quantity of selected data will be found in "Tables of Refractive Indices," Volume 2, "Oils, Fats and Waxes," by R. Kanthack and J. N. Goldsmith, which was published in 1921 by Adam Hilger of London.

Optical Rotation (Polarization). Optical rotation or activity is the property which some substances have of rotating the plane of polarized light. Some substances have the power of turning the plane of polarized light to the right (dextro-rotary) and others to the left (levo-rotary). Most fats and oils show very litttle optical activity, but castor, croton and those oils which contain glycerides of chaulmoogric and hydnocarpic acids are notable exceptions. The slight optical activity observed in the case of other fats and oils is, with few exceptions, due to the presence of small quantities of various sterols, all of which show a marked optical activity. Lewkowitsch has indicated that it is desirable not to omit the examination of new fats and oils for optical activity because it may well be that a larger number of these substances may occur in nature than has hitherto been observed.

It is now customary to state the optical rotation in terms of the specific rotation. The specific rotation or rotary power is the angular rotation of the plane of polarized light by a column of liquid one decimeter in length, and of unit density. It is calculated by means of the following formula:

$(\alpha) = \frac{r}{l \times d}$ in which α = specific rotation
r = observed angular rotation
l = length of column of liquid in decimeters
d = density of liquid

With solid substances such as fats and fatty acids dissolved in chloroform or other solvent, the formula is $(\alpha) = \frac{100\,r}{l \times c}$, in which c = the number of grams of the substance in 100 cc. of the solution. In stating the specific rotation the solvent used should be given.

In view of the fact that light of different wave lengths is rotated to a different degree by optically active substances, it is necessary to use a monochromatic light of an agreed wave length. Consequently, the light employed is that given by sodium, which corresponds to the D ray of the solar spectrum with a wave length of 0.000588 mm. During the observa-

tion, the liquid (or solution) must be at a known constant temperature. The specific rotation is represented as follows:

$(\alpha)_D^{20°}$ in which *D* indicates that a sodium light was used in making the observation.

The specific rotation [Perkins and Cruz, *Analyst,* **49,** 236 (1924)] for chaulmoogra (*Taraktogenos kurzii*) and related oils is as follows:

Source of Oil	Specific Rotary Power Oil	Fatty Acids
Taraktogenos kurzii	+52.0	+52.6
Hydnocarpus alcale	+49.6	+53.6
Hydnocarpus alpina	+49.5	....
Hydnocarpus anthelminthica	+52.5	+53.6
Hydnocarpus venenata	+52.0	+60.9
Hydnocarpus wightiana	+57.7	+60.4
Ancoba echinata	+48.8	+52.5

The optical rotation of castor oil when read through a 200 mm. tube ranges from +7.6° to +9.7°.

Melting Point. The melting point is the temperature at which a solid assumes the liquid condition. Natural fats and oils, being mixtures of various glycerides and other minor constituents, do not have definite melting points. When heated, these substances soften, depending on their individual nature, through a shorter or longer range of temperature to a final melting point at which the substance is entirely liquid. Some of the fats give a double melting point, that is, they melt, then solidify and melt again at a higher temperature. So far no explanation is known for this phenomenon. Fats that have been melted, and then solidified, give an abnormally low melting point unless they are allowed to stand in the solid condition for some hours or even longer. In most cases if the recently solidified fat is allowed to stand for 12 or 15 hours, a normal melting point will be obtained, but in the case of cocoa butter it appears necessary to allow it to stand for one or two days. With an individual fatty acid, for example, the melting point is sharp and the same melting point will be obtained directly after solidification.

It should be observed that the presence of moisture in a fat influences the melting point to a considerable extent. Quite a number of methods have been devised to determine the melting point of fats. Most of these methods do not determine the real melting point, but the softening of flow points of fats.

Methods for the melting, softening, and slipping points which have been tested and adopted by the American Chemical Society Committee on Analysis of Commercial Fats and Oils [*Ind. Eng. Chem.,* **18,** 1346 (1926)] will be described.

Melting Point. *Apparatus.* Capillary tubes made from 5-mm. (inside diameter) thin-wall glass tubing drawn out to 1 mm. inside diameter. Length of capillary part of tubes about 5 cm.; length of tube 8 cm.

Standard Thermometer graduated in tenths of a degree.

Beaker, 600 cc. capacity.

Determination. The sample, when melted, should be clear and entirely free from moisture, or incorrect results will be obtained. Melt and thoroughly mix the sample. Dip three of the capillary tubes in the oil so that the melted sample rises to a height of 1 cm. in the tubes.

Fuse the capillary ends of the tubes carefully by means of a small blast furnace and allow them to cool. Place the tubes overnight in a refrigerator at a temperature from 4° to 10° C. Then fasten them by means of a rubber band or other suitable means to the bulb of the thermometer. Suspend the thermometer in the beaker of water (which is agitated by air or by mechanical means) so that the bottom of the bulb of the thermometer is immersed to a depth of about 3 cm. Increase the temperature of the water gradually at the rate of about 0.5° C. per minute. Before finally melting to a perfectly clear fluid, the sample becomes opalescent and usually appears clear at the top, bottom and sides before becoming clear at the center. Continue the heating until the contents of the tube become uniformly clear and transparent. Report this temperature as the melting point. (The melting point of oils may be determined in general according to the above procedure, taking into consideration the lower temperature required.) It is usually only a fraction of a degree above the opalescent point noted. The thermometer should be read to the nearest 0.5° C.

Softening Point. *Apparatus.* Straight capillary tubes made from tubing of 1 mm. inside diameter of medium wall thickness. Length of tube 7.5 cm.

Determination. Melt the sample and mix thoroughly. Dip three of the tubes described above in the oil or fat to a depth of 1 cm. Chill at once by means of ice and place tubes in a tight container, pack in ice and hold at this temperature overnight.

Fasten the tubes with a rubber band or other suitable means to the bulb of a thermometer graduated in tenths of a degree. Suspend the thermometer in a 600-cc. beaker of water (agitated by mechanical means or air) so that the bottom of the bulb is submerged about 3 cm. The temperature of the water should be about 10° C. lower than the expected softening point. Raise the temperature of the water gradually at the rate of about 1° C. per minute at first, slowing down to 0.5° C. per minute as the softening point is approached. The temperature at which the column rises in the capillary tube is taken as the softening point of the sample.

This method is of limited application and definite knowledge of its limitations is required for its satisfactory use. A fat or fat mixture does not have a sharply defined softening point comparable with the melting point of a pure substance. In the hands of different operators the method yields good results (±0.3°) when applied to such fats as coconut oil, stearins, hard hydrogenated oils, hard tallows and other homogeneous fatty substances; less satisfactory results are obtained (±2°) on lard, soft tallows, grease and similar fats and the method is quite unusable on lard compounds or mixtures of hard and soft fatty mixtures and emulsions (range +5° or more).

Slipping Point. Modified Bailey Whitner method [*Cotton Oil Press,* **5,** No. 10, 30 (1922)] for lard, lard substitutes, butter, margarin, emulsions and fatty products in their natural or prepared state.

Apparatus. Thermometer graduated in tenths of a degree. Melting point cups made of brass cylinders, medium walls 1 cm. diameter by 1 cm. high, soldered to a brass or copper spiral and bent so that they may be attached to the thermometer.

Heating Apparatus. Tripod and burner or other suitable apparatus.

Determination. Fill the melting point cups with the sample as received by forcing the material into them from the bottom until the plug of fat projects above the top of the cup. Cut off the excess so that the cup is completely filled. Take care that none of the sample is smeared around the bottom of the cup and that the cup is solidly packed. Attach two or more of the cups to the thermometer in such a way that they will hang opposite the bulb of the thermometer and in close proximity to it. Suspend the thermometer in a saturated salt solution in a 600-cc. beaker to a depth of 8 cm. Heat the bath at the rate of 1° C. per minute with constant agitation by air or by mechanical means, slowing down the heating toward the last to 5° C. per minute. The thermometer is read when the fat rises from the cup and the temperature is recorded as the slipping point.

Comments. The slipping point method gives excellent results on manufactured products in the form of emulsions and mixtures which have been beaten with water or air, such as butter, margarin, lard compound, etc. It applies equally well to lard, tallow, or any manufactured product of a fatty nature as manufactured, since it measures the slipping point of the product as it exists. The determination, when properly made, is capable of giving results that agree within ±0.2°. As the slipping point varies according to the manipulation of the product during manufacture, it is difficult and often impossible to reproduce in the laboratory the conditions of manipulation of a given sample sufficiently well to obtain the same slipping point after the sample has been melted or modified. Therefore, it is essential that this test be made on the original sample.

Titer Apparatus. Two-liter, low-form Griffin beaker; 450-cc. wide-mouth bottle having a height of 190 mm. and inside diameter of neck 38 mm.; test tubes 100 mm. long having a diameter of 25 mm., and these may have an etched line 57 mm. from the bottom to indicate the weight to which they are to be filled; saponification vessel which may be a flask, beaker, or casserole of suitable size; stirrer of glass, Nichrome or Monel metal with a diameter of 2 to 3 mm., having one end bent at a right angle in the form of a loop of 19 mm. diameter, the other end being formed for hand or mechanical stirring; a laboratory thermometer, calibrated from 0° to 150° C.

Titer thermometer. Minus 2 to plus 68° C. in 0.2-degree graduations, having a total length from 375 to 385 mm.; stem shall be made of suitable thermometer tubing of 6 or 7 mm. diameter. May be plain front or of the magnifying lens type. Red reading mercury is preferable but not

obligatory; bulb length 15 to 25 mm. and diameter not less than 5.5 mm., but not greater than that of the stem. It shall be made of normal Corning or other equally suitable glass; minimum length of graduated scale 300 mm.; length of unchanged capillary between lowest graduation mark and bulb, 13 mm.; expansion chamber large enough to permit heating the thermometer to at least 85° C.; length of unchanged capillary between uppermost graduation mark and expansion chamber, not less than 10 mm.; tubing above mercury shall be evacuated or filled with nitrogen or other suitable gas; all graduation lines, figures, and letters to be clear-cut and distinct; each degree mark to be longer than other graduations; at each multiple of 2 degrees, graduations are to be numbered; the words "45 mm. immersion" are to be etched on stem, and a line shall be etched around the stem 45 mm. above the bottom of the bulb; the error at any point on the scale, when the thermometer is standardized at 45 mm. immersion, shall not exceed 0.2° C.; thermometer shall be standardized at intervals of approximately 10° C. and for an average temperature of the emergent mercury column of 25° C.

Assembly apparatus. The salt mouth bottle weighted with 400 g. of lead shot is placed in the 2-liter beaker on a sheet of cork and held firm by means of 3 pieces of cork placed at equal distances apart near the shoulder of the bottle. Through a hole previously made in one of these corks, suspend the laboratory thermometer so that the bottom of the bulb will be about 2.5 cm. from the bottom of the beaker which serves as a water bath. A suitable hole is cut in the bottle cork to hold the test tube firmly in place. In the center of the cork, fitting the test tube, a hole is cut through which the titer thermometer is inserted and held firm. Also a second hole is cut through which the stirrer is operated up and down.

Reagents. Caustic Glycerin Solution: Dissolve 250 grams of solid potassium hydroxide in 1250 grams of glycerin (dynamite or C.P. grade) with the aid of heat. To avoid foaming do not heat mixture above 135° C.

Sulfuric Acid. Prepare a solution containing 30 per cent by weight of acid as follows: Add 32 cc. of sulfuric acid sp. g. 1.84 to 140 cc. of distilled water.

Method. Weigh 110 grams of caustic glycerin solution into the saponification vessel, stir while heating to 150° C., then add 50 cc. of oil or melted fat and reheat while stirring, but not above 150°, until complete saponification has been obtained. To the slightly cooled solution, add 250 cc. of water and after solution of the soap has taken place, add while stirring 50 cc. of the sulfuric acid and boil until the fatty acid layer is completely clear. Siphon off the lower aqueous-acid solution. Add 250 cc. of water and boil for 2 or 3 minutes, making certain that all the fatty acids have completely melted and form a clear layer. Siphon off water and repeat treatment until wash water is neutral to methyl orange indicator. Carefully remove the fatty acids to a flask so as not to include any drops of water. Filter them while entirely melted through any rapid filter paper. Heat the filtered acids on a hot plate to 130° C. to remove

traces of moisture and pour them into the test tube, filling it to a height of 57 mm. from the bottom. The fatty acids should not be held at 130° nor should they be reheated to this temperature more than once. The acids must be completely freed from moisture before putting them in the test (titer) tube.

Fill the 2-liter beaker in which is fixed the 450-cc. bottle to hold the titer tube, so that the water level will be 1 cm. above that of the fatty acids. The temperature of the water should be adjusted to 20° C. for all samples having titers of 35° C. or higher, and 15° to 20° C. below the titer point for those having titers below 35° C. Suspend the tube containing the melted fatty acids in the bottle by means of the hole in its cork made for this purpose. Insert the stirrer and the titer thermometer in the fatty acids to the immersion mark on it so that the latter will be equidistant from the sides of the tube. Then stir at the rate of 100 complete up-and-down motions per minute. The stirrer should move through a vertical distance of about 3.8 cm. Stirring should be started while the temperature of the acids is at least 10° C. above the titer point. Stir at the directed rate until the temperature remains constant for 30 seconds, or begins to rise in less than a 30-second interval. Discontinue stirring immediately and observe the increase in temperature. Report as titer the highest point reached by the thermometer. Duplicate determinations are expected to agree within 0.2° C.

Comments. The method is both rapid and satisfactory when conducted as directed. Care must be taken that saponification is complete in all cases. This is usually indicated by a change in the appearance of the soap which finally becomes homogeneous. In some cases, the further addition of a small quantity of the caustic glycerin solution may be found necessary to obtain complete saponification.

Critical Temperature of Dissolution or Turbidity Point. The turbidity point is determined by heating the oil and a solvent, such as acetic acid or alcohol, in which most of the oils are soluble only at elevated temperatures until the mixture is clear, then allowing it to cool slowly until the first permanent turbidity (caused by the separation of the oil) is obtained, at which point the temperature is noted and is known as the turbidity point.

Glacial acetic acid was first employed by Valenta [*J. Soc. Chem. Ind.*, **3**, 643 (1884)], but owing to the difficulty of preparing and maintaining the strength of the acid the test devised by Crismer [*Analyst*, **20**, 209 (1895)], in which alcohol is used in place of acetic acid, is now much more commonly employed. In the case of the Valenta procedure, it was found that slight variations in the strength of the glacial acetic acid caused wide differences of the turbidity point for a given oil. After the alcohol, which is used in the Crismer test, is adjusted to proper strength, there is no difficulty in keeping the reagent so that it will give satisfactory results. Free fatty acids, depending upon the quantity present, affect both methods similarly in that they lower the true values of the oils. Consequently, corrections of the turbidity points observed are made, as

will be shown below for the Crismer method. The corrections vary somewhat for the different groups of animal and vegetable oils.

In 1918, Fryer and Weston suggested as a further improvement in the Crismer method the use of a mixture consisting of equal volumes of 92 per cent alcohol and amyl alcohol in place of the methylated spirits employed by Crismer.

In both the Valenta and the Crismer tests pure expressed almond oil is used as a standard, and the solvents employed in these tests are adjusted by the addition of the necessary quantity of water so as to bring the turbidity point for the almond oil to 70° C., after correcting for the acidity of this oil.

Precautions must be taken to have the almond oil as well as the oils to be tested entirely free from moisture, because its presence will seriously affect the results of the tests. Also, it is equally important to use thoroughly dried apparatus for making the tests.

The different groups of oils show for the most part a wide range of turbidity point temperatures. Marked differences have been noted amongst the individuals of a given group of oils, and in some cases these differences are considerably larger than the range of Crismer values usually found for a given oil. In some instances this test will be found of value in the examination of oils suspected of being adulterated.

Modified Crismer Turbidity Test. The following modification of the Crismer test is essentially that of Fryer and Weston, *Analyst,* **43,** 3 (1918).

Reagents. Pure dry expressed almond oil low in acidity.

Alcohol. Mix equal volumes of 92 per cent ethyl alcohol by volume and pure amyl alcohol. Determine the turbidity point, using the almond oil as described below: Adjust the alcoholic mixture by the addition of water so as to bring the turbidity point to 70° C. for the almond oil, making allowance for its acidity as directed. The quantity of water to be added is about 0.11 per cent for each degree centigrade that the turbidity point has to be raised.

Preparation of Oils. To 25- or 30-cc. portions of the samples to be tested add about 2 grams of anhydrous sodium sulfate, shake and let stand for 30 minutes. Filter through folded filters into clean, dry flasks or small bottles. Carefully determine the acidity as oleic acid of each sample, using 5- or 10-gram portions in the usual manner.

Apparatus. An accurate thermometer graduated to fifths of a degree. The bulb of the thermometer should be moderately large.

Test Tubes. Test tubes 12.5 cm. × 1.3 cm. (5 × 0.5 inches). These may be calibrated with a diamond pencil or file at 2 and 4 cc. above the bottom of the tubes. Select a sound cork to fit these tubes and cut a hole in the center for the thermometer. Cut a notch in the side of the cork, through which a stirrer can be operated. A supply of ordinary-sized test tubes is necessary for heating samples of oils to be tested.

Stirrer. A small copper wire of suitable length with a horizontal circular loop of such a size that it can be raised and lowered outside of

the thermometer, which is placed in the center of the test tube during the test.

Beakers. Two of 400 cc. capacity.

Determination. Heat a portion of the dried sample to be tested in a test tube placed in one of the beakers half full of boiling water for about 5 minutes, then pour into one of the clean, dry, calibrated test tubes to the 2-cc. mark. Add the alcoholic reagent to the 4-cc. mark. Suspend the test tube by means of a clamp in the second beaker containing 200 cc. of warm water. Insert the stirrer through the notch in the cork, and adjust the thermometer so that the bulb is covered with the liquid, being careful that it does not touch either the sides or bottom of the test tube. Heat the water in the beaker slowly while stirring the mixture in the test tube until it becomes homogeneous and clear. Note the temperature of the thermometer and continue the heating about 5° C. above this point. Remove the stirrer from the test tube and quickly replace the cork carrying the thermometer. Remove the flame and allow the water bath to cool. Take as the turbidity point the temperature at which the first definite turbidity or cloudiness appears. The slight traces of turbidity which form at the top of the liquid as it cools quickly disappear as they move downward, and are ignored. The definite turbidity usually begins near the bottom of the tube, then quickly spreads throughout the whole solution during which the temperature change is considerably less than a degree. This point is very definite and readily distinguishable. The test cannot be repeated using this mixture, as the turbidity point will invariably be lower than that first obtained, due to the loss of some of the ethyl alcohol through volatilization. Therefore, a duplicate test can be made only with fresh portions of the oil and alcoholic reagent. Duplicate determinations should agree within half of a degree.

Correction for Acidity of Oils Tested. Multiply the acidity of each sample tested by the correction given in the table for one per cent acidity as oleic acid, according to the classes to which the samples belong, and add this correction to the temperatures observed.

Classes of Oil	Typical Oil	Fall in Turbidity Temperature for Each Per Cent of Acidity ° C.
Marine	Whale	1.95
Drying	Linseed	2.05
Semi-drying	Cottonseed	2.03
Semi-drying	Rape	1.61
Non-drying	Almond	2.07
Non-drying	Coconut Palm kernel	2.01
Non-drying	Palm	1.72
Non-drying	Butter fat	1.54
Non-drying	Lard	2.13

Comments. Unless every detail is observed in preparing the oil and alcoholic reagent, as well as in making the tests, unsatisfactory results will be obtained. As in the case of the other characteristics of the oils,

such as the iodine number, saponification value, etc., the Crismer test will show more or less variation with a given kind of pure oil from different sources and a range of two and often more degrees is to be expected.

CRISMER TESTS FOR VARIOUS OILS (FRYER AND WESTON)

Fat or Oil	Acidity (as Oleic) Per Cent	Observed Crismer Value	Correction Factor for Acidity	Corrected Value
Perilla	5.5	49.0	2.05	60.3
Linseed	2.0	58.3	2.05	62.4
Tung	0.9	74.0	2.05	75.8
Soybean	1.2	65.0	2.05	67.0
Niger	2.2	57.5	2.05	60.0
Sunflower	2.2	59.5	2.05	64.0
Corn	2.8	62.5	2.03	68.2
Cotton	0.1	65.0	2.03	65.2
Sesame	4.0	60.5	2.03	68.1
Rape	0.6	82.3	1.61	83.3
Almond	0.9	68.2	2.07	70.1
Peanut	1.1	72.0	2.07	74.3
Olive	0.7	67.8	2.07	69.2
Olive	1.8	65.5	2.07	69.2
Olive	3.6	61.5	2.07	69.0
Cacao	2.9	71.0	1.72	76.0
Chinese vegetable tallow	6.9	54.0	1.72	65.9
Palm	0.1	68.0	1.72	68.2
Lard	0.9	70.8	2.13	72.7
Tallow	0.1	72.5	2.13	72.7
Butter fat	1.9	43.0	1.54	46.0
Coconut	0.0	34.0	2.01	34.0
Coconut	1.6	30.0	2.01	33.2
Palm kernel	0.0	40.0	2.01	40.0

The Crismer values given in the following table were determined in the author's laboratory according to the modified method described. All of the oils for which results are given were of known purity.

Oil	Acidity (as Oleic)	Observed Value	Correction for Acidity	Corrected Value
Almond	0.65	68.8	1.36	70.16
Olive	0.35	70.0	0.71	70.71
Olive	0.63	69.6	1.28	70.88
Olive	0.98	68.4	1.95	70.35
Rape	0.14	82.6	0.30	82.90
Rape	0.51	80.2	1.05	81.25
Rape	0.21	83.4	0.44	83.88
Rape	3.50	75.4	7.24	82.64
Cottonseed	0.0	67.2	...	67.20
Corn	0.0	63.6	...	63.60
Apricot kernel	0.35	66.4	0.73	67.13
Peanut	9.02	49.1	18.68	67.78
Peanut	0.66	66.0	1.36	67.36
Peanut	0.77	61.0	1.60	62.60

With each of the oils, the Crismer values given in this table have been checked by duplicate tests.

Soluble and Insoluble Fatty Acids. The percentage of insoluble fatty acids is known as the "Hehner Value." As usually determined, it also includes the unsaponifiable constituents of the fat.

Soluble Acids. Evaporate the neutralized solution obtained from the determination of the saponification value to dryness on the steam bath. Add such an amount of 0.5*N* hydrochloric acid that its volume plus the quantity used in the titration for the saponification value will be 1 cc. in excess of that required to neutralize the 25 cc. of the alcoholic potassium hydroxide added, and place on steam bath until the separated fatty acids form a clear layer on the surface of the liquid. Fill to neck with hot water and cool in the ice water until the cake of fatty acids is entirely hard. Pour the liquid contents of the flask through a filter (not folded) into a liter flask. Fill the saponification flask again with hot water, set on the steam bath until the fatty acids collect at the surface, then cool by immersing flask in ice water, and when the fatty acids are entirely solid, filter as before into the liter flask. Repeat the treatment with hot water three times, cooling and collecting the washings in the liter flask each treatment. Titrate the combined washings with 0.1*N* alkali, using phenolphthalein as indicator. Subtract 5 cc. for the 1 cc. excess of 0.5*N* acid added from the number of cc. of 0.1*N* alkali used, and multiply by 0.0088 to obtain the weight of soluble acids as butyric acid. Calculate the percentage of soluble acids.

Insoluble Acids. Allow the flask containing the cake of insoluble fatty acids from the previous determination and the paper through which the soluble fatty acids were filtered to drain and dry for 12 hours. Transfer the cake, together with as much of the fatty acids as can be removed from the filter paper, to a weighed, wide-mouth flask. Then place the funnel containing the filter in the neck of the flask and wash the paper thoroughly with hot absolute alcohol. Remove the funnel, evaporate the alcohol, dry the residue for two hours at 105° C., cool and weigh. Again heat for two hours, cool and weigh. If necessary, heat further until weight is constant. In cases where the iodine number of the oil is above 145, the acids should be dried at 105° C. in an atmosphere of carbon dioxide to prevent oxidation. Calculate the percentage of insoluble acids.

Viscosity. The measurement of the viscosity of oils is of little or no importance except in the case of those products such as castor, rape, neatsfoot and lard oils which are going to be used alone or in mixture with mineral oils as lubricants. Consequently, the determination of the viscosity and the numerous types of viscosimeters used will not be described. Those interested in this determination should consult Thorpe's "Dictionary of Applied Chemistry," Archbut and Deely's "Lubrication and Lubricants," or other books dealing with this subject.

Determination of Chemical Characteristics

Acid Value. The acid value is a measure of the quantity of free fatty acids and is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of substance.

Solutions. An accurately standardized 0.1*N* and a 0.25*N* solution of potassium hydroxide.

Neutral Alcohol. Add 2 cc. of a one per cent alcoholic solution of phenolphthalein to 1000 cc. of approximately 95 per cent alcohol by volume or alcohol denatured with methanol and titrate to a faint pink color with the 0.1*N* solution of potassium hydroxide.

Determination. Weigh 10 grams of the sample into a 200-cc. Erlenmeyer flask (take from 2 to 5 grams in the case of products containing large quantities of free fatty acids); add 50 cc. of the neutral alcohol and heat for 10 minutes on the steam bath; add 1 cc. of phenolphthalein solution (*see* saponification value) and with constant shaking titrate the mixture with the 0.1*N* potassium hydroxide solution until the pink color persists for a minute. Vigorous agitation is necessary to bring the fatty acids in contact with the standard alkali solution. Calculate the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of the sample.

Comments. In cases where the acid value exceeds 20, it is preferable to take a 5- or 10-gram portion of the sample and titrate with a 0.25*N* potassium hydroxide solution. An 0.5*N* alkali solution is used for titrating low-grade crude palm oils. The free fatty acids are still commonly given in the trade as the percentage of oleic acid (per cent of palmitic acid for palm oil and of butyric acid for coconut and palm kernel oils), although it has been shown that the free fatty acids of a given oil contain saturated and unsaturated acids in about the same proportions as in the glycerides [*Cotton Oil Press,* 7, No. 2, 35 (1923)].

This determination in the case of crude cottonseed, pumpkin and some other oils not only includes the free fatty acids but also more or less resinic acids and other constituents which react readily with the alkali hydroxide.

Another method which is also used to considerable extent is based on using equal volumes of neutral alcohol and benzene (C_6H_6) and titrating the free fatty acids without previously heating the mixture of oil and solvents.

The following references may be of interest:

"Determination of Acidity of Oils and Fats by the Quinhydrone Electrode in Non-Aqueous Solutions," Seltz and Silverman, *Ind. Eng. Chem., Anal. Ed.* 2 1 (1930).

"Determination of Acid Value of Fats and Oils by the Electro-Titerometric Method," Kremann and Muss, *J. Soc. Chem.*, 40, 896A (1921).

Saponification Value (Koettstorfer Number). The number of milligrams of potassium hydroxide required to saponify one gram of fat or oil is known as the saponification value. The method for the determination of this value is as follows:

Alcoholic Potassium Hydroxide. Crush 40 grams of the best grade of potassium hydroxide in a sizable mortar. Add 45 grams of pure granulated calcium oxide and grind the mixture as quickly as possible to a fine powder. Measure 1000 cc. of 95 per cent of alcohol. Mix about 100 cc. of it with the powdered alkalies and transfer to a flask,

rinsing the mortar with several portions of the alcohol. Then add the remainder of the alcohol and shake thoroughly until the potassium hydroxide is in solution. Invert a small beaker over the neck of the flask and allow the solution to stand until the calcium hydroxide has completely settled. Filter into liter glass-stoppered bottle. The solution prepared in this manner remains practically colorless for a long time. The method for this reagent was devised by Malfatti, [*Chem. Abs.*, **6**, 200 (1912)].

Standard Acid. Prepare accurately several liters of 0.5*N* hydrochloric acid solution.

Indicator. Dissolve one gram of phenolphthalein in 100 cc. of 95 per cent alcohol.

Determination. Weigh accurately from 2.5 to 3 grams of the sample in a small glass shell vial (15 × 35 mm.) and transfer to a 200-cc. Erlenmeyer flask. Add exactly 25 cc. of the alcoholic potash solution from a burette. Stopper the flask with a cork through which a 2-foot glass tube with an inside diameter of 0.25 inch is inserted to serve as an air condenser. Place flask on steam bath and gently boil contents for 30 minutes. Remove the cork and add six drops of phenolphthalein solution and titrate with 0.5*N* hydrochloric acid solution. Also titrate two 25-cc. portions of the alcoholic potash solution, previously heated to about 50° C. with the 0.5*N* hydrochloric acid. If the quantity of standard acid used in these two titrations differs more than 0.1 cc., repeat the titrations. Deduct from the volume of standard acid required to neutralize 25 cc. of the alcoholic potash solution, that used in the titration of the saponified sample, to get the volume of standard acid equivalent to the potassium hydroxide required for the saponification of the sample. Calculate the saponification value, which is the number of milligrams of potassium hydroxide required to saponify one gram of the sample. In all cases duplicate determinations should be made. The calculated results should agree within less than 1 or be repeated. The resulting soap solution in the case of deep-colored products is often so dark as to obscure the end point. In such cases a 2 per cent alcoholic solution of alkali blue 6 B may be used in place of phenolphthalein as indicator.

As the solution of alcoholic potash solution is subject to change, it is necessary to determine its value by titration with the 0.5*N* hydrochloric acid solution as directed above, each day that saponification values are to be determined.

In the case of the waxes, saponification can usually be completed only by boiling them with alcoholic potash for three or four hours.

Saponification Equivalent. The term *saponification equivalent* refers to the weight of fat saponified by 56.104 parts of potassium hydroxide. The saponification equivalent is readily calculated from the saponification value, using it as a divisor and 56.104 as a dividend. The saponification equivalent of the fatty acids or esters of monohydric alcohols is identical with their molecular weight, but in the case of the glycerides it is one-third of their molecular weight. It is generally considered preferable to give the saponification value instead of the saponifi-

cation equivalent, and thereby avoid possible confusion with the former term which, with few exceptions, is the one used.

Ester Value. By the term *ester value* is meant the quantity of potassium hydroxide required to saponify the esters present, and it is found by subtracting from the saponification value the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of the sample being examined. Only in cases of those products which contain large quantities of free fatty acids does the ester value differ perceptibly from the saponification value.

Unsaponifiable Matter. The term *unsaponifiable matter* includes all those substances which are not saponified by alkali, but which are soluble in ether and petroleum ether. In the case of fats and oils, the unsaponifiable matter consists of sterols and small quantities of other alcohols and hydrocarbons. In marked contrast to the fats and oils, the waxes yield large quantities of unsaponifiable matter which consists chiefly of the higher monohydric alcohols.

The Modified Kerr-Sorber Method, which gives very satisfactory results, will be described.

Reagents

Concentrated Potassium Hydroxide Solution. Dissolve 100 grams of potassium hydroxide in 100 cc. of water.

Dilute Potassium Hydroxide Solution. Dissolve 11.2 grams of potassium hydroxide in 1000 cc. of water.

Phenolphthalein Solution. Dissolve one gram of phenolphthalein in 100 cc. of alcohol.

Ethyl Alcohol. Approximately 95 per cent by volume.

Ether. U. S. P. grade.

Determination. Accurately weigh 5 grams of the sample of fat oil into a 200-cc. Erlenmeyer flask. Add 30 cc. of alcohol and 5 cc. of the concentrated alkali solution. Mix thoroughly by rotating the flask. Boil the mixture, using a reflux condenser for twenty minutes. In the case of waxes use 1- or 2-gram portions, 5 cc. of alkali solution, and heat for at least two hours. Cool to about 30° C., add 50 cc. of ether, mix, and carefully transfer to a 500-cc. separatory funnel. Rinse the flask with two successive 50-cc. portions of ether, add to the separatory funnel, and mix the contents thoroughly. Wash the saponification flask with 100 cc. of the dilute alkali solution and pour into the separatory funnel in a slow, steady stream. Rotate the funnel gently to secure better contact of the solutions, but do not shake. Shaking at this stage causes stubborn emulsions. Allow the liquids to separate completely, then slowly draw off as much of the soap solution as possible. Do not withdraw any emulsion that may be formed. Keep the volume of ether at about 150 cc. by replacing that dissolved by the wash solutions. Further treat the ether solution with two successive 100-cc. portions of the wash solution in the same manner as described above. Add 30 cc. of water to the ether solution and mix by rapid rotation of the separatory funnel. When the layers have separated, withdraw the water. Repeat this treatment by shaking the water and ether thoroughly until the

washings are free from alkali, as shown by testing with phenolphthalein solution. Three washings usually suffice. Transfer the ether quantitatively to a weighed 250-cc. Erlenmeyer flask. Distill the ether, using a water bath, then dry the flask and residue in an oven heated to 100° or 105° C., until a constant weight is obtained. Calculate the percentage of unsaponifiable matter.

Comments. It is important to follow in detail all the directions as given, if accurate results are desired In connection with distillation of the ether, it is preferable to employ a suitable spray trap between the flask and the condenser to eliminate any possible loss of unsaponifiable matter. It will be observed that this method, in contrast to others, is based upon the solution of the unsaponifiable matter in ether and the removal of dissolved soap by washing with a dilute solution of potassium hydroxide, which is necessary to prevent the formation of acid soaps which cannot be removed from the ether.

Iodine Number (or Value). The iodine number may be defined as the number of grams of iodine absorbed by 100 grams of fat or other substance. As the absorption of iodine alone by the unsatuated acids or their esters is exceedingly slow, it is customary to use it in combination with mercuric chloride, bromine or chlorine. The iodine number of an oil indicates the class to which it belongs. Oils having an iodine number below 100 may be considered as belonging to the non-drying class. Iodine numbers from 100 to 130 indicate semi-drying oils and those above 130 the drying oils. The iodine number of fats and oils is subject to more or less variation. In the case of vegetable oils, the differences are due in part to variety, environment and seasonal variations. For example, the iodine number of olive oil from different sources varies from about 81 to 91.

As there are a number of radically different methods in use, it is important in reporting iodine numbers to indicate the method used, because these methods do not give identical results.

For detailed information of the various methods that have been suggested for the determination of the iodine number B. M. Margosches' work entitled "Die Jodzahlschnellmethode und die Uberjodzahl der Fett" (Ferdinand Enke, Stuttgart, 1927) should be consulted.

The following references may be of interest:

"Results with Kaufmann's Method for Determining Iodine Number," W. Trappe, *Biochem. Z.*, **296**, 174 (1938); *Chem. Abs.*, **33**, 420 (1939).

"The Iodine Number Determination Without Iodine," H. P. Kaufmann, *Fette u. Seifen*, **47**, 4 (1940).

"Wijs Iodine Numbers for Conjugated Double Bonds," W. C. Forbes and H. A. Neville, *Ind. Eng. Chem. Anal. Ed.*, **12**, 72 (1940).

"Woburn Iodine Absorption Method," J. D. Mikusch and C. Frazier, *Ind. Eng. Chem. Anal. Ed.*, **13**, 782 (1941).

In connection with the preparation of the Hanus and Wijs solutions, it should be noted that their stability is dependent upon the quality of the acetic acid used. If the acid contains any reducing substance, as shown by the potassium dichromate test described in B. L. Murray's "Standards and Tests for Reagent Chemicals" (D. Van Nostrand Co.,

New York), Hanus and Wijs solutions made with it will remain but a short time in a usable condition. All acetic acid to be used for these purposes should be tested, because at times even that labelled as conforming to the dichomate test has been found to contain some reducing substances.

The Hanus, Wijs, and Kaufmann procedures will be described.

Reagents

Potassium Iodide Solution. Dissolve 45 grams of pure potassium iodide in 300 cc. of water and preserve the solution in a blue or dark amber-colored bottle.

Starch Paste. Mix about 1 gram of powdered starch in 20 cc. of cold water and pour the mixture into 500 cc. of boiling water. Boil for 10 minutes. Cool and preserve the solution in a glass-stoppered bottle. Add 5 cc. of chloroform as a preservative and shake the mixture. This preparation keeps in excellent condition for six months and often much longer.

Sodium Thiosulfate Solution. Boil about 1500 cc. of water in a flask for 30 minutes to render it sterile. After boiling, invert a small beaker over the neck of the flask while the water is cooling. Dissolve 24.8 grams of sodium thiosulfate in the boiled water, cooled to room temperature, and dilute to 1000 cc. Weigh accurately 0.4 to 0.5 gram of pure powdered iodine in duplicate and transfer to a 250-cc. glass-stoppered bottle. Add about 15 cc. of the potassium iodide solution and shake until the iodine is dissolved. Add 100 cc. of water, mix and titrate with the sodium thiosulfate solution until the larger part of the iodine color has been discharged. Add about 1 cc. of the starch paste and slowly continue the titration with constant shaking until the blue color just disappears. Calculate the value of 1 cc. of the solution in terms of iodine to six decimal places.

Wijs Method

Reagents. Wijs Solution. Dissolve 13 grams of powdered resublimed iodine in 1000 cc. of pure glacial acetic acid (99 to 99.5 per cent). The acid may be warmed to facilitate the solution of the iodine, but it should be cooled to room temperature before proceeding with the preparation of this regeant. Take 10 cc. of the iodine solution in a 300-cc. flask, add 50 cc. of water, and titrate the iodine with the standard thiosulfate solution, using starch paste as an indicator. Set aside in a flask about 30 cc. of the iodine solution and pass into the remainder dry chlorine gas until the color of the solution does not appear to further change. Remove 10 cc. to a 300-cc. flask, add 10 cc. of the potassium iodide solution, 50 cc. of water, and titrate as before with the standard thiosulfate solution. Sufficient chlorine should be added to double the titration of the original iodine solution, but little chlorine in excess of this requirement can be present. Continue the titration of 10-cc. portions of the solution after each further addition of chlorine that may be necessary before the halogen content of the solution is doubled. Then

add the reserved 30-cc. portion of the iodine solution and mix thoroughly. A slight excess of iodine is not objectionable, but there must be no free chlorine in the Wijs solution. Preserve the solution in a blue or amber-colored, glass-stoppered bottle. Place the date of the preparation on the bottle and discard this solution when it is a month old. It should be observed that the Wijs solution is far more sensitive toward light than is the case with the Hanus solution.

Determination. Weigh accurately 0.15 gram to 0.25 gram of the sample, preferably in a 1-cc. glass shell vial, and transfer to a clean, dry 250- or 300-cc. glass-stoppered bottle. In the case of fats, weigh the vials, add the melted sample, and when at room temperature weigh. Portions of about 0.5 gram can be used to advantage in the case of coconut, palm kernel or other fats having low iodine numbers. In the case of drying oils, not over 0.2 gram should be taken for analysis. Add about 15 cc. of chloroform or carbon tetrachloride and shake gently until the sample is dissolved. In the case of very hard fats or fatty acids, sometimes it is necessary to slightly warm the contents of the titration bottle in order to dissolve the samples. Add from a burette exactly 25 cc. of the Wijs solution (the excess of iodine should be from 50 to 60 per cent of the quantity added, that is, from 100 to 150 per cent of the quantity absorbed by the portion taken for analysis). The directions given above for the quantities of various kinds of oils, etc., to be taken for analysis insure a proper excess of the Wijs reagent, which is necessary in order to get a maximum absorption of halogen. Moisten the stopper with the potassium iodide, but guard against the use of a quantity sufficient to run down inside the bottle. Stopper the bottle and let it remain in a dark place for thirty minutes; then add 15 cc. of the 15 per cent potassium iodide solution and 75 cc. of water. Mix and titrate the iodine solution with the sodium thiosulfate solution. Titrate rapidly with constant rotation of the contents of the titration bottle until most of the red color of the solution has disappeared. Add 1 cc. of the starch paste, insert stopper, and shake thoroughly, but not so hard as to break the glass vial (if one is used), then continue the titration slowly from this point until the blue color just disappears. Make two blank determinations in the same manner as that employed with the actual analysis. As variation in the temperature affects appreciably the titer of the Wijs solution on account of the high coefficient of expansion of the acetic acid, it is essential that the blanks and determinations on the sample be made at the same time. The number of cubic centimeters of standard sodium thiosulfate solution required by the blank titration, less the quantity used in the actual determination, gives the quantity of sodium thiosulfate solution equivalent to the iodine absorbed by the sample taken for analysis. Calculate the weight of iodine absorbed, divide this by the weight of the sample, and multiply this result by 100 to get the iodine number.

Hanus Method

Reagents. The 0.1*N* sodium thiosulfate, the potassium iodide, and the starch solutions used are described under the Wijs method.

Hanus Solution. Dissolve 13.815 grams of powdered iodine in 825 cc. of glacial acetic acid (99.5 per cent) in a bottle or flask. The mixture may be heated slightly, if necessary, in order to dissolve the iodine completely. When the solution is at room temperature, measure 25 cc. from a burette into a 200-cc. Erlenmeyer flask. Add 50 cc. of water, 10 cc. of the 15 per cent potassium iodide solution, and titrate with 0.1*N* thiosulfate. Put 200 cc. of glacial acetic acid into a 300-cc. flask and add 3 cc. of pure bromine. Mix and measure exactly 5 cc. into a flask. Add 10 cc. of the potassium iodide solution and 50 cc. of water. Titrate this solution with the 0.1*N* sodium thiosulfate solution. Calculate the quantity of the bromine solution required exactly to double the halogen content of the remaining 800 cc. of the iodine solution as follows:

$$A = \frac{B}{C}$$

A = cc. of bromine solution required; B = 800 × the thiosulfate equivalent of 1 cc. of the iodine solution; C = the thiosulfate ≡ 1 cc. of the bromine solution. The finished solution should contain 13.2 grams of iodine per 1000 cc. Keep the solution in a glass-stoppered bottle and when not in use store it in a dark place. The following example will illustrate the calculations in the preparation of the Hanus solution.

Example. 138.15 grams of iodine are dissolved in 8250 cc. of glacial acetic acid. Thirty cc. of bromine is dissolved in 2000 of acetic acid. A titration of 50 cc. of the iodine solution showed that 1 cc. equals 1.1 cc. of the 0.1*N* thiosulfate solution. A titration of 5 cc. of the bromine solution showed that 1 cc. equals 4.6 cc. of the thiosulfate solution. Then the quantity of bromine solution required to double the halogen content of the remaining 8200 cc. of iodine solution is equivalent to $\frac{8200 \times 1.1}{4.6}$ or 1961 cc. Upon mixing the two solutions in this proportion, there is obtained a total volume of 10,161 cc., which contains 135.3 grams of iodine. In order to reduce this solution to the proper strength, which is 13.2 grams of iodine per liter, $10{,}161 \times 13.2 = 134.1$; $135.3 - 134.1 = 1.2$ grams of iodine in excess or $\frac{1.2 \times 1000}{13.2} = 91$ cc. of acetic acid, which must be added. Reference: "Association Official Agricultural Chemists' Methods for Analysis," **1925**, p. 287.

Determination.—Follow exactly the directions given for the Wijs method on page 393.

Comments. The Hanus solution, when stored in a dark place, keeps in a satisfactory condition for a year or longer. The Hanus method usually gives results from about 2 to 4 per cent lower than those obtained by the Wijs method. The Wijs method gives abnormally high results with sterols, but most fats and oils contain less than 1 per cent of these substances. On the other hand, wool wax contains a considerable quantity of sterols (cholesterols). By either method, duplicate

analyses should not differ by more than one unit; otherwise they should be repeated.

Kaufmann Method

Reagents. The 0.1*N* sodium thiosulfate, the potassium iodide, and the starch solutions used are described under the Wijs method.

Kaufmann Solution. Saturate 1 liter of pure methyl alcohol, using about 150 grams of finely powdered anhydrous sodium bromide. Filter the solution and add to it 8.0 grams of bromine. Keep the solution in a blue or amber glass-stoppered bottle.

Chloroform. Pure and free from alcohol.

Determination. Weigh accurately 0.10 to 0.15 gram of drying oils, 0.20 gram of semi- or non-drying oils or 0.30 to 0.4 gram of solid fats in a shell vial and place it in a 250- or 300-cc. glass-stoppered bottle. Add 15 cc. of chloroform and rotate it until the sample is dissolved. Add from a burette exactly 40 cc. of the bromine solution, rotate to mix the solutions, and allow the stoppered bottle to stand in a shaded place for 2 hours for drying oils or one hour for other fats and oils. Then add 15 cc. of the 15 per cent potassium iodide solution and 75 cc. of distilled water. Mix and titrate with the standard sodium thiosulfate solution in the usual manner.

Make two blank determinations in the same manner as that employed with the actual analysis. The number of cubic centimeters of sodium thiosulfate required by the blank titration, less the quantity used in the actual determination, gives the quantity of thiosulfate solution equivalent to the bromine absorbed by the sample taken for analysis. Calculate the iodine number in the usual manner.

Comments. The results obtained by this method agree closely with those given by the Hanus procedure. The stability of the Kaufmann bromine reagent is shown by the fact that it undergoes very little change after storage for 6 or 7 weeks.

F. R. Earle and R. T. Milner [*Oil and Soap*, **16**, 69 (1939)] stated that a minimum of two hours was required for the reaction of the reagent with the sample taken for analysis.

Thiocyanogen Value. The procedure to be described for the determination of the thiocyanogen value, which was originated by H. P. Kaufmann, is essentially that of the Committee on the Analysis of Commercial Fats and Oils of the American Chemical Society [*Ind. Eng. Chem. Anal. Ed.*, **8**, 233 (1936)]. By means of this value and the iodine number, the percentages of oleic, linoleic and saturated acids can be calculated, provided other unsaturated acids are absent. Also the percentages of oleic, linoleic, and linolenic acids can be calculated, provided the quantity of saturated acids is known.

Recently, further investigations on the reaction of thiocyanogen with oleic, linoleic, and linolenic acids made by Riemenschneider and Wheeler [*Oil and Soap*, **16**, 219 (1939); Kass, *et al., ibid.*, **17**, 50, 118 (1940)] have shown that it reacts quantitatively with oleic acid and its esters; but in the case of linoleic acids or its esters the reaction somewhat exceeds

that required to saturate one double bond, whereas in the case of linolenic acid, the two double bonds which react with thiocyanogen fail to do so completely. As the reaction of the thiocyanogen is not strictly quantitative with either linoleic or linolenic acids (which was contrary to the assumption of Kaufmann and associates), it has been found necessary to pay attention to conditions such as the concentration of the thiocyanogen reagent and the excess of it used, the time allowed for the reaction, and the temperature of the reacting substances, if the equations given below for calculating the proportions of acids (oleic, etc.) are to be used. These equations are based on using a 0.2*N* thiocyanogen solution and allowing it to react with the sample for a period of 24 hours at 20° C.

Method

Apparatus. It should be noted that all glassware (as well as chemicals) used must be free from moisture. All glassware should be cleansed with cleaning mixture, water, alcohol, and ether, and then dried in an oven at 105° C. for an hour or longer.

Reagents. Acetic acid. Place 2 liters of glacial acetic acid (99.5 to 100 per cent) and 100 cc. of acetic anhydride (90 to 100 per cent) in a 3-liter Florence flask. Into the neck of the flask insert a large test tube (provided with a cork having inlet and outlet tubes through which cold water is passed) to serve as a condenser. By means of an oil bath, reflux the mixture for 3 hours at a temperature of approximately 135° C. After the anhydrous acid has cooled to room temperature, transfer it to cleaned, dried, glass-stoppered bottles.

Lead thiocyanate. Dissolve 250 grams of the finest pure neutral lead acetate in 500 cc. of distilled water. Dissolve likewise 250 grams of pure potassium thiocyanate in 500 cc. of distilled water. To this solution, while stirring, add slowly that of the lead acetate. Collect the precipitated lead thiocyanate on a Büchner funnel, washing it successively with distilled water, alcohol, and ether. Dry the lead thiocyanate as much as possible by drawing air through it. Remove it from the funnel and dry it on a watch glass in a phosphorus pentoxide desiccator for 8 to 10 days. This lead thiocyanate should be a greenish or yellowish-white crystalline material, but if the product is at all discolored, it must be discarded. Precipitated lead thiocyanate may be kept for a period not exceeding two months.

Preparation of an 0.2 solution of Thiocyanogen. For the preparation of 1 liter of solution, suspend 50 grams of the dry lead thiocyanate in 500 cc. of the anhydrous acetic acid. Dissolve 5.1 cc. of pure bromine in another 500 cc. of the anhydrous acetic acid. Each of these solutions is to be placed in glass-stoppered bottles which have been previously thoroughly cleaned and dried. Add the bromine solution slowly in small portions to the suspension of lead thiocyanate, shaking vigorously after each addition until the solution is completely decolorized. After all the bromine solution has been added, allow the precipitated lead bromide and excess of lead thiocyanate to settle, then filter the solution as rapidly as possible. A 13-cm. Büchner funnel and a qualitative filter, together

with two 2-liter pressure flasks, are used for the filtration. They are previously dried for an hour at 105° C. The entire solution is filtered by suction into one of the filter flasks; then the funnel is transferred to the second one and the solution is refiltered. The filtrate should be perfectly clear. It is stored in dried, glass-stoppered, brown bottles and kept in a cool place (16° to 21° C.).

This solution should not be exposed to air, heat or light for any length of time. Also it cannot be used after its decomposition exceeds 0.2 cc. of 0.1*N* sodium thiosulfate solution for 25 cc. over a period of 24 hours. This rate of decomposition should not be exceeded in less than 7 days after the preparation of the solution.

Potassium Iodide. Prepare 250 cc. of a 15 per cent solution using pure potassium iodide.

Method. Weigh from 0.1 to 0.3 gram of oil accurately into a dry 125-cc. glass-stoppered Erlenmeyer flask. Add from a pipette exactly 25 cc. of the thiocyanogen solution, rotate the solution and allow it to stand in a dark place at a temperature of 20°. The size of the sample taken for analysis is governed largely by the expected thiocyanogen absorption. The excess of thiocyanogen used over that absorbed by the sample should be at least 100 per cent, but preferably less than 150 per cent, although a greater excess appears to do no harm. At the end of the 24-hour reaction period, add 10 cc. of a 15 per cent solution of potassium iodide quickly and all at once, while rotating the contents of the reaction flask. (If the potassium iodide solution is not added all at once and quickly to the thiocyanogen solution, some hydrolysis of the latter reagent will take place.) Then add 30 cc. of distilled water and titrate the liberated iodine with 0.1*N* thiosulfate solution, using starch as an indicator. At least three blanks should be made along with the samples under examination. The number of cubic centimeters of thiosulfate solution required by the blank titration, less that used in the actual determination, gives the quantity equivalent to the thiocyanogen absorbed by the sample of oil. Calculate the weight of iodine equivalent to the thiocyanogen absorbed, divide this by the weight of the sample, and multiply this result by 100 to get the thiocyanogen value.

The desired calculations can be made using the following equations:

	Iodine No.	Thiocyanogen Value
Linoleic acid glyceride (x)	173.20	90.59
Oleic acid glyceride (y)	86.01	86.01
Saturated acid glycerides (z)	0	0

(1) $x + y + z = 100$
(2) $173.20x + 86.01y + 0z = 100$ (iodine number)
(3) $90.59x + 86.01y + 0z = 100$ (thiocyanogen value)

The following formulas are derived by solving these equations.

x (per cent of linoleic acid glyceride) = 1.210 (Iod. No.—SCN value)
y (per cent of oleic acid glyceride) = 2.438 (SCN value—1.274 Iod. No.)
z (per cent of saturated acid glycerides) = 100—($x + y$).

It must be remembered that z includes also the percentages of unsaponifiable matter.

Formulas for calculations of the free fatty acids are as follows:

	Iodine No.	Thiocyanogen Value
Linoleic acid	181.0	96.3
Oleic acid	89.9	89.9
Saturated acids	0	0

$x + y + z = 95.5$ (per cent)
$181.0x + 89.9y + 0z = 100$ (Iod. No.)
$96.3x + 89.9y + 0z = 100$ (SCN value)

From these equations the following are obtained:

x (per cent of linoleic acid) = 1.181 (Iod. No.—SCN value)
y (per cent of oleic acid) = 2.377 (SCN value—1.265 Iod. No.)
z (per cent of saturated acids + Unsapon.) = $95.5—(x + y)$

It is assumed that the fatty acids together with the unsaponifiable matter amount to 95.5 per cent of the fat or oil under examination. In cases where the unsaponifiable matter exceeds one per cent, it is preferable to prepare the fatty acids (after separation of the unsaponifiable matter) and use them for determination of the thiocyanogen value in place of the original sample.

The application of the method to oils which contain linolenic acid is as described, except that it is necessary to know the percentage of the saturated and unsaturated acids, if it is desired to calculate the quantities of the unsaturated acids in the sample. Equations for these calculations are as follows:

Acids	Iod. No.	SCN Value
Linolenic (x)	273.7	167.3
Linoleic (y)	181.0	96.3
Oleic (z)	89.9	89.9

(1) $273.7x + 181.0y + 89.9z = 100$ (Iod. No.)
(2) $167.3x + 96.3y + 89.9z =$ (SCN value)
(3) $x + y + z = 95.5$—(sat. acids + unsapon.)

These equations are resolved into the following:

(4) $106.4x + 84.7y = 100$ (Iod. No.—SCN value).
(5) $106.4x + 8.58y = 137.47$ SCN value—123.59 (95.5—sat. acids + unsapon.)

The percentage of linoleic acid is obtained by substituting the proper values for the iodine number, the thiocyanogen value, and that for the saturated acids and unsaponifiable matter added together, simplifying and subtracting equation (5) from (4), and solving for y. The percentage of linolenic acid is then obtained by substituting the value for y in either equations (4) or (5), and solving them for x. The percentage of oleic acid is obtained by substituting the values for x and y in either equation (1) or (2) and solving for z.

Diene Value. The observation of Diels and Alder [*Ann.*, **460**, 98 (1938)] that maleic anhydride and a group of related substances react readily with conjugated dienes, attracted the attention of Kaufmann and Baltes [*Fette u. Seifen*, **43**, 93 (1936)], who applied the reaction to the determination of elaeostearic acid. Afterwards, Kaufmann, Baltes, and Büter [*Ber.*, **70**, 903 (1937)] proposed several alternative procedures

for this determination. Ellis and Jones [*Analyst*, **61**, 812 (1936)] have described also a procedure based on the maleic anhydride reaction. These various methods have been used with several preparations of pure elaeostearic acid in the author's laboratory. The Kaufmann procedures gave values ranging from 75 to 78, whereas that of Ellis and Jones gave values ranging from 89.0 to 89.6, in each case using portions of several different specimens of acid. The calculated diene value of elaeostearic acid is 91.2. The method to be given is essentially that previously described by Ellis and Jones.

Method

Reagent. Distill the maleic anhydride twice, shortly before preparation of the reagent. Dissolve 60 grams of the purified product in one liter of reagent-grade toluene. Prepare a 0.5*N* sodium hydroxide solution in the usual manner and standardize it, with pure maleic acid, using phenolphthalein as indicator.

Apparatus. Have at least 4 inner spiral tube type condensers with water jackets from 20 to 25 cm. long and which have ground joints to fit 250-cc. flasks. An oil bath is required in which 4 of the flasks attached to supported condensers can be heated at one time.

Determination. Weigh accurately in duplicate portions about 3 grams of the sample into the 250-cc. flasks. Filter the maleic anhydride reagent, and add exactly 25 cc. of it to each of these flasks, and also to each of the two other empty 250-cc. flasks (blank determinations). Attach the flasks to the condensers arranged above the oil bath. (If the joints between the condensers and flasks are well made, no lubricant is required, but in cases where there is some leakage, this can be stopped by applying a little paste of powdered graphite and Vaseline to the upper third of the joint.) Lower the flasks into the oil bath heated to about 120° C. After heating for 3 hours, allow the solutions in the flasks to cool somewhat and add 5 cc. of water through the condenser. Heat for 15 minutes in the oil bath at a temperature of about 105° C. Cool the flasks and contents to room temperature. Wash each condenser tube with 5 cc. of ether, then with 20 cc. of distilled water. In each case, detach the flasks from the condensers and transfer the contents to separatory funnels. Rinse each flask, first with 20 cc. of ether, used in 3 portions, and then three times with 8-cc. portions of water, the rinsings being added to the contents of the separatory funnel. Mix the contents of the separatory funnel in each case by rotating and gently shaking it. Allow the mixtures to stand until the "layers" separate. Transfer the aqueous solutions to 250-cc. flasks for titration. In each case wash the non-aqueous solution with two 25-cc. portions of distilled water, adding them to the titration flasks. Titrate each solution with 0.5*N* sodium hydroxide solution, in the usual manner, using phenolphthalein indicator.

The diene value, which is expressed in terms of iodine equivalent to the maleic anhydride used by one gram of the sample, is calculated by using the following equation:

Diene value $= 6.346 \frac{b - a}{w}$, in which a = cc. of $0.5N$ sodium hydroxide used in the titration, b = cc. of solution used in the titration of the blank experiments, and w = weight of sample taken.

Comments. The method is applicable to the determination of the diene value for use in calculating the quantity of elaeostearic acid in tung or similar oil.

To obtain satisfactory results, the directions, as given, must be followed. The method is applicable only to freshly expressed or extracted oils, when the diene value is to be used in connection with the calculation of the quantity of elaeostearic acid in the oil. It should be noted that hydroxyl groups, peroxides, and some other oxidation products, react with maleic anhydride [*cf.* Bickford, Dollear, and Markley, *Oil and Soap,* **15, 256** (1938)].

Volatile Fatty Acids. The volatile fatty acids include those which can be separated from the saponified fat or oil by distillation with steam. With the exception of butter fat, coconut, palm kernel and a few other oils, the rest of these products yield but little volatile fatty acids. It should be understood that the impossibility of removing all the volatile acids from the non-volatile acids has prevented the formulation of a method whereby a sharp but quantitative separation can be accomplished. Consequently the analyst must content himself with approximate methods which, when conducted under uniform conditions, will give comparable results. The volatile acids, depending upon the composition of the fat or oil, consist chiefly of those in the series from butyric to lauric acids. Butter fat yields butyric along with other volatile acids, but coconut and the various palm kernel oils do not contain this acid. The volatile acids are divided into two groups, depending upon their solubility or insolubility in water. The soluble acids are best determined by the Reichert-Meissl and the insoluble acids by the Polenske methods. The Reichert-Meissl value is defined as the number of cubic centimeters of $0.1N$ potassium hydroxide solution required to neutralize the soluble volatile fatty acids from five grams of the sample. The Polenske number is defined as the number of cubic centimeters of the $0.1N$ potash solution required to neutralize the insoluble fatty acids from five grams of the sample. The directions for both determinations, using a single portion of the sample, are as follows:

Reagents

Glycerin Sodium Hydroxide Solution. Add 20 cc. of a 1 : 1 sodium hydroxide solution to 180 cc. of pure glycerin.

Dilute Sulfuric Acid Solution. Dilute 200 cc. of sulfuric acid to 1000 cc. with water.

Pumice Stone. Use powdered pumice which has been strongly ignited.

Standard Alkali. Prepare accurately a $0.1N$ solution of potassium hydroxide.

Indicator. A 1 per cent alcoholic solution of phenolphthalein.

Determination. Weigh accurately 5 grams of the sample into a clean, dry flask of about 300 cc. capacity. (Fig. 1). Add 20 cc. of the glycerin sodium hydroxide solution. Heat over an asbestos-covered wire

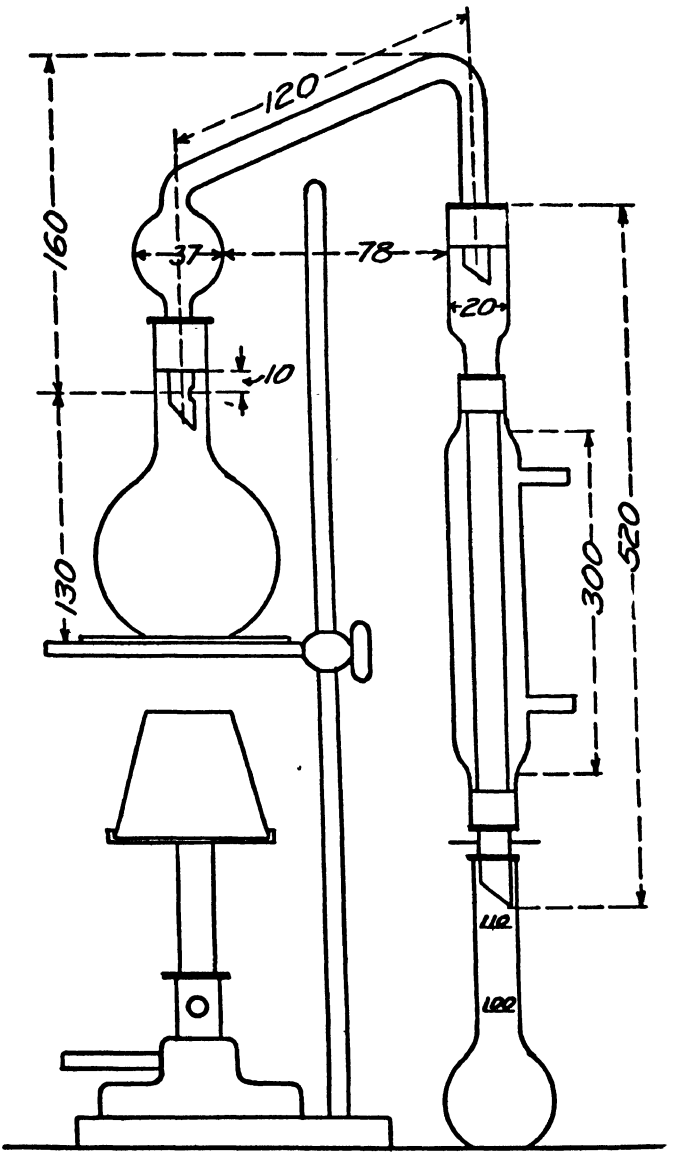


FIG. 1.—Apparatus for Reichert-Meissl and Polenske Determinations.

gauze until complete saponification takes place, as shown by clarification of the mixture. Shake the mixture by rotating the flask if undue foaming occurs. Add carefully 130 cc. of recently boiled water, then 10 cc.

of the dilute sulfuric acid and about 1 gram of the powdered pumice stone. Distill without previously melting the separated fatty acids, using apparatus of the dimensions given in the figure. The 300-cc. dis-

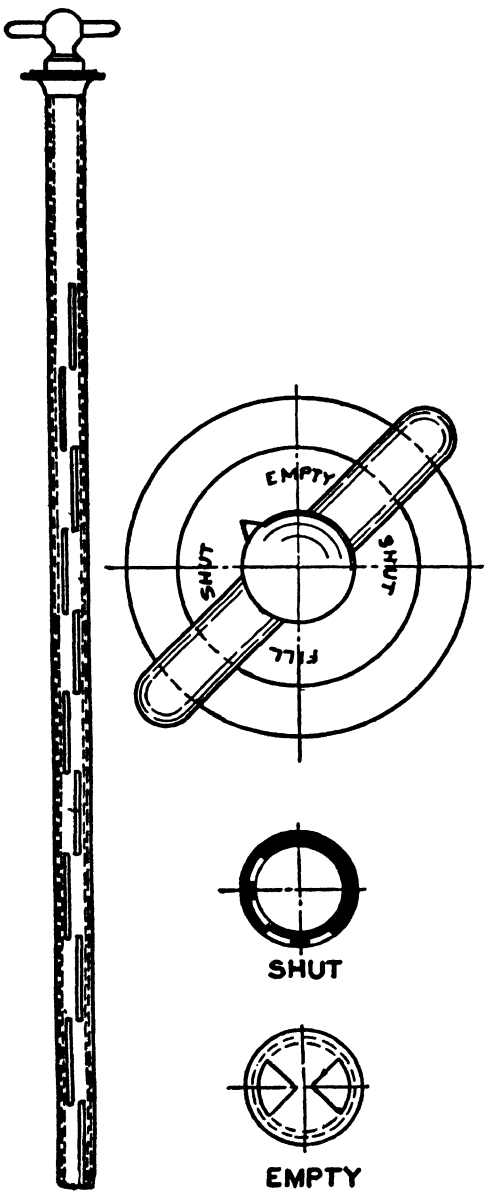


FIG. 2.—Sampling Tube.

tilling flask should rest on a piece of stout asbestos board provided with a 5-cm. hole in the center. The flame should be regulated so as to collect 110 cc. of the distillate in as near thirty minutes as possible, and the

distillate must come over at a temperature not higher than 18° or 20° C. When a 110 cc. of the distillate has been collected, remove the flame and substitute for the receiving flask a 25-cc. cylinder to catch any drops of the distillate that may fall later. Mix the contents of the flask containing the disillate and immerse the flask almost completely in water at 15° C. for fifteen minutes. Filter the distillate through a dry 9-cm. filter paper. Titrate 100 cc. of the filtrate with the 0.1*N* potassium hydroxide solution, using six drops of the phenolphthalein solution as indicator. The pink color should persist for two minutes. Make a blank determination, using the same proportions of reagents as directed above. After correcting for the blank determination, the Reichert-Meissl value equals the number of cubic centimeters of 0.1*N* potassium hydroxide solution times 1.1.

Remove the remainder of the soluble acids from the insoluble acids upon the filter paper by washing with three successive 15-cc. portions of water, previously passed through the condenser, the 110-cc. receiving flask and the 25-cc. cylinder. Dissolve the insoluble acids by passing three successive 15-cc. portions of neutral 95 per cent alcohol through the filter, each portion having been previously passed through the condenser, the 25-cc. cylinder, and the 110-cc. receiving flask. Titrate the combined alcoholic washings with the 0.1*N* potassium hydroxide solution in the same manner as directed for the titration of the soluble acids. The Polenske number is the number of cubic centimeters of 0.1*N* potash solution required to neutralize the insoluble volatile acids obtained from five grams of the sample. All determinations should be made in duplicate. Unless every detail is followed exactly as directed, satisfactory results cannot be obtained.

Acetyl and Hydroxyl Values. Hydroxy acids and alcohols, when heated with acetic anhydride, undergo a change which consists in the substitution of the acetyl radical for the hydroxyl. The acetyl value may be defined as the number of milligrams of potassium hydroxide required for the neutralization of the acetic acid obtained by the saponification of one gram of the acetylated product. The only commercial oil which has a high acetyl value is castor oil, which gives values from about 142 to 150. The figures for other common fats and oils range from 2.5 to 20. It should be noted that old oils frequently contain more or less diglycerides which, having a hydroxyl group, will react with acetic anhydride and give an abnormally high acetyl value. For example, a five-year-old sample of cottonseed oil was examined which gave an acetyl value of 34.6, while another sample of the same age, containing but little free fatty acids, gave a value of 10.7. The difference between the acetyl value of the sample and that of the mixed methyl esters prepared from it corresponds to the quantity of diglyceride (and monoglyceride, if present), according to Grün [*Öl Fett ind.*, **1**, 339 and 364 (1919)].

Although quite a number of methods have been proposed for the determination of acetyl value, only the well-known André-Cook procedure will be described.

Determination. Boil 30 cc. of the sample with an equal volume of

pure acetic anhydride under a reflux condenser for two hours. Pour the mixture into 500 cc. of water in an 800-cc. beaker and boil gently for fifteen minutes while bubbling a stream of carbon dioxide through the solution to prevent bumping. Siphon the water off as much as possible. Repeat the boiling with water twice more. Transfer the acetylated oil to a 500-cc. pear-shaped separatory funnel and wash with two 200-cc. portions of slightly warm water. Separate as much of the water as possible, then add five grams of anhydrous sodium sulfate and shake thoroughly. After standing half an hour, filter through a folded filter in an oven heated to about 105° C.

Determine the saponification value in duplicate of both the original sample and the acetylated portion as described under saponification value. Calculate the acetyl value, using the following formula:

$$A = \frac{S' - S}{1 - 0.00075S'}$$

A = Acetyl value; S is the saponification of the sample; S' is the saponification value of the acetylated product.

The hydroxyl value (H), which is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of the sample, can be calculated by the following formula:

$$H = \frac{S - S}{1 - 0.00075S'}$$

The acetyl value can be calculated from the hydroxyl value as follows:

$$A = \frac{H}{1 + 0.00075H}$$

Comments. In order to obtain satisfactory results, it is necessary to follow the directions exactly as given in every detail. Duplicate saponification values of the sample or acetylated product should not differ by more than 0.5; otherwise they should be repeated.

Attention is called to the following references:
"Determination of the Hydroxyl Number," W. Normann and E. Schildknecht, *Fettchem. Umschau.*, **40**, 194 (1933); *Oil and Soap*, 11, 36 (1934).
"Determination of the Acetyl Number of Fats," K. Täufel, *et al.*, *Chem. Umschau.*, **42**, 141 (1935); *Chem. Abs.*, **30**, 887 (1936).
"Hydroxylated Acids of Fats: An Improved Method of Determination," P. G. Hafner, R. H. Swinney and E. S. West, *J. Biol. Chem.*, **116**, 691 (1936).
"Acetyl Value of Triglycerides," F. Hawke, *J. South African Chem. Inst.*, **21**, 88 (1938); *Brit. Chem. Abs.*, **B1939**, 170.

Separation of Saturated and Unsaturated Acids. Several methods have been proposed for the separation of saturated from unsaturated acids. These are based upon the insolubility of the barium, magnesium, lead, and thallium salts of the saturated acids in alcohol, ether, or other solvent. The separation is not complete with any of these methods, and this is due in some cases to the solubility of the salts of the saturated acids

as well as the insolubility of some of the salts of the unsaturated acids. The lead salt ether, which will be described, gives good results when made according to these directions.

The Lead-Salt Ether Method. Reference: Baughman and Jamieson, [*Cotton Oil Press,* **6,** No. 1, 41 (1922)].

Reagents. Prepare 1000 cc. of a 20 per cent solution of lead acetate.

Potassium Hydroxide Solution. (a) Dissolve 50 grams of potash in 50 cc. of water; (b) dissolve 30 grams in 200 cc. of water.

Acetic Acid. Dissolve 25 cc. of glacial acetic acid in 50 cc. of water.

Alcohol. 95 per cent.

Ether. U. S. P. grade.

Determination. Weigh accurately 10 (or 20) grams of the sample into a 200-cc. Erlenmeyer flask. Add 30 cc. of alcohol and 8 cc. of the concentrated potassium hydroxide solution. Mix thoroughly and heat on the steam bath for about 30 minutes. Add a slight excess of acetic acid, using phenolphthalein as an indicator, and dilute potassium hydroxide solution, while rotating the contents of the flask, until a distinct pink color is obtained. Heat a mixture of 60 cc. (120 cc. for 20-gram sample) of lead acetate solution and 60 cc. of water to boiling in a liter flask. Add the neutralized soap solution cautiously to avoid any loss, rinsing the saponification flask with 5 cc. of alcohol, then with small volumes of hot water. Boil the mixture gently for about five minutes, shake thoroughly and cool under running water, rotating the flask so as to cause all the precipitated lead soaps to adhere to the sides and bottom of the flask. When cold, pour off the aqueous solution, taking precautions to lose none of the lead soap (always pour into a large beaker so that the solution can be examined for particles of lead soap). Usually, the solution is slightly turbid, due to some basic lead acetate, and no particles or globules of lead soap are to be seen. Wash the flask and lead soap twice with cold water and allow the flask to drain for ten minutes. Remove the last drops of water by means of a thin roll of filter paper held by forceps, being careful only to press lightly against the precipitate. Add about 120 cc. of ether and shake by rotating the flask for about 5 minutes. Connect the flask with a reflux condenser and gently boil until the lead soap is completely disintegrated (or dissolved). Remove the flask and rinse down the sides of the flask with sufficient ether to make the final volume about 150 cc. Invert a close-fitting beaker over the neck of the flask and place it in an ice-box for at least fifteen hours. Place a 7-cm. ordinary filter paper in a 7.5-cm. diameter Büchner funnel, turn on full suction and then fit in a hardened filter paper cut to 8 cm. in diameter, as snugly as possible. Decant the ether solution from the separated lead soaps, using only sufficient suction to draw the ether through the filter. Too much suction causes the ether to evaporate so rapidly that the filter may become clogged with the separated unsaturated acid lead soaps or ice. Transfer the precipitate to the filter, by rinsing the flask with small portions of ether. Keep the funnel covered as much of the time during filtration as possible to prevent the evaporation of the ether. If at any time filtration proceeds so fast as to cause

the mass of lead soap to crack, the cracks should be closed by pressing with a small spoon or spatula; otherwise the precipitate cannot be properly washed. Then rinse the spoon free from precipitate with ether. Wash the precipitate from 8 to 10 times with ether, finally allowing the suction to continue until the precipitate cracks in numerous pieces. Without delay, separate as much as possible of the precipitate with a spoon and transfer it without loss to a 500-cc. separatory funnel containing about 50 cc. of ether. Wash off any precipitate adhering to the spoon and neck of the separatory funnel with ether. Transfer the filter paper to the liter flask. Shake the contents of the separatory funnel thoroughly to disintegrate the lumps of lead salt and let stand for about 20 minutes. Add 20 cc. of hydrochloric acid previously diluted with 10 cc. of water and shake thoroughly for 2 minutes to decompose all of the lead soap. Add a few cc. of hydrochloric acid and water to the liter flask containing the filter paper, shake thoroughly to decompose any precipitate adhering to the flask and filter, then wash into the separatory funnel with small alternate portions of ether and water until all the fatty acids and lead chloride are removed from the flask. Again shake the contents of the separatory funnel with a rotary motion and allow to stand for 10 minutes. Withdraw the lower aqueous solution slowly, taking precautions not to remove any emulsion or undecomposed lead soap. Lead soap, if present, will be in the form of lumps which float on top of the aqueous solution. When it is present, add a few cubic centimeters of hydrochloric acid and shake again, then add about 20 cc. of water, shake, and let stand until the layers have separated. Withdraw the aqueous solution. Wash the ether with successive 25-cc. portions of water until the washings are free from hydrochloric acid. Dehydrate the ether with about 2 grams of anhydrous sodium sulfate. Transfer the ether solution to a weighed 300-cc. Erlenmeyer flask. Rinse the separatory funnel and sodium sulfate with several small portions of ether to remove all the fatty acids. Care should be taken not to allow any of the sodium sulfate to fall into the weighed flask. Distill the ether so as not to lose any of the fatty acids, and heat in an oven warmed to about 110° C. until the weight is constant. Obtain the weight of the saturated acids and save them for later investigation.

Transfer the ether solution of the soluble lead soaps to a 500-cc. or a 1000-cc. separatory funnel, rinsing the Büchner filter flask with small quantities of ether. Add a mixture of 30 cc. of hydrochloric acid and 75 cc. of water and shake with a rotary motion for two minutes. After standing for 10 minutes, slowly withdraw the aqueous solution into a beaker. Often drops of the ether solution are entrapped by the lead chloride precipitate and are removed with it. The entrained ether will rise to the surface of the solution in the beaker. In this case, decant the solution from the precipitated lead chloride which has settled, into the separatory funnel. Rinse the beaker and precipitate with small quantities of ether, adding the washings to the separatory funnel. Rotate the contents of the separatory funnel and let stand for 10 minutes. Withdraw the aqueous solution and wash the ether with successive 50-cc.

portions of water until the hydrochloric acid is removed. Transfer the ether solution to a 300-cc. weighed Erlenmeyer flask. Distill the ether, then place flask in an oven heated to about 110° C. for about one hour, while passing a stream of carbon dioxide into the flask to prevent oxidation of the unsaturated acids. Cool in an atmosphere of carbon dioxide. When cold, remove the carbon dioxide and weigh. Repeat this treatment until a constant weight is obtained.

Determine in duplicate the iodine numbers of both the saturated and unsaturated fractions. In all cases in which this method is applicable (see comments), the iodine number of the saturated acid fraction is due chiefly to oleic acid.

The correction for the unsaturated acid present in the saturated acid fraction is calculated as follows:

$$\frac{\text{Iod. No. of Sat. Acid Fraction}}{\text{Iod. No. of Oleic Acid}} \times 100 = A \text{ (percentage of unsaturated acid in saturated acid fraction)}$$

The proper correction is then obtained by means of the formula $\frac{A \times B}{100}$, in which B is the percentage of the impure saturated acids (as found by analysis). This correction is subtracted from the percentage of impure saturated acids and added to the percentage of unsaturated acids actually determined.

When the technique of the lead salt-ether method is mastered and the directions are followed in every detail, duplicate analysis will give closely agreeing results.

Comments. The lead salt-ether method does not give satisfactory results when applied to butter fat, coconut, and palm kernel oils, because they contain saturated acids (below myristic acid in this series), the lead salts of which are so soluble in ether that a considerable proportion of them remain with the lead salts of the unsaturated acids. When an oil contains myristic acid, some of it remains with the unsaturated fraction, because of the slight solubility of the lead salt in cold ether. Sometimes very small percentages of palmitic acid are found also in this fraction (by means of fractional distillation of the esterified unsaturated acid fraction). Also, it should be noted that this method cannot be used with those oils which contain unsaturated acids giving lead salts that are sparingly soluble in ether, such as elaeostearic (tung oil), erucic (rape and mustard oils), chaulmoogric, hydnocarpic, and iso-oleic acids (hydrogenated products). Chaulmoogric and hydnocarpic acids are only found in chaulmoogric, hydnocarpic and a small group of related oils. With the exception of these, the other oils give a saturated acid fraction which should not have an iodine number above 12 and in most cases not above 6 or 7.

The unsaponifiable constituents which, with a few exceptions, amount to a per cent or less of the oil, remain with the unsaturated acids, but when they exceed 2 per cent some is usually found in the saturated acid

fraction. In such cases, corrections should be made for the quantities found in the saturated and unsaturated acids.

The Hexabromide Value. When fats and oils are dissolved in chloroform, ether, or other solvent and are treated with bromine, the bromine addition compounds of the unsaturated acids are formed. Oleic acid gives a dibromide; linoleic acid, a tetrabromide; linolenic acid, a hexabromide, and the highly unsaturated acids of fish oils yield octobromides. The dibromides and tetrabromides are soluble in ether, while the hexa- and octobromides referred to are almost insoluble in cold ether. In the case of vegetable oils, only linolenic hexabromide is precipitated from an ether solution. If the oil is brominated, the brominated glyceride or glycerides are obtained, but if the separated mixed fatty acids are similarly treated the brominated linolenic acid is obtained. In mixtures containing fish oils, the hexabromide and octobromide are precipitated together. In this case, the hexabromide can be extracted from the octobromide by means of boiling benzene.

Formerly, it was customary in the examination of drying oils to precipitate and deterimne the quantity of ether-insoluble brominated glycerides. As drying oils contain varying quantities of mixed glycerides which contain one or two linolenic acid groupings, naturally the results obtained under the best conditions are subject to wide variations as compared with those obtained by the precipitation of linolenic hexabromide from the mixed fatty acids of the sample under examination. The method to be described gives the percentage of the linolenic acid hexabromide that can be precipitated from an ether solution. It should be observed that all the vegetable drying oils, with the exception of tung (Chinese wood) oil, containing varying quantities of isomeric linolenic acids, the hexabromides of which, being soluble in ether, are not precipitated with the so-called *alpha* linolenic acid. The range of hexabromide values, as determined by modern methods on the mixed fatty acids, for pure linseed oil from different sources is usually from about 45 to 52 per cent.

Reagents. Method of Steele and Washburn, *Ind. Eng. Chem.*, **12**, 52 (1920).

Chloroform. Wash 500 cc. of chloroform in a separatory funnel with two 100-cc. portions of water, then dry it with anhydrous calcium chloride or sodium sulfate for 12 hours or longer. Decant from dehydrating reagent and distill. To each 100 cc. of distillate, add 3 cc. of absolute alcohol. Keep reagent in the dark, preferably in a dark blue bottle.

Bromine Solution. Mix one part by volume of bromine with two parts by volume of the prepared chloroform. Make this solution fresh each day. Care must be taken not to use bromine which contains nonvolatile impurities. If 5 grams of bromine leave a weighable residue, it will be necessary to purify it by distillation.

Amylene (C_5H_{10}). This may be purchased or made by the method of Adams [*J. Am. Chem. Soc.*, **40**, 1950 (1918)]. As this reagent is very volatile, it should be kept in a glass-stoppered bottle in an ice-box; cork stoppers are not satisfactory, as they are gradually decomposed.

Wash Ether. Shake 1 or 2 liters of ether with 10 per cent of its volume with ice-cold distilled water. Separate the water and repeat the washing 3 times. Dry the washed ether with fused calcium chloride for a day. Decant the ether through a folded filter into another flask. Add several grams of thinly sliced sodium and warm gently on a steam or water bath, using a long reflux condenser, until the evolution of hydrogen has practically ceased and freshly cut sodium remains bright in the ether. Distill the ether directly into a perfectly dried bottle. A tube of suitable diameter should be attached to the condenser, so that it extends several inches into the bottle; add 3 grams of finely powdered hexabromide for each 1000 cc. of distilled ether. Shake at intervals for 2 or 3 hours, or allow the mixture to stand for about 18 hours. Then place the bottle in an ice-water bath for 3 hours. The temperature of the ether solution should not be above 2° C. Decant the ether rapidly through a sizable folded filter into a dry bottle of suitable size and keep tightly stoppered to prevent evaporation.

Preparation of Hexabromide for Ether Reagent. Dissolve 5 grams of linseed oil fatty acids in 20 cc. of chloroform and place mixture in a centrifuge tube. Place this tube in a freezing mixture and add slowly with frequent shaking bromine until a slight reddish color remains permanent. Add a few drops of amylene to remove the excess of bromine. Whirl in the centrifuge until the precipitate has settled, then pour off the chloroform. Mix the precipitate with 20 cc. of cold absolute ether, using a rod or spatula to disintegrate the lumps thoroughly. Centrifuge and decant as before. Repeat this treatment three times more. After drying, the hexabromide is powdered and preserved for the preparation of the ether reagent.

Preparation of Fatty Acids. Place about 50 grams of linseed or other oil to be tested in a 1500-cc. Erlenmeyer flask. Add 40 cc. of a 36 per cent (sp. g. 1.4) solution of sodium hydroxide and 40 cc. of 95 per cent alcohol. Heat the mixture for 30 minutes on a steam bath, add 1000 cc. of hot water and insert a 2-hole rubber stopper, carrying a glass tube which extends nearly to the surface of the solution. Pass a stream of carbon dioxide through the tube and heat until the alcohol has been removed. Cool and acidify the solution with 1 : 1 hydrochloric acid. Insert a 3-hole stopper, provided with 2 glass tubes arranged as for a wash bottle, leaving the third hole in the stopper for the escape of the carbon dioxide. The inlet tube should extend to just above the layer of fatty acids and the outlet tube should reach to the bottom of the flask. The upper portion of the outlet tube should not extend downward more than two inches outside of the flask, to prevent siphoning. Pass carbon dioxide into the flask and boil gently until the layer of fatty acids is clear. To facilitate the boiling, some capillary tubes may be used. Remove as much water as possible without losing any of the fatty acids, by closing the hole in the stopper used as a vent for the escape of carbon dioxide. The pressure will force the aqueous solution through the outlet tube. Add 500 cc. of hot water to flask and shake to wash the fatty acids. Allow the fatty acids to separate, then remove the water as before.

Repeat the washing until the wash water gives no reaction to methyl orange. Before removing the last wash water, heat until the fatty acid layer is clear. After removing as much water as possible by the outlet tube, the stopper and tubes are removed, and the remaining water is removed with a pipette. Filter the hot fatty acids through a folded filter into a dry bottle placed in an oven heated to about 50° C., in an atmosphere of carbon dioxide to prevent oxidation of the unsaturated acids. If the acids are to be kept more than a day, the air space in the bottle should be filled with carbon dioxide and the sample should be placed in an ice-box.

Method. Weigh accurately 1 gram of the fatty acids into a weighed centrifuge tube which is approximately 6.5 inches long and one inch in diameter. Dissolve the fatty acids in 10 cc. of the chloroform reagent and place the tube in a freezing mixture of finely crushed ice and hydrochloric acid so as to reduce the temperature to about −5° C. Add the bromine solution from a burette under a hood, at the rate of two drops per second while shaking the tube, until the mixture has a permanent orange color. Then add 0.5 cc. more of bromine solution rapidly, shake thoroughly, and allow the tube to remain for 10 minutes more in the ice bath. Remove the tube and add amylene drop by drop with shaking until the bromine color has disappeared. Attach the tube to a source of vacuum, maintaining a pressure not lower than 40 mm. and evaporate the chloroform carefully by placing the tube in a water bath heated from 50° to 60° C. The tube must be constantly shaken to prevent bumping of the mixture. Toward the end of the evaporation, when the contents of the tube become more viscous, rotate and tilt the tube so that the oil will flow about half way up the sides and thus present more surface for the evaporation. When practically all the chloroform has evaporated, place the evacuated tube in a water bath heated to about 60° C. for 15 minutes. It is very important to remove all of the chloroform before proceeding with the next step. Place 20-cc. portions of the prepared wash ether into 4 dry test tubes, stopper and cool to zero in an ice bath. Detach the tube from the source of vacuum and place it in a bath of finely cracked ice and water. When the tube is thoroughly cooled, pour down the sides 20 cc. of the cold ether from one of the test tubes. Thoroughly stir the bromide mixture with a weighed glass rod, breaking all the lumps. Return the tube to the ice bath for two minutes, then whirl in the centrifuge until the precipitate has settled into a hard cake and the supernatant liquor is clear. Return the tube to the ice bath for 2 minutes, then pour off the ether, avoiding any loss of precipitate. Repeat the washing of the hexabromide precipitate three times in exactly the same manner as described, using 20 cc. of ether and rubbing the precipitate thoroughly each time with the weighed rod. Dry and weigh the stirring rod to get the weight of any adhering precipitate. After the fourth washing and the decantation of the ether, carefully incline the tube and tap it gently so as to spread the precipitate part way up the tube. Then warm the tube until most of the ether has evaporated by placing it in a water bath heated to 50° to 60° C. Attach the suction and heat for 15 minutes at

70° C. Detach, wipe off the tube and dry to constant weight in an oven heated to about 110° C. The hexabromide should be pure white. Add the weight of bromide adhering to the stirring rod to that of the precipitate in the tube. The total weight of the precipitate times 100, divided by the weight of the fatty acids taken, gives the percentage of hexabromide which is the hexabromide value.

Comments. Unless the directions are followed in every detail as described, satisfactory results cannot be obtained. When this method is applied to oils, for example, such as soybean oil, which contain but little linolenic acid, it is best to cool the chloroform solution, after the addition of bromine for 2 or 3 hours instead of 10 minutes as directed by Steele and Washburn. If there is any question in regard to the purity of the oil, the melting point of the hexabromide should be taken. The melting point should not be lower than 177° C. and not higher than 181° C. Octobromides do not melt, but char when heated. "The Hexabromide Test for Determining the Purity of Linseed Oil," by H. A. Gardner (*Am. Pt. and Var. Mfs. Assoc. Circ.* **99**, 1920) contains considerable analytical data.

Detection of Fish Oils. The following method has been proposed by Eisenchiml and Copthorne [*Ind. Eng. Chem.*, **2**, 28 (1910)]: Dissolve 100 drops of the sample in a test tube in 6 cc. of a mixture of equal volumes of chloroform and glacial acetic acid. Add bromine from a small burette drop by drop, until a slight excess is shown by the color of the chloroform solution. Allow the mixture to stand for 10 minutes, then place the test tube in a beaker containing boiling water. The linseed or other vegetable drying oil hexabromides dissolve rapidly, but the bromides from fish oils, depending upon the quantity present, give a sandy precipitate or a cloudy appearance to the solution. It is stated that fish oils which have been heated for some time to 260° C. or higher do not give the test. The method has been found very useful in testing linseed oils of doubtful purity. It is capable of detecting the presence of as little as five per cent of fish oil.

Test for Boiled Oil. *Reagent:* Dissolve 1 cc. of freshly distilled aniline in 10 cc. of carbon tetrachloride in a flask and add a few drops of bromine previously dissolved in several volumes of carbon tetrachloride. Then add aniline cautiously, while shaking the solution until the precipitated bromide dissolves. To 5 cc. of the oil to be tested, add a few drops of the reagent and shake. A deep brown color indicates a boiled oil. No color is given by raw oil.

Determination of Ash. Weigh a thin 50-cc. porcelain dish. Add about 15 cc. of the oil to be tested and carefully weigh the amount. Place the dish on a stone slab or on the floor of the hood. Ignite by playing the flame of a burner on the surface of the oil and allow it to burn quietly until most of the oil is burned, then transfer the dish to a muffle or over a flame and continue heating at a low temperature, but not over a dull red heat, until all the carbonaceous matter is burned. Cool, weigh and calculate the percentage of ash.

The test is made particularly in connection with the examination of

drying oils suspected of containing driers. For example, boiled linseed oil of good quality may contain up to 0.05 per cent of ash. Oils free from driers give very little ash.

When desired, the ash may be dissolved in dilute nitric acid to which a little hydrogen peroxide has been added; then the lead, if present, may be determined by any accurate method.

Tests for Rosin and Mineral Oils. Rosin and mineral oils increase the quantity of unsaponifiable matter over that normally present. When appreciable quantities of rosin oil are present, the flash point of the mixture will be lower than that of vegetable oils. The flash point of rosin oil ranges from about 155° to 160° C. The flash point of linseed oil, for example, is approximately 240° C.

Liebermann-Storch Test. Place 2 cc. of the oil to be tested and 2 cc. of acetic anhydride in a test tube. Shake thoroughly for a half minute and allow the mixture to stand until the layers have separated. Remove a portion of the lower acetic anhydride layer with a glass tube and place a few drops on a white porcelain surface. Add one drop of sulfuric acid (10 cc. of acid sp. g. 1.84 and 12 cc. of water) so that it will mix slowly. Rosin or rosin oil gives a characteristic fugitive violet color. Old samples of boiled oil sometimes give a color similar to that given by rosin. In such cases, shake the oil with an equal volume of alcohol. Let the mixture stand until the alcohol separates. Remove 5 cc. of the alcohol to a porcelain crucible and evaporate the alcohol. Add a few drops of acetic anhydride and mix thoroughly by rotating the crucible, then add a drop of the sulfuric acid. In the presence of rosin or rosin oil, a fugitive violet color is produced. It should be observed that sterols and terpenes also give blue, green, or violet colorations with these reagents. Some fish oils give a color similar to that given by rosin, but their presence can be detected by the method already given. According to H. Wolf [*Chem. Umschau* **34**, 17 (1927)], some pure linseed oils give the rosin test.

Holde's rapid test for rosin and mineral oil is as follows: Dissolve a piece of sodium hydroxide, the size of a pea, in a large test tube or a 100-cc. Erlenmeyer flask in a few drops of water and add 15 cc. of absolute alcohol. To this solution, add 10 drops of the sample to be tested, and boil vigorously for two minutes, being certain that no unreacted oil remains on the sides of the tube or flask. Then add 50 cc. of hot water. A slight turbidity indicates the presence of rosin or mineral oil. As little as 0.5 per cent of these impurities can be detected by this test.

Detection of Rape Oil. The following method is based on that of Tortelli and Fortini [*Chem. Zeit.*, **34**, 689 (1910)]. Also see "Olive Oil," Chapter II, for other tests.

Reagents. Ten per cent solutions of acetic acid and lead acetate, and a saturated solution of sodium carbonate.

Alcoholic Potash. 60 grams of potassium hydroxide dissolved in 500 cc. of 90 per cent alcohol (by volume).

Method. To 20 grams of the sample to be tested in a 250-cc. flask add 50 cc. of the alcoholic potash solution and boil gently for 30 minutes using a reflux condenser. Neutralize to phenolphthalein with the dilute acetic acid solution. Heat a mixture of 200 cc. of lead acetate solution and 100 cc. of water in a 500-cc. Erlenmeyer flask to boiling. Add the saponified solution of the sample. After shaking with a rotary motion, cool the mixture under running water while turning the flask so as to collect the precipitated lead soaps on the sides. When cold, decant the solution and wash the flask and precipitate with three 200-cc. portions of warm water. Finally, allow the flask to drain for a few minutes. Then remove the remainder of the water with a roll of filter paper. Add 80–90 cc. of ether and shake thoroughly for several minutes. Connect this flask to a reflux condenser and boil the ether gently for 30 minutes to disintegrate the precipitate. Remove the flask from the condenser, invert a small beaker over the neck, and place flask in a water bath at 15° for one hour. Filter the insoluble lead soaps on a small Büchner funnel, using very gentle suction. Return the precipitate to the flask and repeat treatment with ether as previously directed. Filter and wash the precipitate using about 40 cc. of ether. Combine the ether solutions and transfer them to a 500-cc. separatory funnel. Add 100 cc. of about a 20 per cent solution of hydrochloric acid, shake thoroughly, and allow the layers to separate. Then withdraw the lower aqueous layer. If undecomposed lead salt remains suspended in the lower part of the ether, repeat the treatment with acid. Wash the ether with three 100-cc. portions of water. Dehydrate the ether solution with about 2 grams of anhydrous sodium sulfate. Transfer the ether to an Erlenmeyer flask and distill. Dissolve the residue in 40 cc. of 95 per cent alcohol and add, while shaking, a saturated solution of sodium carbonate until the sodium carbonate begins to precipitate. Distill the alcohol, and after distributing the residue around the sides of the flask, dry in an oven heated to 110° C. for about 4 hours, and finally in a vacuum desiccator for at least about 12 hours. Boil the dried residue with 50-cc. portions of absolute alcohol and filter after each treatment, using a hot water funnel until the soluble soaps are extracted. Combine the alcoholic filtrates, distill the alcohol, and dry the residue as directed above. Place 0.5 gram of the dried residue in a large test tube and dissolve by warming it with 20 cc. of absolute alcohol. Suspend a thermometer in the solution and note the temperature when it becomes turbid.

The following results are given by Tortelli and Fortini.

Oil	Turbidity Temperature ° C.
Olive	20-24
Equal vols. of olive and rape	35-40
80% of olive and 20% of rape	30-35
90% of olive and 10% of rape	30-34
Cottonseed	14-16
Sesame	18-20
Peanut	18-22

Modified Bertram Method for the Determination of Saturated Acids. This method may be used for the determination of saturated acids in oils, fats or fatty acids except those of *Palmae* and *Umbelliferae*. It appears in many cases that the results obtained are slightly high, due to the presence of a small quantity of hydroxy-acids in the saturated acids as weighed.

The method as described by S. H. Bertram is given in *Z. Untersuch. Lebensm.*, **55**, 179 (1928).

Method. Accurately weigh 5 grams of the sample and proceed as described under the determination of unsaponifiable matter, saving the alkali-alcoholic soap solution for the determination of the saturated acids in the following manner: Transfer the soap solution to a casserole and heat on a steam bath until most of the alcohol is removed. Then heat carefully over a flame until the remainder of the alcohol is volatilized. After cooling somewhat, add about 300 cc. of water and heat until the soaps have dissolved, transfer to a two-liter flask, rinse the casserole several times with hot water, and add the rinsings to the flask. Be certain that all the soap is completely dissolved before proceeding with the method. Cool the solution to room temperature (not above 25° C.) and add a solution made by dissolving 35 grams of potassium permanganate in 750 cc. of water. After standing 12 to 18 hours with an occasional shaking, the solution must still show an excess of permanganate. If the solution is not violet-colored, a further addition of permanganate solution must be made, in which case it is necessary to allow the oxidation reaction to proceed for 12 hours more. Distinctly acidify the solution with 1:2 sulfuric acid and add sufficient powdered sodium bisulfite to decolorize the solution and dissolve the precipitated manganese oxides when the solution is heated. Continue the heating on a steam bath until the fatty acids have entirely separated from the aqueous solution. Cool and transfer to a separatory funnel of suitable size. Extract three or four times, using 200- to 250-cc. portions of petroleum ether. Combine the petroleum ether extracts in a separatory funnel and wash them with three 100-cc. portions of water. Transfer to a flask and distill off the solvent as completely as possible, then remove the remainder by heating in an oven at 110° C. for an hour. Treat the residue with 200 cc. of hot water and an excess of ammonium hydroxide. Heat until the residue is dissolved, add 30 cc. of a 10 per cent ammonium chloride solution and an excess of a 15 per cent solution of magnesium sulfate. After cooling, filter off the precipitate and wash thoroughly with water. Transfer the precipitate to the flask with water and decompose the magnesium soaps by heating with slight excess of dilute sulfuric acid; then repeat the precipitation of the magnesium soaps, by the addition of ammonium chloride and hydroxide. Filter, wash, and return the precipitate to the original flask and completely decompose it as before by heating with dilute sulfuric acid. Cool, transfer to a separatory funnel and extract the fatty acids, using three 200-cc. portions of petroleum ether. Combine the petroleum ether extracts and wash with two 50-cc. portions of water. Then transfer to a flask and distill the solvent until the volume is reduced to about

50 cc. Transfer to a weighed flask, distill off as much as possible of the solvent and heat the residue of saturated fatty acids in an oven at 110° C. until a constant weight is obtained. Calculate the percentage of saturated acids.

T. P. Hilditch and J. Priestman (*Analyst,* **1931,** 354) have recommended that the alkali-soap solution be heated to 35° C. before adding the potassium permanganate solution, but the temperature should not be permitted to rise above 50° C. For comments on this and other procedures for the determination of saturated acids, the original article should be consulted.

Comments. The method is not applicable to oils such as those from the seeds of the *Umbelliferae,* which contain petroselinic (6:7-oleic) acid which upon oxidation with permanganate may yield lauric and palmitic acids. When applied to coconut, palm kernel or myristica oils, very low results are obtained due to the loss of part of the lauric and the acids of lower molecular weight present in these oils. When properly conducted, the method is capable of giving duplicate results within ±0.5 per cent. The results obtained by this method have been compared with those by the lead-salt ether procedure in the case of several oils in which the latter method could be used, and it was found that the results by the Bertram method were 0.5 to 1 per cent higher. This was due in part to the presence of some hydroxy acids, as previously mentioned.

Determination of Solid Fatty Acids. The method to be described is a modification of the Twitchell lead-salt-alcohol procedure [*Ind. Eng. Chem.,* 13, 806 (1921)] by Baughman and Jamieson [*Oil and Fat Ind.,* 7, 331 (1930)], and is based on using the original sample instead of the insoluble fatty acids, which in many cases has been shown to be a decided advantage, and in particular, the analyses of hydrogenated oils. The method is as follows: Weigh into a 300-cc. Erlenmeyer flask a quantity of the sample that is estimated (if possible) to contain 1 to 1.5 grams of solid acids, but in no case a portion larger than 6 grams. Saponify with an excess of alcoholic potash (40 grams per liter) in the usual manner. Forty cc. are sufficient for 6 grams of fat. After saponification, add a few drops of phenolphthalein indicator solution, neutralize the excess of alkali with glacial acetic acid from a burette and add one drop in excess. Add sufficient 95 per cent alcohol to bring the volume to 150 cc. Dissolve 5 grams of lead acetate in 50 cc. of alcohol. Heat both solutions to boiling and pour the lead acetate solution into the soap solution. Allow this to cool slowly to room temperature and leave it overnight in a refrigerator approximately 15° C. Filter through an 11-cm. filter paper and wash flask and precipitate with cold 95 per cent alcohol until the washings, diluted with water, remain clear. Wash the precipitate completely from the filter through a wide-stem funnel into the flask, using about 100 cc. of alcohol. Add 0.5 cc. of glacial acetic acid and heat to boiling. The precipitate will gradually dissolve. Cool slowly to room temperature and allow the solution to stand overnight in the refrigerator. Filter and wash with alcohol as before. Transfer the precipitate from the filter and flask into a 500-cc. separatory funnel with

ethyl ether. Add 25 cc. of 1 : 1 hydrochloric acid to decompose the lead salts. Also decompose the small quantity of lead salt adhering to the flask with a small quantity of dilute acid and wash into the separatory funnel with ether. Rapidly rotate the solution to assist the decomposition of the lead salts. Withdraw the acid solution and wash the ether solution of the fatty acids with 50-cc. portions of water until the washings give no turbidity with silver nitrate solution. Dehydrate the ethereal solution with about 6 grams of anhydrous sodium sulfate. Pour the solution through a 7-cm. filter paper into a weighed 200-cc. Erlenmeyer flask. Wash the separatory funnel, sodium sulfate, and filter paper repeatedly with small quantities of ether to remove all of the fatty acids. Distill the ether so as not to lose any of the acids, and heat the residue in an oven at approximately 110° C. until the weight is constant. When hydrogenated products are being examined, the solid acids will contain iso-oleic acid, and in this case an atmosphere of carbon dioxide in the oven should be used. After each heating period, when the flask has reached room temperature, remove the carbon dioxide prior to weighing. Calculate the percentage of solid acids. When iso-oleic acid is present, the quantity can be calculated approximately from the iodine number of the solid acids.

The method devised by L. V. Cocks, B. C. Christian and G. Harding [*Analyst,* **56,** 368 (1931)] for the determination of solid acids is as follows: Dissolve 3.500 grams of freshly prepared fatty acids in a 300-cc. Erlenmeyer flask in 50 cc. of 92–3 per cent (by weight) alcohol. Heat the solution to about the boiling point and add 50 cc. of a hot alcoholic (92–3 per cent) solution containing 3.45 grams of lead acetate (use 1 gram in 50 cc. of alcohol in cases where solid acids amount to less than 25 per cent of the fatty acids). Heat the mixture to the boiling point, allow it to cool slowly, and to stand overnight in a place where the temperature is not below 15° nor above 20° C. Next day, stir the solution and transfer as much as possible of the crystalline lead salts to a carefully fitted filter paper in a 10-cm. Büchner funnel. After removing the alcohol from the precipitate and filtering, transfer the Büchner funnel to another suction flask. Wash the 300-cc. Erlenmeyer flask with five 20-cc. portions of petroleum ether (Dist. 40° to 60° C.), transferring each portion to the lead salts in the Büchner funnel with gentle suction. Set the funnel aside for later treatment of the lead salts. Distill the petroleum-ether filtrate, using a water bath. To the residue, add 20 cc. of the 92-3 per cent alcohol and 1 drop of glacial acetic acid from a pipette. Connect the flask with a reflux condenser and boil the solution until all the lead salt has dissolved. Allow the solution to stand for 3 hours at 15° to 20° C. Then filter the crystalline lead salts and wash them with 20 cc. of the cold 92–3 per cent alcohol. Transfer the lead salts and those set aside in the Büchner funnel to a 500-cc. separatory funnel containing 150 cc. of ethyl ether. Add 50 cc. of 1 : 3 nitric acid, rotate the solution, then shake it until all the lead salts are decomposed. Withdraw the aqueous solution and wash the ether 4 times, using 50-cc. portions of water. Dehydrate the ethereal solution with about 5 grams

of anhydrous sodium sulfate. From this point, finish the analysis as described under the other method. Determine the iodine number of the solid acids and use this for calculating the quantity of unsaturated acids on the basis that they have an iodine number of 90, unless unsaturated acids other than iso-oleic acids are present.

These investigators have found that this method gives distinctly more accurate results for the solid unsaturated acids than the original Twitchell procedure. They state that, in all but extreme cases not likely to be encountered in practice, the results obtainable by their method are within 3 units per cent of that actually present.

The Detection of Cholesterol and Phytosterols in Mixtures of Animal and Vegetable Fats by the Digitonin Method. Transfer 50 grams of the melted sample to a 200-cc. Erlenmeyer flask and add 20 cc. of a one per cent alcoholic solution of digitonin. Shake vigorously for 15 minutes, then allow the mixture to stand until the layers of alcohol and fat have separated. The lower fat layer should be quite clear, while the upper alcoholic solution contains a bulky flocculent precipitate of the digitonin-sterol compounds. Withdraw the fat as completely as possible, avoiding the loss of any of the precipitate. Add 100 cc. of ether to the alcoholic solution in the separatory funnel, mix gently, and filter on a plain filter paper (not folded). Wash filter and precipitate with ether until free from fat and allow the precipitate to stand until dry. Transfer the precipitate to a 50-cc. Erlenmeyer flask and add about 3 cc. of acetic anhydride. Insert a crucible cover over the neck of the flask and boil the contents gently for about 30 minutes while the flask rests on an asbestos-wire gauze; when cold, add 30 to 35 cc. of alcohol, 60 per cent by volume, and mix thoroughly. Filter, and wash the precipitate four or five times with the 60 per cent alcohol, then dissolve it on the filter with a fine stream from a wash bottle of hot alcohol, 80 per cent by volume. Place the filtrate in the ice-box for several hours, or in a water bath maintained at about 10° C. Collect the crystalline acetates upon a filter, wash with cold 80 per cent alcohol and then dissolve in a minimum quantity of hot absolute alcohol, receiving the filtrate in a small beaker. Add 2 drops of water and warm if not perfectly clear. Allow the alcohol to evaporate spontaneously, stirring the contents occasionally to mix the deposit of crystals that form upon the edges with the main body of the liquid. As soon as a good deposit of crystals has formed, filter them upon a hardened filter, wash twice with cold alcohol, 90 per cent by volume, and dry them at 100° C. for 30 minutes. Then determine the melting point. The melting point of cholesteryl acetate is 114° C. and that of phytosteryl acetate is usually from 125° C. to 138° C. The melting point of the first crop of crystals usually gives definite information as to the presence or absence of phytosterol, but the conclusion indicated should be confirmed by recrystallizing the crystals from absolute alcohol and again determining the melting point. If the crystals are pure cholesteryl acetate, the melting point of the recrystallized acetate should agree with that first obtained. If phytosteryl acetate is present, however, a higher melting point will be noted, as it is less soluble in alcohol than cholesteryl acetate.

Alcoholic Extraction Method. Place 250 grams of the melted sample in a flat-bottomed liter flask; stopper the flask with a 3-holed cork, and insert through these holes the following: (1) A reflux condenser; (2) a right-angled glass tube, one arm of which reaches to a point 6 mm. above the surface of the melted fat, the other end being closed a short distance from the flask by means of a short piece of rubber tubing and a pinch cock; (3) a glass tube bent so that one arm reaches down to the bottom of the flask and the other serves as a delivery tube for a 700-cc. round-bottomed flask containing 500 cc. of 95 per cent alcohol.

Place the flasks which contain the melted sample and the alcohol on the steam bath and heat so that the alcohol vapor passes through the melted fat in the liter flask and is condensed in the reflux condenser, finally collecting in a layer over the melted sample. After all of the alcohol has passed in this manner into a flask containing the fat, disconnect the flask from which the alcohol has been distilled and attach a tube to the short piece of rubber tubing attached to the right-angled glass tube [*see* (2) above], and siphon the alcoholic layer back into the alcohol distillation flask. Reconnect this flask as before and again distill the alcohol through the melted sample of fat as previously directed. When the alcohol has been distilled, siphon it back to the distillation flask and extract a third time in the same manner. Discard the fat and reserve the alcoholic extract, which now contains practically all the sterols originally present in the sample. Concentrate the alcoholic solution to about 250 cc. and while still hot add 20 cc. of (1:1) potassium hydroxide solution. Boil for 10 minutes to insure complete saponification of the dissolved fat, cool to room temperature, and pour the solution into a 2000-cc. separatory funnel containing 500 cc. of ether. Shake so as to insure thorough mixing and add 500 cc. of water. Rotate the separatory funnel gently to avoid the formation of a stubborn emulsion, but be careful to mix the water thoroughly with the alcohol-ether soap solution. A clear sharp separation of the ether and aqueous layers should take place. After standing for 10 minutes, withdraw slowly the lower aqueous layer, which contains most of the soaps. Wash the ether solution as directed for the first water treatment, with three 150-cc. portions of approximately fifth normal potassium hydroxide solution (11 grams of alkali in 1000 cc. of solution). Then wash with three 150-cc. portions of water, shaking thoroughly the ether solution and water. Dry the ether with about 5 grams of anhydrous sodium sulfate for 30 minutes, transfer it to a distilling flask of suitable size, and distill the ether until the volume is reduced to about 20 cc. Transfer to a 50-cc. Erlenmeyer flask and distill the remainder of the ether. Dry the residue for an hour in an oven heated to about 105° C. When the residue is dry, acetylate, and proceed from this point as directed under the digitonin method.

Limitation of the Method. The detection of the presence of small quantities of vegetable fats and oils in admixture with animal fats by means of the phytosteryl acetate test is relatively easy, if the directions are closely followed, as small amounts of phytosterol are readily detected

in the presence of much larger quantities of cholesterol; but the detection of animal fats when mixed with those of vegetable origin is much more difficult and cannot be accomplished by present methods unless the amount of animal fat is relatively large.

Also, it should be noted that vegetable shortenings containing hydrogenated soybean oil give a sterol test which indicates animal fat, although none is present.

Allen and Moore [*J. Soc. Chem. Ind.*, **46**, 433T (1927)] called attention to the fact that the major portion of the phytosterols in sunflower seed oil gives an acetate which melts at 119° C., and that a mixture of equal quantities of this acetate and cholesteryl acetate melts at 121° C. Previously, Power and Browning, and later Stuart, had shown that some phytosteryl acetates melted below 125° C., the lower limit given under the digitonin method. With this information it is evident that the present methods are not suitable for the detection of animal fats and oils in those of vegetable origin, but that the methods are still of use for the detection of vegetable in animal fats. With the exception of soybean oil, noted above, the other hydrogenated commercial oils apparently yield sterol acetates which melt at the same temperatures as those obtained from the original oils.

Attention is called to "The Detection of Animal Fat in Mixture with Vegetable Fat" by J. A. Broge, *Fette u. Seifen*, **46**, 131 (1939), and to the "Identification of Animal Fats and Oils, Particularly the Detection of Hardened Fish Liver Oils in Mixed Fats," S. H. Bertram, *Ole, Fette, Wachse*, **2**, 13 (1937), *Brit. Chem. Abs.* **B-1937**, 464, which is based on the color reaction given by trichloracetic acid.

Color Tests. Color tests or reactions are not generally given by the glycerides of a fat oil, but by the various kinds of minor constituents. A large number of such tests have been proposed from time to time, but the great majority of them are entirely useless. Formerly, much stress was laid on these tests, but with the development of more scientific methods for the detection or determination of various oils in admixture with others, but few of the color tests are now used. Even the more important tests which will be described are now limited in regard to their usefulness, due to the developments in the technology of the fatty oil industries and to the increasing number of fats and oils being used on a commercial scale.

Halphen Test for Cottonseed Oil. Place 5 cc. of the sample to be tested in a test tube, together with 5 cc. of carbon disulfide containing one per cent of sulfur and 5 cc. of amyl alcohol. Mix and heat in a saturated salt solution placed under the laboratory hood. The heating should be continued for three hours unless a red or orange color, which is the test, appears sooner. Some prefer to heat in an oil bath, in which case the bath should be gradually heated to about 130° C. and held at that temperature for 30 minutes. As all samples of cottonseed oil do not give the same intensity of color, the test cannot be made quantitative for the estimation of the oil in mixture with other oils. Cottonseed oil, which has been heated in iron vessels for a considerable period of time

above 225° C., gives little or no color with the Halphen reagents. Also, the hydrogenated or hardened oil usually responds only faintly to this test. Many of the seed oils of plants belonging to the *Malvaceae, Tiliaceae* and *Bombacaceae* families [S. Ivanov, *J. Soc. Chem. Ind.*, **617**, B 236 (1928)] respond to the Halphen test, but at present kapok oil is the only other one now of commercial importance.

Test for Cottonseed and Kapok Oils. Milliau [see *Mat. Grasses*, **13**, 5885 (1921)] suggests the following tests: Place 5 cc. of the dehydrated fatty acids, obtained in the usual manner from the sample to be tested, in a test tube with 5 cc. of a one per cent alcoholic solution of silver nitrate. After thorough shaking, allow the mixture to stand at room temperature for 20 minutes. A coffee-brown color will develop if one per cent or more of kapok oil is present. Baobab oil, which as yet is not produced commercially, will also give this color. Cottonseed oil only gives this test when the mixture is heated. As kapok gives the test in the cold or when the mixture is heated, the presence of cottonseed oil cannot be detected by this or any other test. In some cases it is desirable to test the original oil. This is done by dissolving 5 cc. of the oil in 5 cc. of chloroform and shaking the mixture with 5 cc. of the alcoholic silver nitrate; upon standing a half hour at room temperature, 5 per cent of either cottonseed or kapok oils in admixture with other oils can readily be detected.

Modified Villavecchia Test for Sesame Oil. To 5 cc. of the oil to be tested in a test tube, add 0.1 cc. of a 2 per cent alcoholic furfural solution, shake, and add 5 cc. of concentrated hydrochloric acid. Shake thoroughly, and let stand for 10 minutes. Then add 5 cc. of water, shake, and note the color. A crimson color shows the presence of sesame oil. The test will detect one per cent or less of sesame oil. Often African and Spanish pure olive oils give a pink or reddish color with the Villavecchia or Baudouin tests, which have been repeatedly mistaken as indicating the presence of sesame oil, but when the test is made as directed above, no color is given by these oils, unless sesame oil is also present.

Test for Conjugated Double Bonds. The following method has been devised by K. Meinel [*Berichte*, **70**, 429 (1937)]: *Reagents.* (1) Make a methyl alcohol solution containing 5 per cent each of bromine and calcium bromide. (2) To 20 cc. of 0.1*N* ammonium thiocyanate methyl alcohol solution, add 2 cc. of nitric acid and 2 cc. of a saturated aqueous solution of ammonium ferric alum. Then add just enough of a 0.3*N* methyl alcohol solution of silver nitrate (while rotating or stirring the solution) to decolorize it. *Method.* Dissolve 5 grams of the oil to be tested in 5 cc. of carbon tetrachloride. Add 9.1 cc. of solution (1) to saturate exactly one of the double bonds of the oil. Then add 50 cc. of distilled water. Extract the mixture with 30 cc. of peroxide-free ether. To the separated ether solution add 30 cc. of reagent (2) and mix by shaking. If no red color appears, shake it again. A red color indicates the presence of conjugated double bonds.

Comments. Unless the reagents are carefully prepared and the directions for making the test followed, satisfactory results cannot be obtained.

A Modified Renard Test for Peanut Oil. Weigh 20 grams of the oil to be tested into a 200-cc. Erlenmeyer flask. Add 10 cc. of a solution containing equal weights of potassium hydroxide and water, mix and add 20 cc. of alcohol. Mix thoroughly for a minute and heat in the steam bath for 30 minutes. Add 4 or 5 drops of phenolphthalein indicator solution and sufficient 20 or 30 per cent acetic acid to neutralize the excess of alkali. Then add, while shaking, enough 15 or 20 per cent solution of potassium hydroxide to give the soap solution a pink color. Pour carefully into a hot solution in a 500-cc. Erlenmeyer flask containing 120 cc. of a 20 per cent lead acetate solution and 120 cc. of water. Rinse the saponification flask twice with 10-cc. portions of hot water and add them to the solution in the 500-cc. flask. Boil for 2 minutes, remove the flame and let stand for 20 minutes, cool under running water, turning the flask slowly backward and forward several times, so as to bring the floating precipitate against the cool sides of the flask where it will become attached. When cold, decant the solution and wash the flask and precipitate several times with cold water. Invert the flask and let it drain for 5 minutes. Rinse flask and precipitate with 10 to 20 cc. of alcohol and drain without delay. Add 200 cc. of ether and let stand with occasional thorough shaking for 15 or 20 minutes; then attach to a reflux condenser and heat on the steam bath for 10 minutes. Remove the flask from the steam bath and rotate the solution, slowly at first and then rapidly. If the precipitate is thoroughly disintegrated or dissolved, no further heating is necessary. Add sufficient ether to bring the final volume up to about 200 cc. Place a small beaker over the neck of the flask and set it in an ice-box for 6 hours or longer. Filter the crystallized lead salts on a hardened filter paper carefully fitted in a small Büchner funnel, using suction just sufficient to draw the ether through the filter. Wash all the precipitate from the flask with ether. Wash thoroughly with small volumes of ether the entire inner surface of the funnel, and precipitate. During the filtration and washing, if the precipitate cracks, close the cracks with a spoon and rinse off the precipitate with ether. Finally, allow the precipitate to dry until it cracks in all directions, then transfer it without delay by a small horn spoon as completely as possible to a 500-cc. separatory funnel containing 25 cc. of ether. Remove the filter to a sheet of hard paper and after scraping off all the precipitate onto the paper, transfer it to the separatory funnel. Add 60 cc. more of ether, stopper and shake thoroughly for at least 1 minute. After standing for 20 minutes, rotate the ether gently and add a mixture of 30 cc. of hydrochloric acid and 15 cc. of water. Rotate the solution with the stopper removed from the separatory funnel, then insert the stopper and shake very thoroughly. After standing for about 10 minutes, remove the stopper, rinse it and neck of the funnel with a little ether; then add 20 cc. of water, pouring it around the neck. Rotate gently, let stand a few minutes, then withdraw the aqueous solution and the precipitated lead chloride. Wash the ether solution with 50-cc. portions of water until the washings are free from hydrochloric acid. If necessary, make further additions of ether to keep the volume about 70 cc. The ether solution,

after the second washing, should be free from precipitate, otherwise it will be necessary to shake again with 5 cc. of hydrochloric acid to decompose the remaining lead soap. Then the ether must be washed as before. Transfer the ether solution to a 200- or 300-cc. Erlenmeyer flask, distill the ether and dry the residue and flask at 110° C. in an oven for one or two hours. Dissolve the fatty acids in 100 cc. of boiling 90 per cent alcohol (by volume) and rotate the flask under running water until the solution is cold; then place in an ice-box for 6 hours or longer. Filter on a filter paper (not folded) and wash twice with 10-cc. portions of the 90 per cent alcohol cooled to 20° C. Wash again with three 10-cc. portions of 70 per cent alcohol (by volume). It is very important to wash the upper edge of the filter with the above-mentioned volumes of alcohol. Dissolve the fatty acids and wash the filter thoroughly with ether, collecting it in a weighed 200-cc. Erlenmeyer flask. Distill the ether and dry the residue and flask to constant weight in an oven heated to about 110° C. Add to the weight of acids in the flask 0.0090 gram to correct for the solubility of the arachidic and lignoceric acids in the 20 cc. of 90 per cent alcohol used for washing them. Twenty times the weight of these acids gives approximately the quantity of peanut oil present. The melting point of the mixed acids should be 71 or higher.

Comments. It is important that the 90 and 70 per cent alcohols used in the Renard test should be carefully prepared and that the directions should be closely followed. Although peanut oil, depending upon its origin, actually contains from about 5.8 to over 7 per cent of arachidic and lignoceric acids, the Renard test gives values usually in the neighborhood of 5.0 per cent. Both on account of the variation in the quantities of these acids in peanut oil and the character of the method, the results can be only approximate. From a qualitative standpoint, the finding of small quantities of these acids for example in an olive oil may not be due to the presence of a little peanut oil, but may indicate rape oil, which is not infrequently used as an adulterant and which contains from one to over two per cent of lignoceric acid. Also, olive oil contains from about 0.1 to 0.2 per cent of arachidic acid; but when the Renard test is applied to these pure oils, in most instances no evidence of this small quantity of arachidic acid is obtained.

The Kerr Method for the Detection of Peanut Oil. This method is based on the separation of arachidic-lignoceric acids as in the case of the Renard procedure [R. H. Kerr, *Ind. Eng. Chem.*, **8**, 904 (1916)].

Reagents. Potassium Hydroxide: 100 grams dissolved in 100 cc. of water. Magnesium Acetate Solution: 10 grams dissolved in a mixture of 100 cc. water and 100 cc. of 95 per cent alcohol. Acetic Acid: 50 cc. of glacial acetic acid dissolved in 150 cc. of 95 per cent alcohol. Sulfuric Acid: 50 cc. dissolved in 150 cc. of water. Alcohol: 90 per cent by volume.

Method. Place 20 grams of the oil to be tested in a 300-cc. Erlenmeyer flask, add 200 cc. of 95 per cent alcohol, and heat to boiling on the steam bath. Add 10 cc. of the potassium hydroxide solution and continue the heating for 10 minutes or longer if necessary to get complete

saponification. Add a few drops of phenolphthalein solution and neutralize the excess of alkali with the alcoholic acetic acid. Then add 30 cc. of the magnesium acetate solution and heat the mixture to boiling. Allow to cool to room temperature with occasional shaking and then place in a refrigerator (10° to 15° C.) until the next day. Filter the magnesium soaps, wash them twice with 50 per cent alcohol and three times with water. Return the precipitate to the flask, add 100 cc. of hot water and 20 cc. of the dilute sulfuric acid. Heat until the separated fatty acids form a clear layer. Cool the covered flask under running water until the acids are thoroughly solidified. Decant the aqueous solution, then rinse the solid acids and flask with cold water. Add 100 cc. of water, heat until acids have entirely melted, cool and decant as before. After draining off the water as completely as possible, dissolve the acids in 100 cc. of hot 90 per cent alcohol, and proceed from this point as described under the Renard test.

It will be observed that this method avoids the use of ether, besides requiring somewhat fewer operations than the Renard test. So far, this method has been used only as a qualitative procedure and it is capable of detecting the presence of 5 per cent of peanut oil in mixture with olive oil.

The Kreis Test for Rancidity. Reference: R. H. Kerr, *Ind. Eng. Chem.*, **10**, 471 (1918). The following reagents will be required: Hydrochloric acid sp. g. 1.19, free from nitrosyl chloride [*cf.* W. C. Porwick, *Oil and Fat Ind.*, **5**, 1071 (1928)]; a 0.1 per cent ether solution of pure phloroglucinol; liquid petrolatum, a highly refined fraction of petroleum.

Method. Place 5 cc. of the oil or melted fat to be tested and 5 cc. of the hydrochloric acid in a test tube. Insert a clean, sound rubber cork and shake vigorously for 30 seconds. Add 5 cc. of the phloroglucinol solution, insert cork, and shake again for 30 seconds, then allow the mixture to stand for 10 minutes. If a pink or red color appears in the lower acid layer, a reaction is obtained, but no attention should be paid to a pale orange, yellow or faintly pink color. When a pink or red color is obtained, make a mixture of one part of the sample to be listed with nine parts of the liquid petrolatum and another mixture of one part of the sample with 19 parts of petroleum. Test as before 5 cc. portions of each of the two mixtures and note the colors. Fats and oils may be divided into 4 classes as follows: (1) Those giving no reaction, (2) those giving a reaction when undiluted, (3) those giving a reaction in dilution 1 to 10 but none in dilution 1 to 20, and (4) those giving a reaction in dilution 1 to 20.

Class 1 represents sound fats and oils which may be expected to withstand severe exposure before turning rancid. Class 2 represents products which have not yet become rancid in so far as odor and taste are concerned, but in which those changes that will later manifest themselves as rancidity, are already in progress. Class 3 represents a late stage of incipient rancidity. These products are well advanced on the road to rancidity and in most cases, it is evident to the senses of smell and taste. Class 4 represents those which have definitely become rancid. It should

be observed that some crude vegetable oils, notably cottonseed oil, give an intense Kreis test, although free from rancidity. The extreme sensitiveness of the Kreis reaction enables one to predict the appearance of rancidity long before it becomes evident to the senses. In view of this sensitiveness, care must be taken in the interpretation of this test, particularly, when pale pink colors are obtained. In commercial dealings, the buyer and seller should come to an agreement upon what color should constitute a positive test and act accordingly.

Crude Glycerin Analysis. The following methods are those recommended by the International Committee (*J. Soc. Chem. Ind.*, **30**, 556 (1911). *Ind. Eng. Chem.*, **3**, 679 (1911).

Sampling. The most satisfactory method available for sampling crude glycerin liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerin sampled by a mutually approved sampler as soon as possible after it is run into drums, but in any case before any separation of salt has taken place. In such cases he shall sample with a sectional sampler, then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of the same made in his certificate, together with the temperature of the glycerin. Each drum must be sampled. Glycerin which has deposited salt or other matter cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerin to be taken including any deposit.

Analysis. 1. *Determination of Free Caustic Alkali.* Put 20 grams of the sample into a 100-cc. flask, dilute with approximately 50 cc. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 cc. of phenolphthalein solution, make up to the mark and mix. Allow the precipitate to settle, draw off 50 cc. of the clear liquid and titrate with normal acid ($N/1$); calculate the percentage of Na_2O existing as caustic alkali.

2. *Determination of Ash and Total Alkalinity.* Weigh 2 to 5 grams of the sample in a platinum dish, burn off the glycerin over a luminous Argand burner or other source of heat (carbon is readily burned off completely without loss of chlorides in a muffle furnace at a dull red heat) giving a low temperature, to avoid volatilization and the formation of sulfides. When the mass is charred to the point that water will not be colored by soluble organic matter, lixiviate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate the water and carefully ignite without fusion. Weigh the ash. Dissolve the ash in distilled water and titrate the total alkalinity, using as indicator methyl orange cold or litmus boiling.

3. *Determination of Alkali Present as Carbonate.* Take 10 grams of the sample, dilute with 50 cc. distilled water, add sufficient $N/1$ acid to neutralize the total alkali found in (2), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube, and then titrate back

with $N/1$ NaOH, using phenolphthalein as indicator. Calculate the percentage of Na_2O. Deduct the Na_2O found in (1). The difference is the percentage existing as carbonate.

4. *Alkali Combined with Organic Acids.* The sum of the percentages of Na_2O found at (1) and (3) deducted from the percentage at (2) is a measure of the Na_2O or other alkali combined with organic acids.

5. *Determination of Acidity.* Take 10 grams of the sample, dilute with 50 cc. distilled water free from carbon dioxide, and titrate with $N/1$ NaOH and phenolphthalein. Express in terms of Na_2O required to neutralize 100 grams.

6. *Determination of Total Residue at 160° C.* For this determination, the crude glycerin should be slightly alkaline with Na_2CO_3, not exceeding 0.2 per cent Na_2O, in order to prevent loss of organic acids. To avoid the formation of polyglycerols, this alkalinity must not be exceeded. Ten grams of the sample are put into a 100-cc. flask, diluted with water and the calculated quantity of $N/1$ HCl or Na_2CO_3, added to give the required degree of alkalinity. The flask is filled to 100 cc., the contents mixed, and 10 cc. measured into a weighed Petrie or similar dish 2.5 inches in diameter and 0.5 inch deep, which should have a flat bottom. In the case of crude glycerins abnormally high in organic residue a smaller amount should be taken, so that the weight of the organic residue does not materially exceed 30 to 40 milligrams.

The dish is placed on a water bath (the top of the 160° C. oven acts equally well) until most of the water has evaporated. From this point, the evaporation is effected in the oven. If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° C. can readily be maintained with the door partially open, and the glycerin, or most of it, should be evaporated off at this temperature. When only a slight vapor is seen to come off, the dish is removed and allowed to cool. An addition of 0.5 to 1 cc. of water is made and by a rotary motion the residue is brought wholly or nearly into solution. The dish is then allowed to remain on the water bath or top of the oven until the excess of water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spurt. The time taken up to his point cannot be given definitely, nor is it important. Usually two or three hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulfuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1.5 mg. per hour is obtained. In the case of acid glycerin a correction must be made for the alkali added; 1 cc. $N/1$ alkali represents an addition of 0.03 gram. In the case of alkali crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to

NaCl. The corrected weight multiplied by 100 gives the percentage of total residue at 160° C.

This residue is taken for the determination of the non-volatile acetizable impurities (see Acetin method).

7. *Organic Residue.* Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (It should be noted that the alkaline salts of fatty acids are converted to carbonates on ignition and that the CO_2 thus derived is not included in the organic residue).

Acetin Process for the Determination of Glycerol. This process is the one agreed upon at a conference of delegates from the British, French, German, and American committees, and has been confirmed by each of the above committees as giving results nearer to the truth than the bichromate method on crudes in general. It is the process to be used (if applicable) whenever only one method is employed. On pure glycerol the results are identical with those by the bichromate process. For the application of this method the crude glycerol should not contain over 60 per cent of water.

Reagents. (*A*) *Best Acetic Anhydride.* This should be carefully selected. A good sample must not require more than 0.1 cc. of normal NaOH for saponification of the impurities when a blank is run on 7.5 cc. Only a slight color should develop during digestion of the blank. The anhydride may be tested for strength by the following method. Into a weighed stoppered vessel, containing 10 to 20 cc. of water, run about 2 cc. of the anhydride, replace the stopper and weigh. Let stand with occasional shaking for several hours, to permit the hydrolysis of all the anhydride, then dilute to about 200 cc., add phenolphthalein and titrate with *N*/1 NaOH. This gives the total acidity due to free acetic acid and acid formed from the anhydride. It is worthy of note that in the presence of much free anhydride a compound is formed with phenolphthalein, soluble in alkali and acetic acid, but insoluble in neutral solutions. If a turbidity is noticed toward the end of the neutralization, it is an indication that the anhydride is incompletely hydrolyzed, and inasmuch as the indicator is withdrawn from the solution, results may be incorrect.

Into a stoppered weighing bottle containing a known weight of recently distilled aniline (from 10 to 20 cc.) measure about 2 cc. of the sample, stopper, mix, cool, and weigh. Wash the contents into about 200 cc. of cold water, and titrate the acidity as before. This yields the acidity due to the original preformed acetic acid, plus one half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated to 100 grams) and double the result, obtaining the cc. *N*/1 NaOH per 100 grams of the sample. 1 cc. *N*/1 NaOH equals 0.0510 anhydride.

(*B*) *Pure Fused Sodium Acetate.* The purchased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or desiccator. It is most important that the sodium acetate be anhydrous.

(*C*) *A Solution of Caustic Soda for Neutralizing, of about N/1 Strength, Free from Carbonate.* This can be readily made by dissolving

pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through asbestos. The clear solution is diluted with water free from carbon dioxide to the strength required.

(*D*) *N/1 Caustic Soda Free from Carbonate.* Prepare as above and carefully standardize. Some caustic soda shows a marked diminution in strength after being boiled: such solutions should be rejected.

(*E*) *N/1 Acid.* Carefully standardized.

(*F*) *Phenolphthalein Solution.* 0.5 per cent phenolphthalein in alcohol and neutralized.

Method. In a narrow-mouthed flask (preferably round-bottomed), capacity about 120 cc., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 grams of glycerin. A Grethan or Lunge pipette will be found convenient. Add about 3 grams of the anhydrous sodium acetate, then 7.5 cc. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside diameter. The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used it should have a preliminary treatment with hot acetic anhydride vapor. Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts from drying on the side of the flask. Allow the flask to cool somewhat, and through the condenser tube add 50 cc. of distilled water free from carbon dioxide at a temperature of about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapors from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test resumed the next day without detriment, bearing in mind that the anhydride in excess is much more effectively hydrolyzed in hot than in cold water. The contents of the flask may be reached, but must not exceed 80° C., until the solution is complete, except for a few dark flocks representing organic impurities in the crude. By giving the flask a rotary motion, solution is more quickly effected. Cool the flask and contents without loosening from condenser. When quite cool, wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground glass connection into the flask, and filter the contents through an acid-washed filter into a liter flask. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 cc. of phenolphthalein solution (*F*), then run in caustic soda solution (*C*) or (*D*) until a faint pinkish-yellow color appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the color developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon dioxide-free water and the alkali subsequently added

drop by drop, mixing after each drop until the desired tint is obtained. Now run in from a burette 50 cc. or a calculated excess of $N/1$ NaOH (D) and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate the excess of NaOH with $N/1$ acid (E) until the pinkish yellow or chosen end-point color just remains (a precipitate at this point is an indication of the presence of iron or aluminum, and high results will be obtained unless a correction is made as to be described). A further addition of the indicator at this point will cause an increase of the pink color; this must be neglected, and the first end point taken. From the $N/1$ NaOH consumed calculate the percentage of the glycerin (including acetylizable impurities) after making the correction for the blank test described below.

1 cc. $N/1$ NaOH = 0.03069 gram glycerin. The coefficient of expansion for normal solutions is 0.00033 per cubic centimeter for each degree centigrade. A correction should be made on this account, if necessary.

Blank Test. As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride, sodium acetate and water as in the analysis. It is not necessary to filter the solution of the melt in this case, but sufficient time must be allowed for the hydrolysis of the anhydride before proceeding with the neutralization. After neutralization it is not necessary to add more than 10 cc. of the $N/1$ alkali (D), as this represents the excess usually present after the saponification of the average soap lye crude. In determining the acid equivalent of the $N/1$ NaOH, however, the entire amount taken in the analysis, 50 cc., should be titrated after dilution with 300 cc. of water free from carbon dioxide and without boiling.

Determination of the Glycerol Value of the Acetylizable Impurities. Dissolve the total residue at 160° C. in 1 or 2 cc. of water, wash into the acetylizing flask, and evaporate to dryness. Then add anhydrous sodium acetate and acetic anhydride in the usual amounts and proceed as described in the regular analysis. After correcting for the blank, calculate the result to glycerol.

Instructions for Calculating the Actual Glycerol Content. (1) Determine the apparent percentage of glycerol in the sample by the acetin process is described. The result will include acetylizable impurities if any are present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylizable impurities are present, these are included in this figure.

Trimethyleneglycol is more volatile than glycerin and can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and

bichromate results on such distillates. The spread multiplied by 1.736 will give the glycol.

Bichromate Process for Glycerol Determination. *Reagents.* (*A*) *Pure potassium bichromate* powdered and dried in air free from dust or organic vapors, at 110° to 120° C. This is taken as the standard.

(*B*) *Dilute Bichromate Solution.* 7.4564 grams of the above bichromate is dissolved in distilled water and the solution made up to one liter at 15.5° C.

(*C*) *Ferrous Ammonium Sulfate.* It is never safe to assume this salt to be constant in composition and it must be standardized against the bichromate as follows: Dissolve 3.7282 grams of bichromate (*A*) in 50 cc. of water. Add 50 cc. of 50 per cent sulfuric acid (by volume), and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulfate, and titrate back with the dilute bichromate (*B*). Calculate the value of the ferrous salt in terms of bichromate.

(*D*) *Silver Carbonate.* This is prepared as required for each test from 150 cc. of 0.5 per cent silver sulfate solution by precipitation with about 4.9 cc. *N*/1 sodium carbonate solution (a little less than the calculated quantity of *N*/1 sodium carbonate should be used as an excess prevents rapid settling). Settle, decant and wash once by decantation.

(*E*) *Subacetate of Lead.* Boil a 10 per cent solution of pure lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(*F*) *Potassium Ferricyanide.* A very dilute, freshly prepared solution containing about 0.1 per cent.

Bichromate Method. Weigh 20 grams of the glycerin, dilute to 250 cc. and take 25 cc. Add the silver carbonate, allow to stand with occasional agitation for about 10 minutes, and add a slight excess (about 5 cc. in most cases) of the basic lead acetate (*E*), allow to stand a few minutes, dilute with distilled water to 100 cc., and then add 0.15 cc. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 cc., and return the filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate (in the great majority of cases 5 cc. is ample, but occasionally a crude will be found requiring more, and in this case another aliquot of 25 cc. of the dilute glycerin should be taken and purified with 6 cc. of the basic lead acetate. Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 cc. of the clear filtrate into a flask or beaker (previously cleaned with bichromate and sulfuric acid). Add 12 drops of sulfuric acid (1:4) to precipitate the small excess of lead as sulfate. Add 3.7282 grams of the powdered potassium bichromate (*A*). Rinse down the bichromate with 25 cc. of water and let stand with occasional shaking until all the bichromate is dissolved (no reduction will take place in the cold).

Now add 50 cc. of 50 per cent sulfuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapors, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulfate (*C*), making spot tests on a porcelain plate with the potassium ferricyadine (*F*). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 gram glycerin = 7.4564 grams bichromate
1 gram bichromate = 0.13411 gram glycerin

The percentage of glycerol obtained above includes any oxidizable impurities present after the purification. A correction for the non-volatile impurities may be made by running a bichromate test on the residue at 160° C.

Notes. (1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerin solution it is essential that the slight excess of lead be precipitated with sulfuric acid, as stipulated.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead carbonate to 0.5 cc.

(4) It is sometimes advisable to add a little potassium sulfate to insure a clear filtrate.

APPENDIX

Sampling Crude Glycerin. The usual method of sampling crude glycerin hitherto has been by means of a glass tube, which is slowly lowered into the drum with the object of taking as nearly as possible a vertical section of the glycerin contained in the drum. This method has been found unsatisfactory, because in cold climates glycerin runs into the tube very slowly, so that the time consumed makes it impossible to take a complete section of the crude. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt contained in the drum.

The sampler has been devised with the object of overcoming the objections to the glass tube as far as possible. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the ports are opened, a continuous slot is formed which enables a complete section to be taken throughout the entire length of the drum. By this arrangement the glycerin flows into the sampler almost instantaneously. There are a number of ports cut at the bottom of the sampler which render it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when the sampler is open or closed. In samplers of larger section (1 in.) it is possible to arrange a third

motion whereby the bottom ports only are open for emptying; but in samplers of smaller dimensions (⅜ in.) this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

The sampler is introduced into the drum with the ports closed; when it has touched the bottom, the ports are opened for a second or two, then closed and withdrawn, and the sampler discharged into the receiving vessel by opening the ports. When the drum contains salt which has deposited, the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum, and it is therefore recommended that the drum be sampled before any salt has deposited. A sampler 1 inch in diameter withdraws approximately 10 oz. from a 110-gal. drum, whereas a sampler ⅜-in. in diameter will withdraw about 5 oz.

Attention is called to recent collaborative studies of the Soap Section of the American Oil Chemists Society, particularly with regard to standardization of the hydrochloric acid solution [*Soap,* **5,** No. 4, 29 (1929)] including that by Hulett and Bonner, *J. Am. Chem. Soc.,* **31,** 390 (1909).

It should be noted that in the valuation of crude glycerin for some purposes, it is necessary to estimate the content of arsenic, sulfides, sulfites, thiosulfates, etc.; but methods for the determination of these substances were not included in the international procedures.

For details (and comparative tables of data) for the determination of glycerin in aqueous solutions by means of the specific gravity and refractive index consult "Glycerol and the Glycols" by J. W. Lawrie (New York, Chemical Catalog Co., Inc., 1928). It also contains the procedure in detail for the determination of water in glycerin.

Also attention is called to Grün and Wirth [*J. Soc. Chem. Ind.,* **38,** 295 A (1919)], who consider that the boiling-point method is the most accurate procedure for the determination of the concentration of aqueous solutions of glycerin, and the data obtained by them are in close agreement with those of Lewis [*J. Soc. Chem. Ind.,* **41,** 97 T (1922)].

L. B. Smith and H. Matthews [*Oil and Soap,* **17,** 58 (1940)] have devised a dichromate procedure for the determination of glycerin in fats and oils after saponification with alcoholic potash, which has been found to give reliable results. They give detailed directions for using their method. Various procedures for the determination of glycerin are discussed and much data are given by A. F. Nelson, *et al.* [*Oil and Soap,* **15,** 10 (1931)].

Nickel in Hydrogenated Fats. The R. H. Kerr modification of the Börner method [*Ind. Eng. Chem.,* **6,** 207 (1914)] is as follows: Heat for 2 or 3 hours on the steam bath with frequent shaking 10 grams of the sample to be tested in a 100-cc. Erlenmeyer flask with 10 cc. of hydrochloric acid, sp. g. 1.12. Separate the fat by filtration through a wet filter paper, receiving the filtrate in a porcelain dish. Evaporate the filtrate on the steam bath to a small volume. Add 2 cc. of nitric acid and

continue the evaporation to dryness. Dissolve the residue in 5 cc. of water, add 1 cc. of a one per cent alcoholic solution of dimethylglyoxime, and a few drops of ammonium hydroxide. A red color or precipitate indicates nickel. The quantity of nickel present can be determined colorimetrically in the usual manner, using a standard nickel chloride or sulfate solution, 1 cc. of which contains 0.05 milligram of nickel.

When samples larger than 10 grams are to be used for the test, the quantity of hydrochloric and nitric acids should be correspondingly increased.

The following procedure has been proposed by Waginaar [*Chem. Abs.*, **20**, 2421 (1926)]. Melt a 20- to 30-gram portion of the sample in a small beaker or flask. Transfer about 5 grams to a 3-inch porcelain dish and heat until fumes appear. Then add a small roll of ignited filter paper. The paper serves as a wick. As the oil is consumed, gradually add the remainder from the beaker. Finally, ash the filter paper and residue. Cool and moisten the residue with 2 cc. of nitric acid. Evaporate to dryness and dissolve the residue in 5 cc. of water and proceed from this point as described in the first method given. One part of nickel in several million of the fat can be detected by this method, according to the originator. Attention is called to the following references: "Nickel in Foods," Normann, [*Chem. Abs.*, **7**, 3622 (1913)]; "The Hygienic Significance of Nickel," K. R. Drinker, L. T. Fairhall, G. B. Gay and C. K. Drinker [*J. Ind. Hygiene*, **6**, 307-56 (1924); *Chem. Abs.*, **19**, 1011 (1925)]. This article contains a bibliography of 100 references and describes the delicate dithio-oxalate test for nickel.

Analysis of Soybeans. The methods given are those found in the 1939-1940 edition of "Rules" of the National Cotton Products Association (U.S.) which were devised and tested by the American Oil Chemists' Society [*Oil and Soap*, **14**, 213 (1937)].

For the determination of "original moisture," weigh accurately 8 to 10 grams, in duplicate, of whole beans into aluminum moisture dishes and heat them for 3 hours at 130° ± 3° C. in a forced-draft oven. Remove dishes from oven, put on covers, and place in a desiccator until cool (30 minutes); then weigh them.

For the determination of ammonia and oil, heat 60 grams of the beans at 130° ± 3° C. in the forced-draft oven for 2 hours. Grind them to a fine meal. For the second moisture determination, weigh 5 grams into a moisture dish, heat for 2 hours at 130° ± 3° C., cover, cool in a desiccator, and weigh.

Extract duplicate 2-gram portions each of the ground dried beans with petroleum ether for 2 hours, as described under *Cottonseed analysis.* Then regrind in a mortar and extract again for 3 hours. Evaporate all the solvent, cool, and allow the flask to remain in the balance room 10 minutes before weighing it. Calculate the percentage of oil. Determine ammonia, using 1.7034 grams of dried ground beans, by the method given under *Cottonseed analysis.*

If a determination of free fatty acids is desired, grind to a fine meal 40 to 50 grams of beans which have been heated for 2 hours in the oven

a 130° C.; extract the oil, and finish the determination as described under *Cottonseed analysis.*

Recalculate the oil and moisture to the original moisture basis of the beans. Report moisture and oil to the first decimal place, and ammonia to the second decimal place.

When it is desired to calculate the approximate yields of oil and press cake from the analytical data obtained for a shipment of beans, assume that the cake will contain 5 per cent of oil and 7.5 per cent of moisture and make the following calculations: Add together the pounds of oil and moisture in a ton of the beans. Subtract this figure from 2000 pounds. The result is pounds of dry, oil-free cake and it equals 87.5 per cent of the total cake. To obtain the available pounds of oil, deduct from the total remaining in the cake. Calculate the ammonia in the cake by dividing the pounds of total ammonia (in a ton of beans) by the weight of the cake and multiply the result by 100. The moisture and manufacturing loss in processing a ton of beans is the difference between the sum of the cake and available oil, and 2000 pounds.

Example. An analysis of beans gave 12.5 per cent moisture, 17.3 per cent oil, and 7.20 per cent ammonia. 2000 lbs. − 596 lbs. (250 lbs. moisture and 346 lbs. oil) = 1404 lbs. of dry, oil-free cake = 87.5 per cent of total cake. (1404 lbs. ÷ 87.5 × 100 = 1604 lbs. of cake. 1604 lbs. × 0.5 = 80 lbs. of oil in the cake. 346 lbs. − 80 lbs. = 266 lbs. of available oil. (144 lbs. ammonia ÷ 1604 lbs. cake) × 100 = 8.97 per cent ammonia in cake. 2000 lbs. of seed − 1604 lbs. of cake + 266 lbs. of oil = 130 lbs., which is the manufacturing loss.

Sampling of Cottonseed. Altogether too frequently, sampling of cottonseed from cars, wagons, etc., is allowed to be made by inexperienced men without supervision. Not infrequently, the samples taken are so small that if properly selected, they could not be representative of the shipment of seed. Unless the sample is representative, it is a useless expense to have it analyzed, because the results obtained are worthless in so far as the grading or evaluation of the seed is concerned. Too much emphasis cannot be placed on the necessity for having representative samples, and further that each portion of the same taken for analysis shall be representative of the sample. Not less than a 50-lb. sample should be drawn from a car of seed. G. S. Meloy [*Cotton Oil Press,* **13,** No. 2, 43 (1929)], who has made a special study of sampling seed, has found it preferable, where possible, to collect the sample as the car is unloaded according to the following directions. The sampler is to be provided with an 8 × 5 × 55 inch receptacle (such as an elevator bucket) attached to a handle long enough so that the sampler can hold this receptacle or ladle in a level position near the top of the seed chute while standing outside immediately in front of the car so as to catch a ladle of the seeds as they are ejected from the car. At regular intervals during the unloading of the car, the sampler is to take not less than 25 ladles of seed (each being 2 lbs. of seed). The sample is collected in a suitable can or other metallic container provided with a tight-fitting cover. The sampler weighs the sample and records the weight of the seed, then passes it

through the shaker cleaner provided with a vent through which a cross-section of the clean seed may pass into a small box. The portion so collected must be representative of the cleaned seed and the vent should be so regulated that not less than 1000 grams of seed shall be obtained. This portion is placed at once in a friction-top can, together with the recorded weight of the original sample and the weight of foreign matter separated from it, and forwarded to the chemist for analysis.

When cars have to be sampled prior to unloading it has been suggested that a trench be dug through the seed as deep as circumstances permit, going from the center to each end of the car; the sample is gathered by thrusting the arm into each side and the bottom of the trench, as far as possible, withdrawing large handfuls of seed each time. This is to be repeated at intervals of about 3 feet throughout the length of the car. The sample, which must weigh not less than 50 lbs., is treated as already described.

For methods of drawing and preparing official samples of cottonseed by licensed cottonseed samplers, as well as for the methods of analysis and grade calculations, a current issue of the Agricultural Marketing Service of the United States Department of Agriculture should be consulted.

Analysis of Cottonseed. The following directions for the analysis of laboratory samples of cottonseed have been selected by the writer and R. S. McKinney [*Oil and Fat Ind.*, 7, 291 (1930)] with a view to their use in connection with the evaluation of the commercial product. The sample of approximately 1000 grams submitted to the chemist in an air-tight container (can or glass jar) by the sampler is expected to be a portion of the cleaned seed representative of the 50-lb. sample drawn from a car or other container. Along with the chemist's sample is to be a statement giving the weight of the original sample drawn and the foreign matter separated from it by the sampler.

Laboratory Examination. The sample shall be examined, and if it is not thoroughly cleaned, the weights reported by the sampler shall be corrected for such additional foreign matter as may be present. The cleaned seed should be quartered, as to be described, and one half be returned to the container and held as a referee sample. The second half is quartered down until the combining of opposite quarters yields 2 samples of about 120 grams. One is used for the free fatty acid determination; the other 120-gram portion is requartered, yielding 2 samples of 60 grams. One of these is used for the moisture determination and the other for the determination of oil and nitrogen (proteins).

Quartering: Place the sample on a large square of heavy smooth paper and mix thoroughly, passing the hands upward through the pile, separating any masses of seed with the fingers. If there is a large percentage of damaged seed present, the greatest care must be taken to get the seed well mixed. When large quantities of bald seed are present, the tendency is for them to segregate at the bottom of the pile. In such cases, it is preferable to remove the bald seeds, and later distribute them uniformly over the thoroughly mixed flattened pile of fuzzy seed. Divide

the flattened pile into four equal parts by cutting twice through it to the bottom with a large spatula. Quadrants 1 and 3 are discarded; 2 and 4 are combined, mixed and requartered. All operations should be carefully but rapidly executed to avoid either a loss or gain of moisture, and the portions of seed not immediately used for analysis should be kept in suitable tight containers.

Original Moisture. The moisture may be determined by either of the two following methods: (1) Crack the seed, preferably by passing them through a plumber's crimper. Weigh duplicate samples of about 5 grams in aluminum moisture dishes (2 to 2½ inches in diameter) and dry for 5 hours at 101° C. in a constant-temperature oven. Remove dish, cover, and let cool to room temperature in an efficient desiccator; then weigh. Calculate the percentage of moisture. One-half hour in the desiccator is sufficient.

(2) Weigh 60 grams of whole seed in a suitable sized moisture dish (about 9 cc. capacity). Dry at 101° C. for 14 hours or overnight. Remove dish, cover, cool in desiccator for one-half hour, and weigh.

Determination of Oil and Nitrogen (Proteins): Apparatus: Fuming oven.—A well-ventilated oven capable of maintaining a temperature of 120° C., the variation being not more than 5° C. in any part of it. Fuming pots.—3-inch flower pots. Clay covers for pots or watch glasses. Grinding mill—Bauer Bros. No. 148 laboratory mill.

Method. Dry 60 grams of seed for 2 hours at 130° ± 1° C. Absorb into inner walls of flower pot 1.5 cc. concentrated hydrochloric acid. The acid is distributed all over the inner walls of the pot and when absorbed the inside must appear dry; otherwise a new pot must be substituted. Place the dried seed in the pot, cover with a watch glass or a clay cover, and place in the fuming oven at 120°C. for one hour. The lint after this treatment should be loose and brittle, but not scorched. Grind the sample in the Bauer mill adjusted to produce a fine meal. After grinding, open the mill and carefully brush out all remaining ground seed onto a sizable smooth sheet of paper. It is important also that the top of the hopper of the mill be fitted with a cover to prevent loss of seed during the grinding. There should be practically no loss of material in grinding. If such loss amounts to more than 1 gram, the whole process should be repeated, starting with another 60 grams of seed, because the material lost is not necessarily representative of the whole. Place the ground sample in a 2-quart fruit jar containing a large, solid-rubber stopper, adjust can top, shake violently for 30 seconds, then transfer the contents to a well-stoppered bottle. This procedure alone has been found satisfactory for obtaining a uniform mixture.

Second Moisture Determination. Weigh 5 grams of the ground sample into a moisture dish and dry for 3 hours in an oven at 101° C. Remove from oven, cover, cool in desiccator for one-half hour, weigh, and calculate loss in weight as per cent of moisture of the fumed sample.

For the determination of oil, the following equipment is needed: Extractors of the Butt type or other continuous percolator types, Allihn condensers with 12-inch jackets and extraction flasks of 120 cc. capacity.

Method. Weigh accurately duplicate samples of the ground fumed seed of 4 to 5 grams, tightly wrap (to prevent channeling of meal) in a 150-mm. filter paper (S.&S. No. 597 or equivalent grade) and rewrap in a second paper in such a manner as to prevent escape of the meal, leaving the top of the second paper open like a thimble. Some prefer to use 2 papers for the second wrapping. Place a piece of absorbent cotton in the top of the thimble to distribute the dropping ether. Place 35 cc. of petroleum ether in the weighed extraction flasks, connect to the extractor, with sound, well-fitting previously extracted corks and extract the sample for 2 hours. The ether should drop into the center of the cotton in the filter paper thimble at a rate of at least 150 drops per minute. The volume of the solvent should be kept approximately constant during the extraction. Remove the sample, allow the adhering solvent to evaporate, then regrind the sample in a mortar, rewrap in the same filter papers, and continue the extraction for one more hour. Disconnect the flask and evaporate the solvent on the steam bath until no trace of it remains, cool and weigh. As the last traces of the petroleum ether are sometimes difficult to detect by odor, in case of doubt heat the flasks again on the steam bath, cool and weigh until a constant weight is obtained.

Example of calculation.

Petroleum-ether extract	1.0255 grams
Original moisture	12.22 per cent
Second moisture	2.54 per cent

$$\text{Per cent of oil in seed} = \frac{1.0255}{5} \times \frac{87.78}{97.46} = 18.46$$

It has been suggested that when large numbers of samples are examined daily, the following procedure be followed: Spread out the weighed sample in a thin layer on a square filter paper and coil tightly into a cylinder. Wrap this as already described in one or two filter papers, and make one 4-hour extraction.

For the determination of nitrogen (ammonia or proteins) the following apparatus and reagents are required: 800-cc. Kjeldahl digestion flasks, a digestion stand with fume pipe to flue for supporting flasks over burners or electric heaters, a distillation stand provided with block tin condensers, 500-cc. flasks or heavy glass wide-mouth bottles for receiving distillate, delivery tubes or adapters, metallic mercury or mercuric oxide, potassium sulfate, sulfuric acid (sp. g. 1.84), granulated zinc (20-mesh), sodium hydroxide solution (sp. g. 1.50), 4 per cent solution of sodium or potassium sulfide, 0.25*N* solution of sodium or potassium hydroxide and 0.5*N* sulfuric acid solution and indicators, either an alcoholic solution of cochineal, methyl red, or a 1 per cent aqueous solution of sodium alizarine sulfonate.

Method. Digest 1.7034 grams of the fumed ground sample in a dry Kjeldahl flask with approximately 0.5 gram of mercury (or 0.7 gram of mercuric oxide), 10 grams of potassium sulfate and 25 cc. of sulfuric acid. Place the flask in an inclined position on the digestion stand and heat somewhat below the boiling point of the mixture until the frothing has ceased. Then increase the temperature and continue the digestion

until the liquid becomes colorless. Allow the solution to cool to about room temperature and add 300 cc. of distilled water, a few granules of zinc, and 25 cc. of the sulfide solution, or sufficient to precipitate all the mercury as sulfide. After thorough mixing, add 60 cc. of the sodium hydroxide reagent, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect flask with condenser, mix contents of flask, and distill into receiving flask or bottle which contains an accurately measured quantity of 0.5*N* sulfuric acid (or other suitable normality) to which has been added 50 cc. of water, until at least 200 cc. of distillate is obtained, taking precautions that the delivery tube extends below the acid solution. Titrate the distillate in the usual manner with 0.25*N* or other suitable strength solution of sodium hydroxide (or potassium hydroxide), using cochineal as indicator. When methyl red is used as the indicator, first heat the distillate to boiling and titrate while hot. Make a blank determination using all the reagents as directed and apply this correction to the titration of the distillates. A description of the apparatus for making 500 determinations a day is given in the *Cotton Oil Press,* **5**, No. 8, 33 (1921). This method (which is commonly used in the United States) directs that the factor weight 1.7034 grams be taken for analysis. This weight is such that if normal solutions were employed for the titration, 1 cc. equals 1 per cent of ammonia, but in actual practice a 0.25*N* alkali and a 0.5*N* acid solution are generally used. The equivalents for one cubic centimeter of a 0.25*N* solution are 0.003502 gram of nitrogen, 0.004258 gram of ammonia, and 0.021888 gram of protein.

Calculate the percentage of nitrogen, ammonia or protein as desired on the basis of the seed in its original condition.

Determination of Free Fatty Acid in Extracted Oil from Seed. Heat about 120 grams of the sample of cottonseed obtained by quartering from 30 to 45 minutes at 105° C. When cool, separate the meats with a laboratory huller. Grind the meats sufficiently to pass through a 1.5-mm. sieve. Mix thoroughly and extract without delay not less than 10 grams with petroleum ether by cold percolation. Remove the solvent by evaporation and weigh the oil. At least 2 grams of oil should be obtained. Add 30 cc. of neutralized alcohol and titrate the free fatty acids with a standard solution of sodium or potassium hydroxide, using phenolphtalein as indicator. The titration is made in the flask in which the oil is weighed. During the titration, the mixture of oil and alcohol must be thoroughly agitated until a pink color in the alcoholic solution is obtained that is not discharged by further shaking. Decinormal alkali solution is used for oils low in free fatty acids, but a quarter or a fifth normal solution is used when the acids are above 5 per cent. Some prefer to add about 2 cc. of petroleum ether, before the titration, as this makes the end point somewhat sharper. Calculate the percentage of free fatty acids as oleic acid by the following formula:

$$\% \text{ F. F. A.} = \frac{28.2 \times \text{Normality of Solution (cc. of Sol. used)}}{\text{Weight of Oil}}$$

TABLE FOR THE CONVERSION OF NITROGEN INTO AMMONIA AND PROTEIN

N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.
.00	.00	.00	.50	.61	3.13	1.00	1.22	6.25	1.50	1.82	9.38
.01	.01	.06	.51	.62	3.19	1.01	1.23	6.31	1.51	1.84	9.44
.02	.02	.13	.52	.63	3.25	1.02	1.24	6.38	1.52	1.85	9.50
.03	.04	.19	.53	.64	3.31	1.03	1.25	6.44	1.53	1.86	9.56
.04	.05	.25	.54	.66	3.38	1.04	1.26	6.50	1.54	1.87	9.63
.05	.06	.31	.55	.67	3.44	1.05	1.28	6.56	1.55	1.88	9.69
.06	.07	.38	.56	.68	3.50	1.06	1.29	6.63	1.56	1.90	9.75
.07	.08	.44	.57	.69	3.56	1.07	1.30	6.69	1.57	1.91	9.81
.08	.10	.50	.58	.70	3.63	1.08	1.31	6.75	1.58	1.92	9.88
.09	.11	.56	.59	.72	3.69	1.09	1.33	6.81	1.59	1.93	9.94
.10	.12	.63	.60	.73	3.75	1.10	1.34	6.88	1.60	1.95	10.00
.11	.13	.69	.61	.74	3.81	1.11	1.35	6.94	1.61	1.96	10.06
.12	.15	.75	.62	.75	3.88	1.12	1.36	7.00	1.62	1.97	10.13
.13	.16	.81	.63	.77	3.94	1.13	1.37	7.06	1.63	1.98	10.19
.14	.17	.88	.64	.78	4.00	1.14	1.39	7.13	1.64	1.99	10.25
.15	.18	.94	.65	.79	4.06	1.15	1.40	7.19	1.65	2.01	10.31
.16	.19	1.00	.66	.80	4.13	1.16	1.41	7.25	1.66	2.02	10.38
.17	.21	1.06	.67	.81	4.19	1.17	1.42	7.31	1.67	2.03	10.44
.18	.22	1.13	.68	.83	4.25	1.18	1.43	7.38	1.68	2.04	10.50
.19	.23	1.19	.69	.84	4.31	1.19	1.45	7.44	1.69	2.06	10.56
.20	.24	1.25	.70	.85	4.38	1.20	1.46	7.50	1.70	2.07	10.63
.21	.26	1.31	.71	.86	4.44	1.21	1.47	7.56	1.71	2.08	10.69
.22	.27	1.38	.72	.88	4.50	1.22	1.48	7.63	1.72	2.09	10.75
.23	.28	1.44	.73	.89	4.56	1.23	1.50	7.69	1.73	2.10	10.81
.24	.29	1.50	.74	.90	4.63	1.24	1.51	7.75	1.74	2.12	10.88
.25	.30	1.56	.75	.91	4.69	1.25	1.52	7.81	1.75	2.13	10.94
.26	.32	1.63	.76	.92	4.75	1.26	1.53	7.88	1.76	2.14	11.00
.27	.33	1.69	.77	.94	4.81	1.27	1.54	7.94	1.77	2.15	11.06
.28	.34	1.75	.78	.95	4.88	1.28	1.56	8.00	1.78	2.16	11.13
.29	.35	1.81	.79	.96	4.94	1.29	1.57	8.06	1.79	2.18	11.19
.30	.36	1.88	.80	.97	5.00	1.30	1.58	8.13	1.80	2.19	11.25
.31	.38	1.94	.81	.98	5.06	1.31	1.59	8.19	1.81	2.20	11.31
.32	.39	2.00	.82	1.00	5.13	1.32	1.61	8.25	1.82	2.21	11.38
.33	.40	2.06	.83	1.01	5.19	1.33	1.62	8.31	1.83	2.23	11.44
.34	.41	2.13	.84	1.02	5.25	1.34	1.63	8.38	1.84	2.24	11.50
.35	.43	2.19	.85	1.03	5.31	1.35	1.64	8.44	1.85	2.25	11.56
.36	.44	2.25	.86	1.05	5.38	1.36	1.65	8.50	1.86	2.26	11.63
.37	.45	2.31	.87	1.06	5.44	1.37	1.67	8.56	1.87	2.27	11.69
.38	.46	2.38	.88	1.07	5.50	1.38	1.68	8.63	1.88	2.29	11.75
.39	.47	2.44	.89	1.08	5.56	1.39	1.69	8.69	1.89	2.30	11.81
.40	.49	2.50	.90	1.09	5.63	1.40	1.70	8.75	1.90	2.31	11.88
.41	.50	2.56	.91	1.11	5.69	1.41	1.71	8.81	1.91	2.32	11.94
.42	.51	2.63	.92	1.12	5.75	1.42	1.73	8.88	1.92	2.38	12.00
.43	.52	2.69	.93	1.13	5.81	1.43	1.74	8.94	1.93	2.35	12.06
.44	.54	2.75	.94	1.14	5.88	1.44	1.75	9.00	1.94	2.36	12.13
.45	.55	2.81	.95	1.16	5.94	1.45	1.76	9.06	1.95	2.37	12.19
.46	.56	2.88	.96	1.17	6.00	1.46	1.78	9.13	1.96	2.38	12.25
.47	.57	2.94	.97	1.18	6.06	1.47	1.79	9.19	1.97	2.40	12.31
.48	.58	3.00	.98	1.19	6.13	1.48	1.80	9.25	1.98	2.41	12.38
.49	.60	3.06	.99	1.20	6.19	1.49	1.81	9.31	1.99	2.42	12.44
2.00	2.43	12.50	2.50	3.04	15.63	3.00	3.65	18.75	3.50	4.26	21.88
2.01	2.44	12.56	2.51	3.05	15.69	3.01	3.66	18.81	3.51	4.27	21.94
2.02	2.46	12.63	2.52	3.06	15.75	3.02	3.67	18.88	3.52	4.28	22.00
2.03	2.47	12.69	2.53	3.08	15.81	3.03	3.68	18.94	3.53	4.29	22.06
2.04	2.48	12.75	2.54	3.09	15.88	3.04	3.70	19.00	3.54	4.30	22.13
2.05	2.49	12.81	2.55	3.10	15.94	3.05	3.71	19.06	3.55	4.32	22.19

TABLE FOR THE CONVERSION OF NITROGEN—*Continued*

N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.
2.06	2.50	12.88	2.56	3.11	16.00	3.06	3.72	19.13	3.56	4.33	22.25
2.07	2.52	12.94	2.57	3.13	16.06	3.07	3.73	19.19	3.57	4.34	22.31
2.08	2.53	13.00	2.58	3.14	16.13	3.08	3.75	19.25	3.58	4.35	22.38
2.09	2.54	13.06	2.59	3.15	16.19	3.09	3.76	19.31	3.59	4.37	22.44
2.10	2.55	13.13	2.60	3.16	16.25	3.10	3.77	19.38	3.60	4.38	22.50
2.11	2.57	13.19	2.61	3.17	16.31	3.11	3.78	19.44	3.61	4.39	22.56
2.12	2.58	13.25	2.62	3.19	16.38	3.12	3.79	19.50	3.62	4.40	22.63
2.13	2.59	13.31	2.63	3.20	16.44	3.13	3.81	19.56	3.63	4.41	22.69
2.14	2.60	13.38	2.64	3.21	16.50	3.14	3.82	19.63	3.64	4.43	22.75
2.15	2.61	13.44	2.65	3.22	16.56	3.15	3.83	19.69	3.65	4.44	22.81
2.16	2.63	13.50	2.66	3.23	16.63	3.16	3.84	19.75	3.66	4.45	22.88
2.17	2.64	13.56	2.67	3.25	16.69	3.17	3.85	19.81	3.67	4.46	22.94
2.18	2.65	13.63	2.68	3.26	16.75	3.18	3.87	19.88	3.68	4.47	23.00
2.19	2.66	13.69	2.69	3.27	16.81	3.19	3.88	19.94	3.69	4.49	23.06
2.20	2.68	13.75	2.70	3.28	16.88	3.20	3.89	20.00	3.70	4.50	23.13
2.21	2.69	13.81	2.71	3.30	16.94	3.21	3.90	20.06	3.71	4.51	23.19
2.22	2.70	13.88	2.72	3.31	17.00	3.22	3.92	20.13	3.72	4.52	23.25
2.23	2.71	13.94	2.73	3.32	17.06	3.23	3.93	20.19	3.73	4.54	23.31
2.24	2.72	14.00	2.74	3.33	17.13	3.24	3.94	20.25	3.74	4.55	23.38
2.25	2.74	14.06	2.75	3.34	17.19	3.25	3.95	20.31	3.75	4.56	23.44
2.26	2.75	14.13	2.76	3.36	17.25	3.26	3.96	20.38	3.76	4.57	23.50
2.27	2.76	14.19	2.77	3.37	17.31	3.27	3.98	20.44	3.77	4.58	23.56
2.28	2.77	14.25	2.78	3.38	17.38	3.28	3.99	20.50	3.78	4.60	23.63
2.29	2.78	14.31	2.79	3.39	17.44	3.29	4.00	20.56	3.79	4.61	23.69
2.30	2.80	14.38	2.80	3.40	17.50	3.30	4.01	20.63	3.80	4.62	23.75
2.31	2.81	14.44	2.81	3.42	17.56	3.31	4.02	20.69	3.81	4.63	23.81
2.32	2.82	14.50	2.82	3.43	17.63	3.32	4.04	20.75	3.82	4.65	23.88
2.33	2.83	14.56	2.83	3.44	17.69	3.33	4.05	20.81	3.83	4.66	23.94
2.34	2.85	14.63	2.84	3.45	17.75	3.34	4.06	20.88	3.84	4.67	24.00
2.35	2.86	14.69	2.85	3.47	17.81	3.35	4.07	20.94	3.85	4.68	24.06
2.36	2.87	14.75	2.86	3.48	17.88	3.36	4.09	21.00	3.86	4.69	24.13
2.37	2.88	14.81	2.87	3.49	17.94	3.37	4.10	21.06	3.87	4.71	24.19
2.38	2.89	14.88	2.88	3.50	18.00	3.38	4.11	21.13	3.88	4.72	24.25
2.39	2.91	14.94	2.89	3.51	18.06	3.39	4.12	21.19	3.89	4.73	24.31
2.40	2.92	15.00	2.90	3.53	18.13	3.40	4.13	21.25	3.90	4.74	24.38
2.41	2.93	15.06	2.91	3.54	18.19	3.41	4.15	21.31	3.91	4.75	24.44
2.42	2.94	15.13	2.92	3.55	18.25	3.42	4.16	21.38	3.92	4.77	24.50
2.43	2.95	15.19	2.93	3.56	18.31	3.43	4.17	21.44	3.93	4.78	24.56
2.44	2.97	15.25	2.94	3.58	18.38	3.44	4.18	21.50	3.94	4.79	24.63
2.45	2.98	15.31	2.95	3.59	18.44	3.45	4.20	21.56	3.95	4.80	24.69
2.46	2.99	15.38	2.96	3.60	18.50	3.46	4.21	21.63	3.96	4.82	24.75
2.47	3.00	15.44	2.97	3.61	18.56	3.47	4.22	21.69	3.97	4.83	24.81
2.48	3.02	15.50	2.98	3.62	18.63	3.48	4.23	21.75	3.98	4.84	24.88
2.49	3.03	15.56	2.99	3.64	18.69	3.49	4.24	21.81	3.99	4.85	24.94
4.00	4.86	25.00	4.50	5.47	28.13	5.00	6.08	31.25	5.50	6.69	34.38
4.01	4.88	25.06	4.51	5.48	28.19	5.01	6.09	31.31	5.51	6.70	34.44
4.02	4.89	25.13	4.52	5.50	28.25	5.02	6.10	31.38	5.52	6.71	34.50
4.03	4.90	25.19	4.53	5.51	28.31	5.03	6.12	31.44	5.53	6.72	34.56
4.04	4.91	25.25	4.54	5.52	28.38	5.04	6.13	31.50	5.54	6.74	34.63
4.05	4.92	25.31	4.55	5.53	28.44	5.05	6.14	31.56	5.55	6.75	34.69
4.06	4.94	25.38	4.56	5.54	28.50	5.06	6.15	31.63	5.56	6.76	34.75
4.07	4.95	25.44	4.57	5.56	28.56	5.07	6.17	31.69	5.57	6.77	34.81
4.08	4.96	25.50	4.58	5.57	28.63	5.08	6.18	31.75	5.58	6.79	34.88
4.09	4.97	25.56	4.59	5.58	28.69	5.09	6.19	31.81	5.59	6.80	34.94
4.10	4.99	25.63	4.60	5.59	28.75	5.10	6.20	31.88	5.60	6.81	35.00
4.11	5.00	25.69	4.61	5.61	28.81	5.11	6.21	31.94	5.61	6.82	35.06

TABLE FOR THE CONVERSION OF NITROGEN—*Continued*

N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.
4.12	5.01	25.75	4.62	5.62	28.88	5.12	6.23	32.00	5.62	6.83	35.13
4.13	5.02	25.81	4.63	5.63	28.94	5.13	6.24	32.06	5.63	6.85	35.19
4.14	5.03	25.88	4.64	5.64	29.00	5.14	6.25	32.13	5.64	6.86	35.25
4.15	5.05	25.94	4.65	5.65	29.06	5.15	6.26	32.19	5.65	6.87	35.31
4.16	5.06	26.00	4.66	5.67	29.13	5.16	6.27	32.25	5.66	6.88	35.38
4.17	5.07	26.06	4.67	5.68	29.19	5.17	6.29	32.31	5.67	6.89	35.44
4.18	5.08	26.13	4.68	5.69	29.25	5.18	6.30	32.38	5.68	6.91	35.50
4.19	5.10	26.19	4.69	5.70	29.31	5.19	6.31	32.44	5.69	6.92	35.56
4.20	5.11	26.25	4.70	5.72	29.38	5.20	6.32	32.50	5.70	6.93	35.63
4.21	5.12	26.31	4.71	5.73	29.44	5.21	6.34	32.56	5.71	6.94	35.69
4.22	5.13	26.38	4.72	5.74	29.50	5.22	6.35	32.63	5.72	6.96	35.75
4.23	5.14	26.44	4.73	5.75	29.56	5.23	6.36	32.69	5.73	6.97	35.81
4.24	5.16	26.50	4.74	5.76	29.63	5.24	6.37	32.75	5.74	6.98	35.88
4.25	5.17	26.56	4.75	5.78	29.69	5.25	6.38	32.81	5.75	6.99	35.94
4.26	5.18	26.63	4.76	5.79	29.75	5.26	6.40	32.88	5.76	7.00	36.00
4.27	5.19	26.69	4.77	5.80	29.81	5.27	6.41	32.94	5.77	7.02	36.06
4.28	5.20	26.75	4.78	5.81	29.88	5.28	6.42	33.00	5.78	7.03	36.13
4.29	5.22	26.81	4.79	5.82	29.94	5.29	6.43	33.06	5.79	7.04	36.19
4.30	5.23	26.88	4.80	5.84	30.00	5.30	6.44	33.13	5.80	7.05	36.25
4.31	5.24	26.94	4.81	5.85	30.06	5.31	6.46	33.19	5.81	7.06	36.31
4.32	5.25	27.00	4.82	5.86	30.13	5.32	6.47	33.25	5.82	7.08	36.38
4.33	5.27	27.06	4.83	5.87	30.19	5.33	6.48	33.31	5.83	7.09	36.44
4.34	5.28	27.13	4.84	5.89	30.25	5.34	6.49	33.38	5.84	7.10	36.50
4.35	5.29	27.19	4.85	5.90	30.31	5.35	6.51	33.44	5.85	7.11	36.56
4.36	5.30	27.25	4.86	5.91	30.38	5.36	6.52	33.50	5.86	7.13	36.63
4.37	5.31	27.31	4.87	5.92	30.44	5.37	6.53	33.56	5.87	7.14	36.69
4.38	5.33	27.38	4.88	5.93	30.50	5.38	6.54	33.63	5.88	7.15	36.75
4.39	5.34	27.44	4.89	5.95	30.56	5.39	6.55	33.69	5.89	7.16	36.81
4.40	5.35	27.50	4.90	5.96	30.63	5.40	6.57	33.75	5.90	7.17	36.88
4.41	5.36	27.56	4.91	5.97	30.69	5.41	6.58	33.81	5.91	7.19	36.94
4.42	5.37	27.63	4.92	5.98	30.75	5.42	6.59	33.88	5.92	7.20	37.00
4.43	5.39	27.69	4.93	5.99	30.81	5.43	6.60	33.94	5.93	7.21	37.06
4.44	5.40	27.75	4.94	6.01	30.88	5.44	6.62	34.00	5.94	7.22	37.13
4.45	5.41	27.81	4.95	6.02	30.94	5.45	6.63	34.06	5.95	7.24	37.19
4.46	5.42	27.88	4.96	6.03	31.00	5.46	6.64	34.13	5.96	7.25	37.25
4.47	5.44	27.94	4.97	6.04	31.06	5.47	6.65	34.19	5.97	7.26	37.31
4.48	5.45	28.00	4.98	6.06	31.13	5.48	6.66	34.25	5.98	7.27	37.38
4.49	5.46	28.06	4.99	6.07	31.19	5.49	6.68	34.31	5.99	7.28	37.44
6.00	7.30	37.50	6.50	7.90	40.63	7.00	8.51	43.75	7.50	9.12	46.88
6.01	7.31	37.56	6.51	7.92	40.69	7.01	8.52	43.81	7.51	9.13	46.94
6.02	7.32	37.63	6.52	7.93	40.75	7.02	8.54	43.88	7.52	9.14	47.00
6.03	7.33	37.69	6.53	7.94	40.81	7.03	8.55	43.94	7.53	9.16	47.06
6.04	7.34	37.75	6.54	7.95	40.88	7.04	8.56	44.00	7.54	9.17	47.13
6.05	7.36	37.81	6.55	7.96	40.94	7.05	8.57	44.06	7.55	9.18	47.19
6.06	7.37	37.88	6.56	7.98	41.00	7.06	8.58	44.13	7.56	9.19	47.25
6.07	7.38	37.94	6.57	7.99	41.06	7.07	8.60	44.19	7.57	9.21	47.31
6.08	7.39	38.00	6.58	8.00	41.13	7.08	8.61	44.25	7.58	9.22	47.38
6.09	7.41	38.06	6.59	8.01	41.19	7.09	8.62	44.31	7.59	9.23	47.44
6.10	7.42	38.13	6.60	8.03	41.25	7.10	8.63	44.38	7.60	9.24	47.50
6.11	7.43	38.19	6.61	8.04	41.31	7.11	8.65	44.44	7.61	9.25	47.56
6.12	7.44	38.25	6.62	8.05	41.38	7.12	8.66	44.50	7.62	9.27	47.63
6.13	7.45	38.31	6.63	8.06	41.44	7.13	8.67	44.56	7.63	9.28	47.69
6.14	7.47	38.38	6.64	8.07	41.50	7.14	8.68	44.63	7.64	9.29	47.75
6.15	7.48	38.44	6.65	8.09	41.56	7.15	8.69	44.69	7.65	9.30	47.81
6.16	7.49	38.50	6.66	8.10	41.63	7.16	8.71	44.75	7.66	9.31	47.88

TABLE FOR THE CONVERSION OF NITROGEN—*Continued*

N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.
6.17	7.50	38.56	6.67	8.11	41.69	7.17	8.72	44.81	7.67	9.33	47.94
6.18	7.51	38.63	6.68	8.12	41.75	7.18	8.73	44.88	7.68	9.34	48.00
6.19	7.53	38.69	6.69	8.14	41.81	7.19	8.74	44.94	7.69	9.35	48.06
6.20	7.54	38.75	6.70	8.15	41.88	7.20	8.76	45.00	7.70	9.36	48.13
6.21	7.55	38.81	6.71	8.16	41.94	7.21	8.77	45.06	7.71	9.38	48.19
6.22	7.56	38.88	6.72	8.17	42.00	7.22	8.78	45.13	7.72	9.39	48.25
6.23	7.58	38.94	6.73	8.18	42.06	7.23	8.79	45.19	7.73	9.40	48.31
6.24	7.59	39.00	6.74	8.20	42.13	7.24	8.80	45.25	7.74	9.41	48.38
6.25	7.60	39.06	6.75	8.21	42.19	7.25	8.82	45.31	7.75	9.42	48.44
6.26	7.61	39.13	6.76	8.22	42.25	7.26	8.83	45.38	7.76	9.44	48.50
6.27	7.62	39.19	6.77	8.23	42.31	7.27	8.84	45.44	7.77	9.45	48.56
6.28	7.64	39.25	6.78	8.24	42.38	7.28	8.85	45.50	7.78	9.46	48.63
6.29	7.65	39.31	6.79	8.26	42.44	7.29	8.86	45.56	7.79	9.47	48.69
6.30	7.66	39.38	6.80	8.27	42.50	7.30	8.88	45.63	7.80	9.48	48.75
6.31	7.67	39.44	6.81	8.28	42.56	7.31	8.89	45.69	7.81	9.50	48.81
6.32	7.69	39.50	6.82	8.29	42.63	7.32	8.90	45.75	7.82	9.51	48.88
6.33	7.70	39.56	6.83	8.31	42.69	7.33	8.91	45.81	7.83	9.52	48.94
6.34	7.71	39.63	6.84	8.32	42.75	7.34	8.93	45.88	7.84	9.53	49.00
6.35	7.73	39.75	6.85	8.33	42.81	7.35	8.94	45.94	7.85	9.55	49.06
6.36	7.73	39.75	6.86	8.34	42.88	7.36	8.95	46.00	7.86	9.56	49.13
6.37	7.75	39.81	6.87	8.35	42.94	7.37	8.96	46.06	7.87	9.57	49.19
6.38	7.76	39.88	6.88	8.37	43.00	7.38	8.97	46.13	7.88	9.58	49.25
6.39	7.77	39.94	6.89	8.38	43.06	7.39	8.99	46.19	7.89	9.59	49.31
6.40	7.78	40.00	6.90	8.39	43.13	7.40	9.00	46.25	7.90	9.61	49.38
6.41	7.79	40.06	6.91	8.40	43.19	7.41	9.01	46.31	7.91	9.62	49.44
6.42	7.81	40.13	6.92	8.41	43.25	7.42	9.02	46.38	7.92	9.64	49.56
6.43	7.82	40.19	6.93	8.43	43.31	7.43	9.03	46.44	7.93	9.64	49.56
6.44	7.83	40.25	6.94	8.44	43.38	7.44	9.05	46.50	7.94	9.66	49.63
6.45	7.84	40.31	6.95	8.45	43.44	7.45	9.06	46.56	7.95	9.67	49.69
6.46	7.86	40.38	6.96	8.46	43.50	7.46	9.07	46.63	7.96	9.68	49.75
6.47	7.87	40.44	6.97	8.48	43.56	7.47	9.08	46.69	7.97	9.69	49.81
6.48	7.88	40.50	6.98	8.49	43.63	7.48	9.10	46.75	7.98	9.70	49.88
6.49	7.89	40.56	6.99	8.50	43.69	7.49	9.11	46.81	7.99	9.72	49.94
8.00	9.73	50.00	8.50	10.34	53.13	9.00	10.94	56.25	9.50	11.55	59.38
8.01	9.74	50.06	8.51	10.35	53.19	9.01	10.96	56.31	9.51	11.56	59.44
8.02	9.75	50.13	8.52	10.36	53.25	9.02	10.97	56.38	9.52	11.58	59.50
8.03	9.76	50.19	8.53	10.37	53.31	9.03	10.98	56.44	9.53	11.59	59.56
8.04	9.78	50.25	8.54	10.38	53.38	9.04	10.99	56.50	9.54	11.60	59.63
8.05	9.79	50.31	8.55	10.40	53.44	9.05	11.00	56.56	9.55	11.61	59.69
8.06	9.80	50.38	8.56	10.41	53.50	9.06	11.02	56.63	9.56	11.62	59.75
8.07	9.81	50.44	8.57	10.42	53.56	9.07	11.03	56.69	9.57	11.64	59.81
8.08	9.83	50.50	8.58	10.43	53.63	9.08	11.04	56.75	9.58	11.65	59.88
8.09	9.84	50.56	8.59	10.45	53.69	9.09	11.05	56.81	9.59	11.66	59.94
8.10	9.85	50.63	8.60	10.46	53.75	9.10	11.06	56.88	9.60	11.67	60.00
8.11	9.86	50.69	8.61	10.47	53.81	9.11	11.08	56.94	9.61	11.69	60.06
8.12	9.87	50.75	8.62	10.48	53.88	9.12	11.09	57.00	9.62	11.70	60.13
8.13	9.89	50.81	8.63	10.49	53.94	9.13	11.10	57.06	9.63	11.71	60.19
8.14	9.90	50.88	8.64	10.51	54.00	9.14	11.11	57.13	9.64	11.72	60.25
8.15	9.91	50.94	8.65	10.52	54.06	9.15	11.13	57.19	9.65	11.73	60.31
8.16	9.92	51.00	8.66	10.53	54.13	9.16	11.14	57.25	9.66	11.75	60.38
8.17	9.93	51.06	8.67	10.54	54.19	9.17	11.15	57.31	9.67	11.76	60.44
8.18	9.95	51.13	8.68	10.55	54.25	9.18	11.16	57.38	9.68	11.77	60.50
8.19	9.96	51.19	8.69	10.57	54.31	9.19	11.18	57.44	9.69	11.78	60.56
8.20	9.97	51.25	8.70	10.58	54.38	9.20	11.19	57.50	9.70	11.80	60.63
8.21	9.98	51.31	8.71	10.59	54.44	9.21	11.20	57.56	9.71	11.81	60.69
8.22	10.00	51.38	8.72	10.60	54.50	9.22	11.21	57.63	9.72	11.82	60.75

TABLE FOR THE CONVERSION OF NITROGEN—*Continued*

N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.	N	NH_3	Prot.
8.23	10.01	51.44	8.73	10.62	54.56	9.23	11.22	57.69	9.73	11.83	60.81
8.24	10.02	51.50	8.74	10.63	54.63	9.24	11.24	57.75	9.74	11.84	60.88
8.25	10.03	51.56	8.75	10.64	54.69	9.25	11.25	57.81	9.75	11.86	60.94
8.26	10.04	51.63	8.76	10.65	54.75	9.26	11.26	57.88	9.76	11.87	61.00
8.27	10.06	51.69	8.77	10.66	54.81	9.27	11.27	57.94	9.77	11.88	61.06
8.28	10.07	51.75	8.78	10.68	54.88	9.28	11.28	58.00	9.78	11.89	61.13
8.29	10.08	51.81	8.79	10.69	54.94	9.29	11.30	58.06	9.79	11.90	61.19
8.30	10.09	51.88	8.80	10.70	55.00	9.30	11.31	58.13	9.80	11.92	61.25
8.31	10.10	51.94	8.81	10.71	55.06	9.31	11.32	58.19	9.81	11.93	61.31
8.32	10.12	52.00	8.82	10.73	55.13	9.32	11.33	58.25	9.82	11.94	61.38
8.33	10.13	52.06	8.83	10.74	55.19	9.33	11.35	58.31	9.83	11.95	61.44
8.34	10.14	52.13	8.84	10.75	55.25	9.34	11.36	58.38	9.84	11.97	61.50
8.35	10.15	52.19	8.85	10.76	55.31	9.35	11.37	58.44	9.85	11.98	61.56
8.36	10.17	52.25	8.86	10.77	55.38	9.36	11.38	58.50	9.86	11.99	61.63
8.37	10.18	52.31	8.87	10.79	55.44	9.37	11.39	58.56	9.87	12.00	61.69
8.38	10.19	52.38	8.88	10.80	55.50	9.38	11.41	58.63	9.88	12.01	61.75
8.39	10.20	52.44	8.89	10.81	55.56	9.39	11.42	58.69	9.89	12.03	61.81
8.40	10.21	52.50	8.90	10.82	55.63	9.40	11.43	58.75	9.90	12.04	61.88
8.41	10.23	52.56	8.91	10.83	55.69	9.41	11.44	58.81	9.91	12.05	61.94
8.42	10.24	52.63	8.92	10.85	55.75	9.42	11.45	58.88	9.92	12.06	62.00
8.43	10.25	52.69	8.93	10.86	55.81	9.43	11.47	58.94	9.93	12.07	62.06
8.44	10.26	52.75	8.94	10.87	55.88	9.44	11.48	59.00	9.94	12.09	62.13
8.45	10.28	52.81	8.95	10.88	55.94	9.45	11.49	59.06	9.95	12.10	62.19
8.46	10.29	52.88	8.96	10.90	56.00	9.46	11.50	59.13	9.96	12.11	62.25
8.47	10.30	52.94	8.97	10.91	56.06	9.47	11.52	59.19	9.97	12.12	62.31
8.48	10.31	53.00	8.98	10.92	56.13	9.48	11.53	59.25	9.98	12.14	62.38
8.49	10.32	53.06	8.99	10.93	56.19	9.49	11.54	59.31	9.99	12.15	62.44
									10.00	12.16	62.50

Determination of Lint on Seed Hulls. Dry to constant weight in a moisture dish 5 grams of hulls, free from meats and seed. Transfer the hulls to a beaker containing 40 cc. of sulfuric acid (sp. g. 1.84). Stir with a glass rod for exactly 30 seconds. Pour immediately into a beaker containing 200 cc. of water. Wash all particles of hulls from the first beaker into the second beaker with 50 cc. more of water. Filter immediately by suction through a linen cloth. Thoroughly washed tracing cloth is recommended. Wash until all the acid is removed, transfer to the original moisture dish and dry at 110° C. to constant weight. Three or more determinations should be made and the average of these agreeing within one per cent reported. Calculate per cent lint on original moisture basis and report as available hull fiber or lint. Multiply this by the factor 0.70 and report as calculated cellulose. This factor takes into consideration the solvent action of the acid on the hulls.

Sampling Oil. The following directions are according to the 1939-40 "Rules" of the National Cottonseed Products Association (U.S.). When oil in barrels is to be sampled, samples shall be drawn from 10 per cent of the barrels selected at random, each sample to be taken from a separate barrel, so as to represent its entire contents, and drawn in such a manner as to prevent any introduction of moisture; each sample so taken shall be sealed and labelled.

In tank cars, a vertical section of the oil from top to bottom of the tank must be taken with an official trier (sampler) which must be furnished by buyer at destination, or seller at shipping point.

This trier has a uniform diameter of two inches and is long enough to take a sample of the entire depth of the tank (usually 10 feet). It is provided with a tight valve at the lower end which allows an unrestricted opening two inches in diameter when fully opened, and is free from leaks when closed. The valve is opened and closed by means of a rod from the top of the trier and so constructed as to take the sample within one-quarter inch or less of the bottom of the tank.

A clean, dry trier must be lowered vertically through the oil with the bottom valve wide open, at a uniform rate, slowly enough to permit the trier to fill as it is lowered. It requires from 10 to 15 seconds to reach the bottom of the tank. The bottom valve is then closed and the trier withdrawn. Several portions of the oil shall be taken in this manner, avoiding any introduction of moisture, and placed in a clean tub or other container. After thorough mixing, a three-gallon sample shall be taken and put into three clean new gallon cans, filling them only within two inches of the top. Each can shall be carefully marked for identification and sealed, but not with sealing wax. One of these portions is sent to a chemist, if requested by either buyer or seller, one to be held in case a second sample is required, and a third for a referee sample.

Attention is called to the following references: "Bibliography of Sampling," D. Wesson [*Oil and Fat Ind.*, **1**, 47 (1924)]; "Sampling Tank Cars," R. W. Perry [*Cotton Oil Press*, **5**, No. 1, 54 (1921)]; "Sampling Committee Report," M. J. Falkenburg [*Cotton Oil Press*, **6**, No. 1, 44 (1922)]; "Sampling Committee Report," P. W. Tompkins [*J. Oil and Fat Ind.*, **1**, 46 (1924)]; "Sampling Deep Sea Tanks," P. W. Tompkins [*Cotton Oil Press*, **5**, No. 10, 29 (1922)].

Too much attention cannot be paid to obtaining proper samples of oil or of anything else. Remember that it is often worse than useless to analyze non-representative samples.

Examination of Crude Oils. Before removing any of the oil, the sample must be warmed, if necessary, to ensure that no solid glycerides ("stearin") remain undissolved. In the case of cottonseed, peanut, soybean, sesame or corn oils, warming until the oil is at 20° C. is usually sufficient. Then mix the sample thoroughly, with the container in an inverted position and proceed to take portions for analysis without delay; otherwise remix sample.

Moisture and Volatile Matter. Weigh 10 grams (accurately) into a weighed metal or porcelain dish and heat gently over a direct flame with a rotating motion, until the oil barely smokes. Cool, weigh and calculate the percentage of moisture and other volatile matter.

Meal and Other Insoluble Matter. Transfer the portion of oil used in the above test to a beaker with the aid of kerosene. Warm until the oil has dissolved and filter through a weighed Gooch crucible. Wash crucible and any residue with petroleum ether until all the oil is removed.

Dry to constant weight at 100° C. Divide the residue obtained by 0.8 and report the per cent of meal or impurities.

Free Fatty Acids. Weigh 7.05 grams of a well-mixed sample of oil into a 4-oz. bottle or 250-cc. flask. Add 50 cc. of 95 per cent alcohol (or U. S. Formula 30) or isoprophylalcohol containing 0.05 per cent of phenolphthalein and previously neutralized with sodium hydroxide solution to a faint pink color. Titrate with a 0.25*N* sodium hydroxide solution until a permanent faint pink color is produced which cannot be removed by violent shaking of the mixture. The per cent of fatty acids as oleic acid is the number of cubic centimeters of 0.25*N* alkali solution used.

The method for testing refined oils is given later.

Refining Loss. The following method is taken from the "Official Methods of Chemical Analysis of the American Oil Chemists' Society."

Apparatus. Scales: 1000 grams capacity, sensitive to ½ gram. Weights: 500 grams to ½ gram. Refining cups: seamless or enameled iron cups, 4 to 4½ inches in diameter and 4 to 4½ inches deep, with a total capacity of about 900 cc.

Refining Apparatus. A mechanical stirrer with two water baths, arranged to hold the refining cups with contents while being stirred. Each water bath contains a false, perforated bottom, properly supported to bear the weight of the refining cups and/or suitable lugs to hold the cups in place, about one inch above the bottom of the bath. Each bath is provided with a water supply and a large drain pipe for emptying rapidly. Gas or steam is provided for heating. One bath is maintained at a temperature of 20° to 24° C. and the other at 63° to 67° C. A single water bath may be used in place of two separate baths, if suitable arrangements are made so that water may be raised from the low temperature to the specified high temperature within 60 seconds. This may be accomplished by introducing live steam or by rapidly emptying the bath and refilling with water previously heated to the required temperature. The water in each bath must be continuously agitated to insure uniform temperature, and the level of the water must be as high as the level of the oil and lye in the refining cups. The paddles are T-shaped with blades one inch wide and 3½ inches over all. They are at right angles to the shaft of the paddle. Each paddle must be driven by gears, actuated by a motor of sufficient capacity to drive all the paddles simultaneously at the specified speeds under a maximum load. The bottom of the paddle must be approximately one quarter inch above the bottom of the refining cup when in use. The speed of the paddles (in the refining cups) in the cold water bath shall be 250 ± 10 r p m and in the hot water bath 70 ± 5 r p m.

Sodium Hydroxide Solutions. These solutions must be of accurately known sodium hydroxide content, free from carbonate and other impurities and must be prepared in the following manner: A super-saturated solution is first prepared by adding to each kilogram of pure dry solid sodium hydroxide broken up into small pieces, ¾ of a kilogram of distilled water. Heat on the steam bath with occasional stirring, for at least

three hours. Then allow to settle and cool for 24 to 48 hours, keeping the vessel covered, to exclude the air as far as possible. During the cooling, a portion of the sodium hydroxide which had dissolved in the hot solution will crystallize, and under these conditions the solution will then contain no measurable amount of carbonate. If such crystals do not separate, the solution is not supersaturated. Decant the solution from the residue, and if not perfectly clear, filter through asbestos. Dilute to the various concentrations required with distilled water which has been previously boiled and cooled. The final strength of the diluted solutions must be adjusted by actual titration and not by specific gravity tests. The important point is to know the exact content of sodium hydroxide rather than the exact specific gravity or Baumé. Only solutions of the strengths given shall be used, and they must be within the limits shown.

Choice of Lye. The maximum amount of sodium hydroxide allowable for refining shall be calculated from the following formulas, for all

SODIUM HYDROXIDE TABLE

Nominal Degrees Baumé at 15° C.	Actual NaOH Content	Allowable Variations Minimum Per Cent	Allowable Variations Maximum Per Cent
10	6.57	6.44	6.70
12	8.00	7.84	8.10
14	9.50	9.31	9.69
16	11.06	10.84	11.28
18	12.68	12.43	12.93
20	14.36	14.07	14.65
22	16.09	15.77	16.41
24	17.87	17.51	18.23
26	19.70	19.31	20.09
28	21.58	21.15	22.01
30	23.50	23.03	23.97

percentages of free fatty acids (F. F. A.) for hydraulic- or hot-pressed oils:

$$\frac{\text{F. F. A.}}{5.2} + 0.54 = \text{Maximum sodium hydroxide.}$$

For expeller (so-called cold-pressed) oil:

$$\frac{\text{F. F. A.}}{4.365} + 0.77 = \text{Maximum sodium hydroxide.}$$

The strengths of lye (expressed in Baumé degrees) to be used for refining oils of various F. F. A. shall be as follows:

Per Cent F. F. A.	Hydraulic Oil ° Bé.	Expeller Oil ° Bé.
1.5 or less	12 and 14	16 and 20
1.6 to 3.0	12 and 16	16 and 20
3.1 to 4.0	14 and 18	16 and 20
4.1 to 5.0	16 and 20	16 and 20
5.1 to 7.5	18 and 22	20 and 26
7.6 to 10.0	20 and 24	20 and 26
10.1 to 15.0	20 and 26	20 and 30
Over 15.0	22 and 28	20 and 30

Solutions of sodium hydroxide must not be over three months old when used.

The following tables show the required percentage of each strength of lye allowable.

Refining Test. Place 500 grams of the thoroughly mixed sample of crude oil in a weighed refining cup and place in the cold water bath of the refining equipment. Start the agitator at slow speed and adjust the temperature of bath and oil to 20° to 24° C., using ice in the bath, if necessary, to get the desired temperature. Increase the speed of the agitator to 250 ± 10 r p m, add the calculated quantity of sodium hydroxide solution (weighed in a small beaker or flask) as quickly as possible, but avoiding any splashing, and continue the agitation for 15 minutes (45 minutes in the case of expeller oils or other slow "breaking" type of oil from the time the lye is added. Then transfer without delay to the 65° C. water bath and stir at 70 ± 5 r p m for twelve minutes. The temperature of the oil must then be 60° to 65° C. Adjust the temperature of the

LYE REQUIRED FOR HYDRAULIC- OR HOT-PRESSED OILS

F. F. A. (%)	80% of Max. NaOH	12° (80%)	14° (80%)		F. F. A. (%)	Max NaOH	16° Max.	20° Max.
0.5	0.51	6.4	5.4		4.1	1.33	12.0	9.3
0.6	0.52	6.6	5.5		4.2	1.35	12.2	9.4
0.7	0.54	6.7	5.6		4.3	1.37	12.4	9.5
0.8	0.55	6.9	5.8		4.4	1.39	12.6	9.7
0.9	0.57	7.1	6.0		4.5	1.41	12.7	9.8
1.0	0.58	7.3	6.2		4.6	1.43	12.9	9.9
1.1	0.60	7.5	6.3		4.7	1.45	13.1	10.1
1.2	0.62	7.7	6.5		4.8	1.47	13.3	10.2
1.3	0.63	7.9	6.6		4.9	1.49	13.5	10.3
1.4	0.65	8.1	6.8		5.0	1.50	13.6	10.4
1.5	0.67	8.3	7.0				18° Max.	22° Max.
					5.1	1.52	12.0	9.4
	Max. NaOH		16°-80%	16° Max.	5.2	1.54	12.1	9.6
					5.3	1.56	12.3	9.7
1.6	0.85	8.5	6.2	7.7	5.4	1.58	12.5	9.8
1.7	0.87	8.7	6.3	7.9	5.5	1.60	12.6	10.0
1.8	0.89	8.9	6.4	8.0	5.6	1.62	12.8	10.1
1.9	0.91	9.1	6.6	8.2	5.7	1.64	12.9	10.2
2.0	0.93	9.3	6.7	8.4	5.8	1.66	13.1	10.3
2.1	0.95	9.5	6.9	8.6	5.9	1.68	13.2	10.4
2.2	0.97	9.7	7.0	8.8	6.0	1.70	13.4	10.6
2.3	0.99	9.9	7.1	8.9	6.1	1.71	13.4	10.7
2.4	1.01	10.1	7.3	9.1	6.2	1.73	13.6	10.8
2.5	1.03	10.3	7.4	9.3	6.3	1.75	13.8	10.9
2.6	1.05	10.5	7.6	9.5	6.4	1.77	14.0	11.0
2.7	1.07	10.7	7.8	9.7	6.5	1.79	14.1	11.1
2.8	1.08	10.8	7.9	9.8	6.6	1.81	14.3	11.2
2.9	1.10	11.0	8.0	10.0	6.7	1.83	14.4	11.4
3.0	1.12	11.2	8.1	10.1	6.8	1.85	14.6	11.5
					6.9	1.87	14.7	11.6
		14° Max.	18° Max.		7.0	1.89	14.9	11.7
3.1	1.14	12.0	9.0		7.1	1.91	15.1	11.9
3.2	1.16	12.2	9.2		7.2	1.93	15.2	12.0
3.3	1.18	12.4	9.3		7.3	1.95	15.4	12.1
3.4	1.20	12.6	9.5		7.4	1.97	15.5	12.2
3.5	1.22	12.8	9.6		7.5	1.99	15.7	12.4
3.6	1.23	13.0	9.7					
3.7	1.25	13.2	9.9					
3.8	1.27	13.4	10.0					
3.9	1.29	13.6	10.2					
4.0	1.31	13.8	10.4					

F. F. A. (%)	Max. NaOH	20° Max.	24° Max.	F. F. A. (%)	Max. NaOH	20° Max.	26° Max.
7.6	2.0	14.0	11.2	11.1	2.67	18.6	13.6
7.7	2.02	14.1	11.3	11.2	2.69	18.7	13.7
7.8	2.04	14.2	11.4	11.3	2.71	18.9	13.8
7.9	2.06	14.3	11.5	11.4	2.73	19.0	13.9
8.0	2.08	14.5	11.6	11.5	2.75	19.1	14.0
8.1	2.10	14.6	11.7	11.6	2.76	19.2	14.0
8.2	2.12	14.8	11.9	11.7	2.78	19.4	14.1
8.3	2.14	14.9	12.0	11.8	2.80	19.5	14.2
8.4	2.16	15.0	12.1	11.9	2.82	19.6	14.3
8.5	2.18	15.2	12.2	12.0	2.84	19.8	14.4
8.6	2.19	15.3	12.3	12.1	2.86	19.9	14.5
8.7	2.21	15.4	12.4	12.2	2.88	20.0	14.6
8.8	2.23	15.5	12.5	12.3	2.90	20.2	14.7
8.9	2.25	15.7	12.6	12.4	2.92	20.3	14.8
9.0	2.27	15.8	12.7	12.5	2.94	20.4	14.9
9.1	2.29	15.9	12.8	12.6	2.95	20.5	15.0
9.2	2.31	16.1	12.9	12.7	2.97	20.7	15.1
9.3	2.33	16.2	13.0	12.8	2.99	20.8	15.2
9.4	2.35	16.4	13.2	12.9	3.01	21.0	15.3
9.5	2.37	16.5	13.3	13.0	3.03	21.1	15.4
9.6	2.38	16.6	13.4	13.1	3.05	21.2	15.5
9.7	2.40	16.7	13.5	13.2	3.07	21.4	15.6
9.8	2.42	16.9	13.6	13.3	3.09	21.5	15.7
9.9	2.44	17.0	13.7	13.4	3.11	21.7	15.8
10.0	2.46	17.1	13.8	13.5	3.13	21.8	15.9
				13.6	3.15	21.9	16.0
				13.7	3.17	22.1	16.1
				13.8	3.19	22.2	16.2
				13.9	3.21	22.3	16.3
			26° Max.	14.0	3.23	22.5	16.4
10.1	2.48	17.3	12.6	14.1	3.24	22.6	16.5
10.2	2.50	17.4	12.7	14.2	3.26	22.7	16.6
10.3	2.52	17.6	12.8	14.3	3.28	22.8	16.7
10.4	2.54	17.7	12.9	14.4	3.30	23.0	16.8
10.5	2.56	17.8	13.0	14.5	3.32	23.1	16.9
10.6	2.57	17.9	13.1				
10.7	2.59	18.0	13.1				
10.8	2.61	18.2	13.2				
10.9	2.63	18.3	13.3				
11.0	2.65	18.5	13.4				
						22° Max.	
14.6	3.34	23.2	17.0	18.1	4.02	25.0	18.6
14.7	3.36	23.4	17.1	18.2	4.04	25.1	18.7
14.8	3.38	23.5	17.2	18.3	4.06	25.2	18.8
14.9	3.40	23.7	17.3	18.4	4.08	25.4	18.9
15.0	3.42	23.8	17.4	18.5	4.10	25.5	19.0
				18.6	4.11	25.6	19.0
				18.7	4.13	25.7	19.1
				18.8	4.15	25.8	19.2
				18.9	4.17	25.9	19.3
		22° Max.	28° Max.	19.0	4.19	26.1	19.4
15.1	3.44	21.4	15.9	19.1	4.21	26.2	19.5
15.2	3.46	21.5	16.0	19.2	4.23	26.3	19.6
15.3	3.48	21.6	16.1	19.3	4.25	26.4	19.7
15.4	3.50	21.8	16.2	19.4	4.27	26.5	19.8
15.5	3.52	21.9	16.3	19.5	4.29	26.7	19.9
15.6	3.54	22.0	16.4	19.6	4.30	26.8	19.9
15.7	3.56	22.1	16.5	19.7	4.32	26.9	20.0
15.8	3.58	22.3	16.6	19.8	4.34	27.0	20.1
15.9	3.60	22.4	16.7	19.9	4.36	27.1	20.2
16.0	3.62	22.5	16.8	20.0	4.38	27.2	20.3
16.1	3.63	22.6	16.8				

F. F. A. (%)	Max. NaOH	22° Max.	28° Max.
16.2	3.65	22.7	16.9
16.3	3.67	22.8	17.0
16.4	3.69	22.9	17.1
16.5	3.71	23.1	17.2
16.6	3.73	23.2	17.3
16.7	3.75	23.3	17.4
16.8	3.77	23.4	17.5
16.9	3.79	23.6	17.6
17.0	3.81	23.7	17.7
17.1	3.82	23.8	17.7
17.2	3.84	23.9	17.8
17.3	3.86	24.0	17.9
17.4	3.88	24.1	18.0
17.5	3.90	24.3	18.1
17.6	3.92	24.4	18.2
17.7	3.94	24.5	18.3
17.8	3.96	24.6	18.4
17.9	3.98	24.7	18.4
18.0			

LYE REQUIRED FOR EXPELLER OR WHOLE SEED PRESSED OILS

F. F. A. (%)	Max. NaOH	16° (80%)	20° (80%)	20° Max.	F. F. A. (%)	Max. NaOH	20° Max.	26° Max.
0.5	0.88	6.4	4.9	6.1	5.1	1.94	13.5	9.9
0.6	0.91	6.6	5.0	6.3	5.2	1.96	13.6	10.0
0.7	0.93	6.7	5.2	6.5	5.3	1.98	13.8	10.1
0.8	0.95	6.9	5.3	6.6	5.4	2.01	14.0	10.2
0.9	0.98	7.0	5.4	6.8	5.5	2.03	14.1	10.3
1.0	1.00	7.2	5.6	7.0	5.6	2.05	14.3	10.4
1.1	1.02	7.4	5.7	7.1	5.7	2.07	14.4	10.6
1.2	1.04	7.5	5.8	7.2	5.8	2.10	14.6	10.7
1.3	1.07	7.7	5.9	7.4	5.9	2.12	14.8	10.8
1.4	1.09	7.8	6.1	7.6	6.0	2.14	14.9	10.9
1.5	1.11	8.0	6.2	7.7	6.1	2.17	15.0	11.0
1.6	1.14	8.2	6.3	7.9	6.2	2.19	15.2	11.1
1.7	1.16	8.4	6.5	8.1	6.3	2.21	15.4	11.2

Table continued on page 449.

water bath, if necessary, within the limits specified to obtain this final oil temperature. Stop agitator and allow to settle in a water bath at 65° C. for one hour. Cool by setting refining cup in a water bath at 20° to 24° C. for at least one hour and a half, and preferably overnight. Weigh the refining cup and contents, and deduct this weight from the weight at the beginning of the test to obtain the loss due to evaporation of moisture. Decant the refined oil into a weighed refining cup, allowing the oil to drain from the soap stock for 30 minutes. This oil is to be used for the determination of its grade. Weigh both the oil and soap stock cups and contents. Melt the soap stock by setting the refining cup containing it in a water bath heated to 75° ± 2° C., without stirring the soap, for 30 minutes. Cool in a cold water bath for 15 minutes or until thoroughly chilled. Decant and drain for 15 minutes any oil into a weighed container. Weigh this oil and add the weight to that of the refined oil previously obtained and subtract it from the previous weight of the soap stock. Repeat the remelting, cooling, and decanting as described above,

LYE REQUIRED FOR EXPELLER OR WHOLE SEED PRESSED OILS—*Continued*

F. F A. (%)	Max. NaOH	16° (80%)	20° (80%)	20° Max.	F. F. A. (%)	Max. NaOH	20° Max.	26° Max.
1.8	1.18	8.6	6.6	8.2	6.4	2.23	15.5	11.3
1.9	1.20	8.7	6.7	8.3	6.5	2.25	15.7	11.4
2.0	1.23	8.9	6.8	8.5	6.6	2.28	15.9	11.5
2.1	1.25	9.0	7.0	8.7	6.7	2.30	16.0	11.6
2.2	1.28	9.2	7.1	8.9	6.8	2.33	16.2	11.7
2.3	1.30	9.4	7.3	9.1	6.9	2.35	16.4	11.9
2.4	1.32	9.5	7.4	9.2	7.0	2.37	16.5	12.0
2.5	1.34	9.7	7.5	9.3	7.1	2.40	16.7	12.2
2.6	1.37	9.8	7.6	9.5	7.2	2.42	16.8	12.3
2.7	1.39	10.0	7.7	9.7	7.3	2.44	17.0	12.4
2.8	1.41	10.2	7.8	9.8	7.4	2.46	17.1	12.5
2.9	1.43	10.3	8.0	10.0	7.5	2.49	17.3	12.6
3.0	1.45	10.5	8.1	10.1	7.6	2.51	17.5	12.7
					7.7	2.53	17.6	12.8
		16° Max.	20° Max.		7.8	2.55	17.8	12.9
					7.9	2.58	18.0	13.1
3.1	1.48	13.3	10.3		8.0	2.60	18.1	13.2
3.2	1.50	13.5	10.5		8.1	2.62	18.3	13.3
3.3	1.53	13.7	10.7		8.2	2.65	18.5	13.5
3.4	1.55	13.9	10.8		8.3	2.67	18.6	13.6
3.5	1.57	14.1	10.9		8.4	2.69	18.7	13.7
3.6	1.59	14.4	11.1		8.5	2.72	18.9	13.8
3.7	1.62	14.6	11.3		8.6	2.74	19.1	13.9
3.8	1.64	14.8	11.5		8.7	2.76	19.2	14.0
3.9	1.66	15.0	11.6		8.8	2.79	19.4	14.2
4.0	1.69	15.2	11.8		8.9	2.81	19.6	14.3
4.1	1.71	15.4	11.9		9.0	2.83	19.7	14.4
4.2	1.73	15.6	12.0		9.1	2.85	19.9	14.5
4.3	1.75	15.8	12.2		9.2	2.87	20.0	14.6
4.4	1.78	16.1	12.4		9.3	2.90	20.2	14.7
4.5	1.80	16.3	12.5		9.4	2.92	20.4	14.8
4.6	1.82	16.5	12.7		9.5	2.94	20.5	14.9
4.7	1.85	16.7	12.9		9.6	2.97	20.7	15.1
4.8	1.88	17.0	13.1		9.7	2.99	20.8	15.2
4.9	1.90	17.2	13.2		9.8	3.01	21.0	15.3
5.0	1.92	17.4	13.3		9.9	3.03	21.1	15.4
					10.0	3.06	21.3	15.5

until the recovered oil from the last remelting does not amount to more than 1.5 grams. In cases where the soapstock does not solidify, the last of the oil can best be removed from the surface of the soap-stock with a pipette.

Filter the oil which was first decanted from the soap stock and measure its color.

Note that any soap stock floating on the surface of the oil, or decanted with the oil, must be recovered and added to the main soap stock before the oil and the soap stock are weighed. This can conveniently be accomplished by decanting the oil through a common tea strainer with a fine-mesh screen which will retain the floating soap stock. Brass or copper refining equipment, unless plated with nickel or tin, should not be used because any copper dissolved by the oil affects its color.

Calculations. Determine the refining loss by the two following methods of calculation, the results of which should check within 0.25 per cent. Report the average of the two methods of calculation. (1) Weight of

crude oil minus weight of refined oil gives refining loss. (2) Weight of soap stock plus loss in evaporation, minus weight of sodium hydroxide solution used gives refining loss.

Note. The above directions are the result of a very extensive investigation made by the Refining Committee of the American Oil Chemists' Society and attention is called to the necessity of following these directions with regard to every detail; otherwise, satisfactory results cannot be obtained.

Crude Peanut Oil. The method of refining shall follow the same general procedure as that described for cottonseed oil, but the oil and alkali should be agitated for 30 minutes. Make 3 refinings using the following strengths and quantities of sodium hydroxide:

Oils with 3 per cent or less of free fatty acids: 12° Baumé sodium hydroxide solution, using 60 per cent of the maximum amount calculated by the formula given for hydraulic-expressed cottonseed oil.

With 16° Baumé sodium hydroxide solution, make one test with 60 per cent and another with 80 per cent of the calculated maximum amount of sodium hydroxide.

Oils containing over 3 per cent of free fatty acids: 16° Baumé sodium hydroxide solution, using 60 per cent of the calculated maximum amount of sodium hydroxide. Make another test with 16° Baumé and a third test with 20° Baumé sodium hydroxide solution, using in each case 80 per cent of the calculated maximum amount of alkali.

A table is given showing the required percentages of each strength of sodium hydroxide to be used.

Crude Coconut Oil. The method of refining shall follow the same general procedure as that described for cottonseed oil. The strength of sodium hydroxide solution to be used shall be 20° Baumé in all cases, the quantity to be calculated as follows: % free fatty acids (as oleic acid) x 1.10 = % of 20° Baumé sodium hydroxide solution.

Add 0.1 per cent of dry table salt to the oil to be refined for each per cent of free fatty acids it contains. Then add the sodium hydroxide solution, agitate (250 r p m) for 5 minutes; transfer to bath (50 to 53° C.) and continue to agitate the mixture at 70 r p m for 5 minutes. Transfer to a bath at 26-30° C. and allow the soapstock to settle for at least 1.5 hours and preferably for overnight, before separating and weighing the oil and soapstock. The weight of table salt added is to be deducted before calculating the refining loss.

Crude Soybean (Hydraulic and Expeller) Oil. The method of refining shall follow the same general procedure as that described for cottonseed oil. The strength of the sodium hydroxide solution shall be 12° Baumé for expeller oil and 20° for hydraulic oil. Two refining tests shall be made on each oil, using the maximum amount of sodium hydroxide as calculated with the formula $\frac{\text{F.F.A.}}{5.2} = 0.54$, and two-thirds of this maximum quantity.

Expeller oil shall be agitated (250 r p m) at 20°-24° C. for 90 minutes after addition of sodium hydroxide solution. Then it shall be trans-

REQUIRED HYDROXIDE FOR REFINING PEANUT OILS
(PERCENTAGES)

F. F. A.	12° Baumé	16° Baumé 60%	16° Baumé 80%	20° Baumé 80%	F.F.A.	16° Baumé 60%	16° Baumé 80%	20° Bé.
0.1	4.2	3.0	4.0		5.1	8.3	11.1	8.4
0.2	4.4	3.2	4.2		5.2	8.4	11.2	8.6
0.3	4.5	3.3	4.4		5.3	8.5	11.3	8.7
0.4	4.7	3.4	4.5		5.4	8.6	11.4	8.8
0.5	4.8	3.5	4.6		5.5	8.7	11.6	8.9
0.6	4.9	3.6	4.7		5.6	8.8	11.7	9.0
0.7	5.0	3.7	4.9		5.7	8.9	11.8	9.1
0.8	5.2	3.8	5.0		5.8	9.0	12.0	9.2
0.9	5.3	3.9	5.2		5.9	9.1	12.1	9.3
1.0	5.5	4.0	5.3		6.0	9.2	12.2	9.4
1.1	5.6	4.1	5.4		6.1	9.3	12.3	9.5
1.2	5.8	4.2	5.6		6.2	9.4	12.5	9.6
1.3	5.9	4.3	5.7		6.3	9.5	12.6	9.8
1.4	6.1	4.4	5.8		6.4	9.7	12.8	9.9
1.5	6.2	4.5	6.0		6.5	9.8	12.9	10.0
1.6	6.4	4.6	6.2		6.6	9.9	13.0	10.1
1.7	6.5	4.7	6.3		6.7	10.0	13.2	10.2
1.8	6.7	4.8	6.4		6.8	10.1	13.3	10.3
1.9	6.8	4.9	6.6		6.9	10.2	13.5	10.4
2.0	7.0	5.0	6.7		7.0	10.3	13.6	10.6
2.1	7.1	5.1	6.9		7.1	10.4	13.7	10.7
2.2	7.3	5.2	7.0		7.2	10.5	13.9	10.8
2.3	7.4	5.3	7.1		7.3	10.6	14.0	10.9
2.4	7.6	5.5	7.3		7.4	10.7	14.2	11.0
2.5	7.7	5.6	7.4		7.5	10.8	14.3	11.1
2.6	7.9	5.7	7.6		7.6	10.9	14.4	11.2
2.7	8.0	5.8	7.8		7.7	11.0	14.6	11.3
2.8	8.1	5.9	7.9		7.8	11.1	14.7	11.4
2.9	8.3	6.0	8.0		7.9	11.2	14.9	11.5
3.0	8.4	6.1	8.1		8.0	11.3	15.0	11.6
3.1		6.2	8.2	6.4	8.1	11.4	15.1	11.7
3.2		6.3	8.4	6.5	8.2	11.5	15.3	11.8
3.3		6.4	8.6	6.6	8.3	11.6	15.4	11.9
3.4		6.5	8.7	6.7	8.4	11.7	15.6	12.0
3.5		6.6	8.8	6.8	8.5	11.8	15.7	12.1
3.6		6.7	8.9	6.9	8.6	11.9	15.9	12.2
3.7		6.8	9.0	7.0	8.7	12.0	16.0	12.3
3.8		6.9	9.2	7.1	8.8	12.1	16.2	12.4
3.9		7.0	9.3	7.2	8.9	12.2	16.3	12.5
4.0		7.1	9.4	7.3	9.0	12.3	16.5	12.6
4.1		7.2	9.6	7.4	9.1	12.4	16.6	12.7
4.2		7.3	9.8	7.5	9.2	12.5	16.8	12.9
4.3		7.4	9.9	7.6	9.3	12.6	16.9	13.0
4.4		7.5	10.1	7.7	9.4	12.7	17.0	13.1
4.5		7.6	10.2	7.8	9.5	12.8	17.1	13.2
4.6		7.7	10.3	7.9	9.6	12.9	17.2	13.3
4.7		7.9	10.5	8.0	9.7	13.0	17.4	13.4
4.8		8.0	10.6	8.1	9.8	13.1	17.5	13.5
4.9		8.1	10.8	8.2	9.9	13.2	17.7	13.6
5.0		8.2	10.9	8.3	10.0	13.3	17.8	13.7

ferred immediately to a bath at 65° C. and stirred at about 70 r p m for exactly 12 minutes; its temperature then must be 60°-65° C.

Hydraulic oil shall be refined in the same manner as described for expeller oil, except that after the addition of sodium hydroxide solution, the agitation shall be for a period of 45 minutes.

Settling of the soapstock. At the end of the 12-minute period of slow agitation, both hydraulic and expeller oils shall be placed in a bath at

65° C. for one hour, and then transferred and held for one hour in the bath at 20-24° C. The oil shall be allowed to stand overnight before pouring it off from the soapstock.

If it has become warm overnight, the stock should be placed in the bath at 20°-24° C. for 30 minutes to harden before attempting to pour off the oil. Weigh and calculate the refining loss as directed under refining of cottonseed oil.

Crude Corn Oil. The apparatus and general procedure shall be exactly as prescribed for hydraulic-pressed cottonseed oil with the following exceptions: The choice of sodium hydroxide shall be a concentration of 16° Bé. in all cases. Two refining tests shall always be made, using respectively one-half and two-thirds of the maximum quantity of sodium hydroxide permitted for hydraulic-pressed crude cottonseed oil having the same free fatty acids. The soapstock may be hardened by chilling in ice water, if necessary, to permit draining of the oil.

Other Oils. Crude oils such as sesame, safflower, poppy, rape and sunflower can be refined according to the directions given for soybean oil. Linseed oil may be refined according to the method for crude cottonseed oil.

Remarks. In cases where the soapstock (refining foots) is so soft that it is impossible to separate the oil by draining, as much of the refined oil as possible is decanted and the remainder removed by a pipette and added to the rest of the oil before it is weighed.

Bleach Test. The scales, refining cups, and stirring machine referred to are those specified under refining, but the T-shaped paddles for agitation are one-half inch wide instead of one inch as used in the refining test. Gas burners or electric heaters may be used for heating the oils to be tested.

Weigh 300 grams of the refined oil into a refining cup. Heat to 120° C. and add 6 per cent of official fuller's earth obtained from the American Oil Chemists' Society. Stir at 250 r p m (± 5) for 5 minutes, not allowing the temperature to fall below 105° C., and filter through filter paper. After sufficient oil has filtered to insure clearness, collect a sample for color reading. Cool and read color immediately as prescribed under *Color*.

Note. According to the rules of the American Oil Chemists' Society, a fresh supply of fuller's earth must be used each year beginning August first; it may be purchased from the Society's Secretary.

Measurement of Color. The following apparatus is used for reading the color of refined oils: The tintometer consists of a light-proof box with a dull black interior which contains a 100-watt "daylight" electric bulb, a block of magnesia with white reflecting surface set at a proper angle to reflect the light vertically upward through the tube containing the sample of oil and through the standard color glasses alongside the tube of oil, and receptacles for holding the tube of oil and the color glasses so that the light passing through both may be observed simultaneously.

Red and yellow standard Lovibond glasses, of suitable numbers, to match the colors of the oils to be examined (in the United States, the red

glasses are to be standardized by the National Bureau of Standards). The minimum standard set shall consist of the following numbers of red and yellow glasses: Red: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 6.0, 7.0, 7.6, 8.0, 9.0, 10.0, 11.0, 12.0, 16.0 and 20.0. Yellow: 1.0, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0 and 35.0. For measuring the color of corn and soybean oils, 50.0 and 70.0 yellow glasses are required in addition to those listed.

Tubes for holding the samples of oil to be examined must have a flat, smooth, polished bottom of clear colorless glass, not less than ¾ inch inside diameter and provided with a mark to indicate an oil column 5¼ inches in depth.

Determination of Color. Fill a tube to a depth of 5¼ inches with the oil to be examined. The oil must be at approximately room temperature and free from turbidity. Unless it is clear and transparent, filter it through a close-texture white filter paper and note on the report that filtration was necessary. If, however, the oil or fat under examination is not completely liquid at 20° C., heat until liquefied and read the color at a temperature not more than 10° C. above that at which it becomes completely liquefied. Place the tube containing the oil in the tintometer and place alongside of it such yellow and red glasses as are necessary, observing the colors of the oil and glasses through the eyepiece. For matching the color, use only one yellow glass: 35 yellow for refined cottonseed and peanut oils; 70 yellow for refined soybean oil; 30 yellow for refined coconut oil; not more than 2 red glasses up to and including 13.0 red, and not more than 3 red glasses above 13.0 red. If an oil is darker than 50 red, report it as 50 plus.

The ratio of yellow to red in determining color shall be made as follows, except when the Association "Rules" specify the yellow or red to be used for determining given grades:

Refined cottonseed oil: 35 yellow with necessary red to obtain best match.

Refined bleached cottonseed oil: 10 yellow to 1 red.

Refined peanut oil: 35 yellow with necessary red, if red is 3.5 or more.

Refined bleached peanut oil: 10 yellow to 1 red, if red is below 3.5.

Refined coconut or palm kernel oils (or bleached oils): 10 yellow to 1 red, if red is 3.9 or more, and 6 yellow to 1 red, if red is less than 3.9.

Refined bleached soybean oil: 10 yellow to 1 red if red is less than 3.5.

Refined corn oil: 70 yellow if red is more than 3.5.

For specifications covering the grades of crude and refined oils a recent or current edition of "Rules" published by the National Cottonseed Products' Association (of the United States) should be consulted.

Remarks and References. Attention is called to the electrically controlled Hardy Recording Spectrophotometer (General Electric Co.), which eliminates all visual errors in colorimetry [*Oil and Fat Ind.*, 6, No. 9, 31 (1929)] and which permits the exact measurement of colors. The colorimeter adopted by the American Oil Chemists' Society in 1929 is a modification of the Wesson Tintometer, and is manufactured by the

A. H. Thomas Co. of Philadelphia, Pa. When desired, a set of 31 Lovibond glasses is also furnished.

References: "Color Grading of Cotton Seed Oil," I. G. Priest, [*Cotton Oil Press,* **3,** No. 3, 86 (1919)]; "Soy Bean Oil," [*ibid.,* **3,** No. 9, 37 (1920)]; "Color Measurement," C. W. Keuffel [*Pt., Oil and Chem. Rev.,* **82,** No. 5, 10 (1926)]; "Munsell Color System" (for measurement of color of solids such as cottonseed or other meals), [*U. S. Bur. of Standards Tech. Paper,* **167**]; "The Lovibond Color System: A Spectrophotometric Analysis of Lovibond Glasses," K. S. Gibson, F. K. Harris and I. G. Priest [*U. S. Bur. Standards Sci. Paper,* **547,** 1927]; "Calibration of Sixty-five 35 Yellow Lovibond Glasses," I. G. Priest, D. B. Judd, K. S. Gibson and G. K. Walker [*Bur. Standards J. Research,* **2,** 793 (1929)].

Cold Test. Fill a 4-ounce sample bottle with a "wintered" oil at 25° C., insert a cork tightly and seal with molten paraffin wax. Submerge the bottle completely in a bucket of finely cracked ice and add cold water until it reaches the top of the bottle. Add more ice when necessary in order to keep the bucket solidly filled with it. After 5½ hours, remove the bottle and examine the condition of the oil. Properly wintered oil will remain clear, brilliant and limpid under the conditions described.

Total Neutral Oil. A method proposed by David Wesson and further studied by Jamieson and Baughman [*Cotton Oil Press,* **6,** No. 4, 33 (1922)] enables the analyst to determine the quantity of neutral oil in a crude cottonseed or other oil as well as the fatty acids and by difference, the quantity of non-oil constituents. Further study by Wesson [*Oil and Fat Ind.,* **3,** 307 (1926)] has shown that in the case of crude oil of prime quality the refinery recovers close to 96.5 per cent of the quantity of neutral oil shown by this method to be present in the crude oil. With crude oils of lower grade, no such definite relation between the refined oil obtained and the neutral oil present was found. However, the method can be used as a basis in the evaluation of crude cottonseed and other oils.

The method has been further studied and described in more detail in connection with the determination of the "break" in linseed oil by Jamieson [*Oil and Fat Ind.,* **3,** 307 (1926)].

The method is as follows: Weigh accurately 10 grams of the sample in a 50-cc. flask and transfer with the aid of petroleum ether to a 500-cc. pear-shaped separatory funnel, using in all 50 cc. of low-boiling solvent (B. Pt. less than 80° C.). Have the stopcock of the separatory funnel lubricated with water. Agitate the oil and solvent until a homogeneous solution is formed. Add 10 cc. of a 14 per cent potassium hydroxide solution, insert the stopper and shake vigorously for 3 minutes. Then add 25 cc. of 50 per cent alcohol and shake for 15 or 20 seconds. Allow to stand until the mixture separates into 2 layers. If the alcohol-alkali solution is allowed to remain in contact with the petroleum-ether solution too long, there is danger of saponifying some of the neutral oil. A contact of one-half hour will not cause a perceptible error, and this time is more than ample to effect a good separation of the layers; usually 15 minutes is sufficient. Draw off the lower layer and the precipitate into a 200-cc. separa-

tory funnel, and rinse the inside of the outlet tube of the 500-cc. separatory funnel with a little petroleum ether. Add 20 cc. of petroleum ether to the contents of the 200-cc. separatory funnel, shake, and allow the layers to separate for about 10 minutes. Draw off the lower layer and the precipitate into a 250-cc beaker. Rinse the inside of the outlet tube of the separatory funnel with petroleum ether into the beaker. Add the upper layer to the main petroleum ether solution of neutral oil in the large separatory funnel. Pour the alcohol-alkali solution back into the 200-cc. separatory funnel and extract with another 20-cc. portion of petroleum ether. Repeat this treatment a third time to insure complete recovery of neutral oil. Save the alkali-alcoholic solution for the determination of the fatty acids. Wash the petroleum-ether solution of the oil three times with 15-cc. portions of 50 per cent alcohol and add the washings to the alkali-alcoholic solution. Transfer the solution of the oil to a weighed 300-cc. Erlenmeyer flask and rinse the separatory funnel with several small portions of petroleum ether. Distill off as much as possible of the solvent by placing the flask in a water bath. Heat the flask in an oven to 120° or 125° C., using an atmosphere of carbon dioxide to prevent oxidation of the oil, until a constant weight is obtained. In most cases 2 hours' heating is sufficient. The carbon dioxide should be removed from the flask each time before it is weighed. Calculate the percentage of neutral oil found.

Place the beaker containing the alkali-alcoholic solution on the steam bath and evaporate the alcohol, taking precautions not to lose any of the solution. Then add 75 cc. of water and when the soap is dissolved, acidify the solution with hydrochloric acid. Cover the beaker and heat on the steam bath until the fatty acids have collected on the top of the solution. Cool until the fatty acids become solid, filter, and wash with water until the fatty acids are free from chlorides. Place the funnel containing the filter paper with the fatty acids in a 250-cc. beaker and heat on a steam bath until the beaker and filter are dry. Dissolve the fatty acids from the filter and funnel by treating them with small portions of petroleum ether, preferably using a fine-jet wash bottle, washing the upper portion of the filter repeatedly. If the solution is turbid, refilter through the original filter, and wash all the fatty acids from the filter paper. Collect the filtrate and washings in a weighed 200-cc. Erlenmeyer flask. Remove the solvent as described for the determination of neutral oil, and weigh. Calculate the percentage of fatty acids. To obtain the percentage of non-oil constituents subtract the sum of the percentages of neutral oil and fatty acids from 100; the resulting figures will include any moisture in the original oil, but when desirable the moisture can be determined and deducted from this result.

When properly conducted, this method will give duplicate results for neutral oil which often do not differ by more than 0.1%. However, it should be understood that the directions must actually be followed in every detail, and to do this requires considerable experience with the method.

Remarks. Occasionally, after the withdrawal of the alcohol-alkali solution, a small quantity of a finely divided precipitate gradually separates from the petroleum-ether solution of the neutral oil. During the washing with 50 per cent alcohol, this precipitate usually settles between the petroleum-ether and alcohol layers, and it is not safe to withdraw it with the wash solutions, as there is danger of losing some neutral oil. In the cases observed, it has been found possible to decant the petroleum ether from this small precipitate. However, if necessary, the precipitate should be removed by filtration. Then the greatest care must be taken to recover all the neutral oil from the filter with petroleum ether.

Jamieson examined samples of 4 commercial crude oils with the following results according to the above directions:

Neutral Oil	Fatty Acids	Non-Fat Substances
	Per Cent	
97.00	0.91	2.09
96.93	0.92	2.15
96.86	0.88	2.26
96.72	0.92	2.26

Duplicate analyses were made on three samples of crude cottonseed oil with the following results:

Oil	Neutral Oil Per Cent
A	94.60 and 94.65
B	95.87 and 95.87
C	94.22 and 94.31

Free Fatty Acids—Refined Oils. Place 50 cc. of alcohol (U. S. Formula 30) in a clean, dry 250-cc. flask and add to it several drops of refined oil. Then add 2 cc. of a 1 per cent alcoholic solution of phenolphthalein solution. Warm the solution by means of a water bath heated to 60-65° C., and titrate it with 0.1*N* sodium hydroxide solution, shaking vigorously until a faint, permanent color is obtained. Weigh 56.40 grams of the refined oil to be tested into the neutralized alcohol and titrate, with occasional warming and vigorous shaking of the mixture, until a faint, permanent pink color is obtained in the supernatant alcohol of the same intensity as that before adding the oil. Multiply the number of cc. of 0.1*N* sodium hydroxide used by 0.05, and report the result as percentage of free fatty acids expressed as oleic acid.

Soap in Refined Oil. Weigh 125 grams of the refined oil into a 500-cc. separatory funnel. Add 25 cc. of concentrated hydrochloric acid and shake vigorously for several minutes. With a pipette, add 100 cc. of water heated to 70° C. Shake vigorously for 2 minutes, then allow the contents of the separatory funnel to stand for about 20 minutes. Transfer 100 cc. of the aqueous solution to a 250-cc. "Pyrex" beaker and evaporate to dryness, using a hot plate on which is an asbestos board. After reaching dryness, continue heating 4 or 5 minutes longer. Remove beaker from hot plate and after it has cooled somewhat, add 50 cc. of

distilled water. Evaporate to dryness and heat as directed above. Repeat this treatment again. Cool and add 10 cc. of distilled water. Add 1 cc. of a 10 per cent solution of potassium chromate solution and titrate any sodium chloride (due to soap in the oil) present with $N/100$ silver nitrate solution. A blank determination should be conducted in parallel with the actual one.

Remarks: It is very important that all glassware be thoroughly cleaned, then rinsed with hydrochloric acid before being used. Also great care should be taken to exclude all oil from the 100 cc. of aqueous solution for analysis, as this interferes with the evaporation and heating of the residue.

Sampling of Slab Press (Oil) Cake. The 1939-1940 edition of "Rules" of the National Cottonseed Products Association gives the following directions: Thirty whole slabs of cake shall be taken from various parts of the freight car, selecting some well down in the piled cake. Each of these slabs of cake shall be divided by imaginary lines into 15 parts, approximately 6 inches square, and designated as A, B, C, and D, as in the accompanying diagram:

A	D	D	D	A
B	C	C	C	B
A	D	D	D	A

From each of the 30 slabs of cake, take one piece as follows: From the first eight slabs of cake, take one piece from a position designated "A" on the diagram; from the next four slabs take one piece from a position designated "B"; from the next six slabs take one piece from a position designated "C," and from the remaining twelve slabs take one piece from a position designated "D." This sample of 30 pieces of cake shall be ground into meal in an attrition mill as promptly as possible by the inspector, so as to meet the standard of fineness required for color measurement (see method). This meal must be thoroughly mixed, quartered to suitable size, and placed in an air-tight container. The packages, marked with car number, initials, and date taken, shall constitute the official sample for the purpose of determining the protein and oil content. When, however, several cars are to be analyzed as one sample, the official inspector shall commingle equal parts by weight of samples from each car and forward the mixture to the chemist.

When slab cake is delivered by truck, 30 whole slabs shall be taken from various parts of each 56-ton lot, and they shall be sampled as described above.

For the purpose of determining the soundness and texture of the cake, four pieces shall be taken of approximately six inches square; one from each of the positions A, B, C, and D as indicated on the diagram; that is, one piece from position A from one of the first eight slabs; one piece from position B from one of the next four slabs; one piece from position C from one of the next six slabs; one piece from position D from one of the next twelve slabs. These four pieces shall be broken, as nearly

as practicable, into halves and four of such pieces put into one package for the buyer, and the other four pieces put into another package, marked so as to identify it, and kept by the inspector for 90 days in case it might be needed for arbitration purposes. After these samples have been drawn, the remaining portions of the 30 slabs of cake shall be returned to the car.

Analysis of Cake and Meal. Apparatus: Aluminum moisture dishes with covers. Dimensions of dishes: 2 inches outside diameter, and ¾ inch high when covered.

American Oil Chemists' Society's official jacketed oven. The jacket of the oven is so constructed that the glycerin solution used in it not only fills the side walls and bottom but also covers the top inner wall to a depth of about one inch. The door is well insulated by asbestos or other suitable insulating material and is equipped with a ventilating shutter. All the seams of the oven are brazed. The oven is supported on an angle-iron base equipped with electric space heating units or other suitable means of heating the glycerin solution. A forced circulation oven, the air of which can be controlled between 100° and 105° C. may be used. The rate and direction of the flow of air shall be such that proper drying will be obtained without danger of blowing any of the sample from the containers.

Preparation of Sample. Grind the sample, if necessary, to uniform fineness and then thoroughly mix without sieving. Both grinding and mixing must be conducted rapidly to avoid loss or gain of moisture by sample.

Determination of Moisture. Weigh 5 grams of the thoroughly mixed sample into the weighed aluminum moisture dish and place in the oven, where it is heated for three hours at 101° C. Then remove from the oven, cover immediately, and cool in a desiccator. Weigh as soon as cool (within 30 minutes) and calculate the percentage of moisture.

Comments. The calcium chloride in the desiccators must be changed frequently in order to maintain a dry atmosphere. The samples must be weighed promptly after they reach room temperature or an increase in weight may occur in the desiccator.

Determination of Oil. Take 5 grams of the sample and extract it with petroleum ether as described under *Analysis of Cottonseed.*

Determination of Proteins. Determine the proteins using 1.7034 grams of the sample by the method given for the analysis of cottonseed.

Color of Cottonseed Cake and Meal. Cottonseed meal must be graded for color as received, without grinding or sifting. Cottonseed cake, to be graded for color, must be ground in an attrition mill, so that not less than 60 per cent and not more than 70 per cent will pass an 8-inch Tyler National Bureau of Standards No. 40 sieve when tested in the following manner: A 10-gram portion of the ground material shall be placed in the sieve and shaken rapidly for two minutes. The portion of the ground sample used for this test must not be for measuring the color. The certificate of analysis must show the actual percentage of ground cake passing through the No. 40 sieve.

Strips 7 inches long and 1 inch wide of the Munsell Color Standards of the following denominations are used: 1.5 yellow, 5/5 red for meal containing 41 per cent or more proteins; 10 yellow, 5/5 red for meal containing 36 per cent of proteins.

A rotating Munsell comparator is used which consists of a 2-inch section of a 2-inch, heavy walled, clear glass tubing mounted on a vertical motor-driven shaft which can be rotated from 2000 to 3000 revolutions per minute. The instrument, with the exception of the glass section, is painted a neutral gray and is mounted in front of a gray background in good daylight free from shadows.

Fill the glass cylinder half full of the sample to be graded, taking care that the upper surface of meal is level throughout. Place the color standard strip (as previously indicated according to the protein content) in the cylinder above the sample, so that it closely fits and covers all the glass not covered by the meal. Rotate and observe from a position about 5 feet distant but not more than a foot above or below the level of the cylinder in such a position as to reduce to a minimum both high lights and shadows. The color of the sample must be equal to or lighter than the standard to establish the grade.

Sampling Soapstock and Acidulated Soapstock. While tank cars are being loaded or unloaded, the sample is collected by means of a by-pass or pet cock (¼ inch or more) in the loading pipe, through which a continual stream of soapstock flows into a barrel. After the tank is loaded or unloaded, the contents of the barrel are thoroughly mixed and 3 one-pound samples are taken. To each, 0.1 per cent of oil of cassia is added; then they are sealed in suitable containers. One sample is sent to buyer, one to seller, and one is reserved.

Analysis of Soapstock and Acidulated Soapstock. Total fatty acids of all soapstocks except those from coconut or palm kernel oils are determined as follows:

Weigh from a weighing bottle 8 to 10 grams of the well-mixed sample of soapstock (or 4 or 5 grams of acidulated soapstock) into a 400-cc. beaker. Add 30 cc. of 95 per cent alcohol and 2 to 3 grams of stick potassium hydroxide (or equivalent of stock alcoholic alkali solution); cover beaker with watch glass and heat it on a steam bath for at least 30 minutes. During this heating, stir the mixture frequently. After completion of saponification, remove the watch glass and continue the heating on the steam bath, with stirring until the alcohol is volatilized. To avoid oxidation, the soap should not be evaporated dryer than to a pasty mass. If necessary, a small amount of water may be added after most of the alcohol has evaporated. After removal of the alcohol, add 200 to 250 cc. of distilled water and heat until all the soap is in solution. Add 3 to 5 drops of methyl orange indicator solution, acidify with 1:1 hydrochloric acid, using only a small excess. Cover beaker with a watch glass and continue heating until the fatty acid layer is clear. Cool in an ice bath or refrigerator until the fatty acids are solid, and filter, using a wet filter paper which will give a clear filtrate. Wash the acids and filter

paper thoroughly with cold water. Use ice water if the fatty acids are liquid at room temperature. Allow fatty acids to dry overnight on filter paper. If they are liquid at room temperature, place the original beaker under the funnel to catch any fatty acids passing through the filter paper. Dissolve the fatty acids with warm petroleum ether. Wash the filter paper thoroughly with the solvent to remove all the fatty acids. Add solvent, if necessary, to make the volume of the filtrate and washings about 125 cc., and then filter through a dry filter paper (not folded) into a weighed flask, washing both beaker and filter paper thoroughly with warm petroleum ether from a fine jet wash bottle. Evaporate or distill the solvent as completely as possible and heat the fatty acids in an oven at 105° C. until a constant weight is obtained. Calculate and report the per cent of total fatty acids.

Soapstock obtained from refining of vegetable oils usually contains from 35 to over 50 per cent of fatty acids, while acidulated soapstock should contain about 95 per cent, if properly prepared.

The total fatty acids of soapstock or acidulated soapstock from coconut or palm kernel oils is determined according to the following procedure: Weigh from a weighing bottle into a 400-cc. beaker an amount of the thoroughly mixed sample that will furnish approximately 5 grams of fatty acids. Add 50 cc. of 95 per cent alcohol and 2 to 3 grams of potassium or sodium hydroxide and heat on steam bath, with occasional stirring until saponification is complete. Continue heating until the alcohol is removed. (This is facilitated by a current of clean air.) Then add 100 cc. of water and heat until the soap is dissolved. Transfer the solution to an extraction cylinder with the aid of hot water, keeping the total volume within 130° C. (The extraction glass-stoppered cylinder having a diameter about 1⅜ and a height of about 12 inches should be graduated at 40, 80 and 130 cc. Acidify, using a slight excess of 1 : 1 hydrochloric acid. Mix by gently rotating the cylinder. When the cylinder and contents have cooled below 50° C., add 50 cc. of petroleum ether, insert stopper and shake thoroughly. Allow the layers to completely separate. Syphon off the petroleum ether solution onto a 9 cm. filter, collecting the filtrate in a 600 cc. beaker. Make at least four more extractions, using 30 cc. portions of solvent. After filtration of these extracts, wash the filter free from fatty acids, using a petroleum ether wash bottle. Add 50 cc. of 95 per cent alcohol redistilled from caustic soda, to which a few drops of phenolphthalein solution have been added. Titrate to color with normal sodium hydroxide solution. Evaporate the petroleum ether by placing the solution on the steam bath and concentrate to a volume of 25 to 30 cc. Transfer solution to a 250-cc. beaker, weighed with a stirring rod, rinsing with alcohol, redistilled from caustic soda. Evaporate the solution on the steam bath and dry the residue to constant weight in an oven heated to 105° to 110° C. In order to calculate the soda soap to fatty acids, a correction must first be made for the neutral salts in the sodium hydroxide solution. Neutralize 20 cc. of this normal solution with 0.5*N* hydrochloric acid, using a

few drops of phenolphthalein solution as indicator. Evaporate to dryness without any loss of salt and dry to a constant weight at 105° to 110° C. From the weight of the residue found, calculate the weight expected if the reagents had been 100 per cent pure. The difference divided by 20 gives the correction per cc. solution for neutral salts. From the weight of the sodium soap obtained subtract the product of the titration of the fatty acids times the factor 0.022 plus the correction for neutral salts. Divide the result by the weight of sample used and multiply by 100 to get the per cent of fatty acids.

Determination of Neutral Oil. Dissolve 10 grams of the sample in 70 to 80 cc. of 50 per cent alcohol, then proceed as described for the determination of neutral oil in the crude product. The soap stocks examined have contained from 17 to 21 per cent of neutral oil.

Remarks. It should be observed that further study is being made of methods for sampling and examining seed, oil, meal and soapstock. For any subsequent changes in procedure that may be authorized, the current edition of the "Rules" of the National Cottonseed Products Association should be consulted.

Refractometric Determination of Oil in Flaxseed

Various refractometric procedures have been devised for the rapid determination of the oil content of different products. These methods are based on the principle that the refractive index of an extract of the material made by a nonvolatile fat solvent whose refractive index differs decidedly from that of the oil extracted, bears a definite relationship to the percentage of oil in the extract. Thus if the refractive indices of both the oil and the solvent are known, and if a known quantity of solvent is intimately mixed with a definite weight of the oleaginous material, the oil content of the material may be calculated from the refractive index of the filtered extract.

The following method by L. Zeleny (U. S. Dept. Agr. Tech. Bull. 554, 1937) has been used successfully for the rapid determination of oil content in flaxseed.

Reagent. A mixture of α-chloronaphthalene (Halowax) and α-bromonaphthalene of such proportions as to have a refractive index of $n_D^{25} = 1.63940 \pm 2$. Such a mixture contains approximately 74 per cent of α-chloronaphthalene and 26 per cent of α-bromonaphthalene by weight but must be carefully adjusted so that the required refractive index is attained. The refractive index temperature coefficient for this mixed solvent is 0.00045 per 1° C.

Special apparatus. (a) A small mill capable of grinding flaxseed finely without expressing the oil. A motor-driven experimental roller flouring mill with 6 x 6 inch steel rolls, corrugated 40 to the inch has been found very satisfactory. The rolls should have a speed differential of about 9:7, and a speed of about 900 r.p.m. for the faster roll.

(b) A high precision refractometer with water jacketed prisms having an accuracy of $n = \pm 0.00002$ within the ranges of 1.473 to 1.482

and 1.606 to 1.640. Two types of refractometer suitable for this work are now available; a dipping type instrument equipped with interchangeable water jacketed prism heads for use with small quantities of liquids, and a modified precision Abbé type instrument.

Method. (1) Obtain a representative sample of about 25 g of the clean seed either by hand quartering or by use of a mechanical sampling device.

(2) Grind the sample as finely as possible, making sure that none of the oil is expressed from the seed during the grinding operation.

(3) Weigh out accurately 2.5 g of the finely ground, well-mixed sample and transfer the weighed sample into a clean 3-inch porcelain mortar which has been previously heated to approximately 60° C. in an oven or on an electric hot plate at low heat.

(4) Add approximately 1 g of reagent-quality sea sand or similar abrasive and exactly 5 ml of the standard Halowax, α-bromonaphthalene mixture. Since this mixture has a very high specific gravity it is highly important to measure its volume very accurately. This is best accomplished with an accurately calibrated 5-ml pipette having a delivery time of not less than 15 seconds.

(5) Grind the mixture vigorously in the mortar for 3 minutes, constantly scraping into the bottom the particles of meal that are thrown against the sides of the mortar.

(6) Filter the mixture through a fine grade of filter paper into a test tube.

(7) When the filtrate has cooled to room temperature, determine its refractive index at 25.0° C. to an accuracy of ± 0.00002. If the reading is made at any temperature other than 25.0°, correct for temperature using the coefficient 0.00042 per 1° C, to be added to the reading if the temperature is above 25.0° and subtracted if the temperature is below that point. It is important that all water jacket temperature readings be made to the nearest 0.1° C.

(8) Using table 1, note the percentage of oil corresponding to the refractive index reading obtained in (7). This is the uncorrected value for oil content.

(9) Place about 2 g of the original ground sample in a quantitative paper filter in a glass funnel and pour over it about 15 ml of petroleum ether, collecting the clear filtrate in a small shallow evaporating dish. Carefully evaporate off the ether on a steam bath or hot plate at low heat, and place the dish in an oven at 105° C. for 20 minutes. Cool the oil thus prepared to room temperature and determine its refractive index at 25.0°. The temperature coefficient for the pure oil is 0.000357 per 1.0°, to be added if the temperature at which the reading is taken is above 25.0°, and subtracted if below that temperature. If preferred, this sample of oil may be prepared by pressing a small sample of the ground seed in a laboratory hydraulic press and filtering the oil so obtained if it is not entirely clear.

(10) From the refractive index of the oil as determined in (9) sub-

tract the value 1.47780 (the refractive index at 25.0° C. of the composite sample of oil used in obtaining the data for table 16). Using this difference, determine from table 17 the correction to be applied to the uncorrected value for oil content as determined in (8). If the difference is positive add the correction; if negative, subtract.

Table 1. Conversion table for determining the percentage of oil in flaxseed from the refractive index of the Halowax, α-bromonaphthalene extract at 25° C.

n_D^{25}	Oil	n_D^{25}	Oil	n_D^{25}	Oil	n_D^{25}	Oil
	Percent		*Percent*		*Percent*		*Percent*
1.61837	28.0	1.61554	32.5	1.61279	37.0	1.61012	41.5
1.61831	28.1	1.61548	32.6	1.61273	37.1	1.61006	41.6
1.61824	28.2	1.61542	32.7	1.61267	37.2	1.61000	41.7
1.61818	28.3	1.61535	32.8	1.61261	37.3	1.60995	41.8
1.61811	28.4	1.61529	32.9	1.61255	37.4	1.60989	41.9
1.61805	28.5	1.61523	33.0	1.61249	37.5	1.60983	42.0
1.61799	28.6	1.61517	33.1	1.61243	37.6	1.60977	42.1
1.61792	28.7	1.61511	33.2	1.61237	37.7	1.60971	42.2
1.61786	28.8	1.61504	33.3	1.61231	37.8	1.60966	42.3
1.61779	28.9	1.61498	33.4	1.61225	37.9	1.60960	42.4
1.61773	29.0	1.61492	33.5	1.61219	38.0	1.60954	42.5
1.61767	29.1	1.61486	33.6	1.61213	38.1	1.60948	42.6
1.61760	29.2	1.61480	33.7	1.61207	38.2	1.60942	42.7
1.61754	29.3	1.61473	33.8	1.61201	38.3	1.60937	42.8
1.61748	29.4	1.61467	33.9	1.61195	38.4	1.60931	42.9
1.61742	29.5	1.61461	34.0	1.61189	38.5	1.60925	43.0
1.61735	29.6	1.61455	34.1	1.61183	38.6	1.60919	43.1
1.61729	29.7	1.61449	34.2	1.61177	38.7	1.60913	43.2
1.61723	29.8	1.61443	34.3	1.61171	38.8	1.60908	43.3
1.61716	29.9	1.61437	34.4	1.61165	38.9	1.60902	43.4
1.61710	30.0	1.61431	34.5	1.61159	39.0	1.60896	43.5
1.61704	30.1	1.61424	34.6	1.61153	39.1	1.60890	43.6
1.61697	30.2	1.61418	34.7	1.61147	39.2	1.60884	43.7
1.61691	30.3	1.61412	34.8	1.61141	39.3	1.60879	43.8
1.61685	30.4	1.61406	34.9	1.61135	39.4	1.60873	43.9
1.61679	30.5	1.61400	35.0	1.61130	39.5	1.60867	44.0
1.61672	30.6	1.61394	35.1	1.61124	39.6	1.60861	44.1
1.61666	30.7	1.61388	35.2	1.61118	39.7	1.60856	44.2
1.61660	30.8	1.61382	35.3	1.61112	39.8	1.60850	44.3
1.61653	30.9	1.61376	35.4	1.61106	39.9	1.60844	44.4
1.61647	31.0	1.61370	35.5	1.61100	40.0	1.60839	44.5
1.61641	31.1	1.61363	35.6	1.61094	40.1	1.60833	44.6
1.61635	31.2	1.61357	35.7	1.61088	40.2	1.60827	44.7
1.61628	31.3	1.61351	35.8	1.61082	40.3	1.60821	44.8
1.61622	31.4	1.61345	35.9	1.61076	40.4	1.60816	44.9
1.61616	31.5	1.61339	36.0	1.61071	40.4	1.60810	45.0
1.61610	31.6	1.61333	36.1	1.61065	40.6	1.60804	45.1
1.61604	31.7	1.61327	36.2	1.61059	40.7	1.60799	45.2
1.61597	31.8	1.61321	36.3	1.61053	40.8	1.60793	45.3
1.61591	31.9	1.61315	36.4	1.61047	40.9	1.60787	45.4
1.61585	32.0	1.61309	36.5	1.61041	41.0	1.60782	45.5
1.61579	32.1	1.61303	36.6	1.61035	41.1	1.60776	45.6
1.61573	32.2	1.61297	36.7	1.61029	41.2	1.60770	45.7
1.61566	32.3	1.61291	36.8	1.61024	41.3	1.60764	45.8
1.61560	32.4	1.61285	36.9	1.61018	41.4		

Sample Determination

Suppose the refractive index as determined in (7) is 1.61149 at 27.3° C.

$$n_D^{27.3} = 1.61149$$

$$n_D^{25} = 1.61149 + [(27.3\text{-}25.0) \times 0.00042]$$

$$= 1.61246$$

Referring to table 1:

$n_D^{25} = 1.61246$ corresponds to an oil content of 37.55 per cent. This is the uncorrected value.

Then suppose the refractive index of the oil as determined in (9) is 1.47960 at 23.3° C.

$$n_D^{23.3} = 1.47960$$
$$n_D^{25} = 1.47960 - [(25.0\text{-}23.3) \times 0.000357]$$
$$= 1.47899$$

Then:

$$1.47899 - 1.47780 = +0.0019$$

Referring to table 2:

A difference of 0.00119 between the refractive index of the oil in the sample under investigation and the sample used in preparing the conversion table indicates a correction of 0.26 per cent of oil for a sample containing approximately 38 per cent of oil. Since the difference is positive the correction is to be added to the uncorrected value.

37.55 per cent + 0.26 per cent = 37.81 per cent oil

Refractometric Determination of Iodine Number in Flaxseed Oils

It has long been known that a general relationship exists between the refractive index and iodine number of animal and vegetable oils. Only recently, however, has it been shown that for certain oils and under certain conditions this relationship is sufficiently exact to enable the iodine number to be determined refractometrically with a fairly high degree of accuracy.

This relationship has been carefully studied in the case of flaxseed oils prepared under certain conditions by Zeleny and Coleman (*Oil and Soap,* **13,** 253-256, 1936), by Hopper and Nesbitt (*Oil and Soap,* **14,** 34-36, 1937), and by Lehberg and Geddes (*Can. J. Res.,* **15c,** 349-361, 1937). The work at each of the three laboratories was entirely independent and the results obtained were in good agreement indicating the fundamental soundness of the observed relationship.

The following method for determining the iodine number (Wijs) of flaxseed oils refractometrically is that described by Zeleny and Coleman.

Special apparatus. A high precision refractometer with water jacketed prisms, having an accuracy of $n = \pm 0.00002$ within the range 1.473 to 1.482. Two types of refractometer suitable for this purpose are now available; a dipping type instrument equipped with interchangeable water jacketed prism heads for use with small quantities of liquids, and a modified precision Abbé type instrument.

Method. (1) Grind a representative sample of the clean flaxseed with a suitable type mill.

(2) Prepare a sample of oil from the freshly ground seed by one of the following methods (a) Press the oil from a small quantity of the ground seed with a small laboratory hydraulic press, filtering the pressed oil if it is not clear; (b) Mix about 2 g of the ground seed with about 20

Table 2. Corrections to be applied to results obtained in the analysis of flaxseed for oil content by the refractometric method

[Values to be added when (n_D^{25} −1.4778) is positive, subtracted when (n_D^{25} −1.4778) is negative]

(Corrections in terms of percent of oil indicated)

n_D^{25} −1.4778	28[1]	29[1]	30[1]	31[1]	32[1]	33[1]	34[1]	35[1]	36[1]	37[1]	38[1]	39[1]	40[1]	41[1]	42[1]	43[1]	44[1]	45[1]	46[1]	47[1]	48[1]
0.0001.....	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03
.0002.....	.03	.03	.03	.03	.04	.04	.04	.04	.04	.04	.04	.04	.05	.05	.05	.05	.05	.05	.05	.05	.06
.0003.....	.05	.05	.05	.05	.05	.06	.06	.06	.06	.06	.06	.07	.07	.07	.07	.07	.08	.08	.08	.08	.08
.0004.....	.06	.06	.07	.07	.07	.07	.08	.08	.08	.08	.09	.09	.09	.09	.10	.10	.10	.10	.11	.11	.11
.0005.....	.08	.08	.08	.09	.09	.09	.10	.10	.10	.11	.11	.11	.11	.12	.12	.12	.13	.13	.13	.14	.14
.0006.....	.09	.10	.10	.10	.11	.11	.11	.12	.12	.13	.13	.13	.14	.14	.15	.15	.15	.16	.16	.16	.17
.0007.....	.11	.11	.12	.12	.12	.13	.13	.14	.14	.15	.15	.16	.16	.17	.17	.17	.18	.18	.19	.19	.20
.0008.....	.12	.13	.13	.14	.14	.15	.15	.16	.16	.17	.17	.18	.18	.19	.19	.20	.20	.21	.21	.22	.22
.0009.....	.14	.14	.15	.15	.16	.17	.17	.18	.18	.19	.19	.20	.21	.21	.22	.22	.23	.23	.24	.25	.25
.0010.....	.15	.16	.17	.17	.18	.19	.19	.20	.20	.21	.22	.22	.23	.24	.24	.25	.26	.26	.27	.27	.28
.0011.....	.17	.17	.18	.19	.20	.20	.21	.22	.22	.23	.24	.25	.25	.26	.27	.27	.28	.29	.29	.30	.31
.0012.....	.18	.19	.20	.21	.21	.22	.23	.24	.24	25	.26	.27	.27	.28	.29	.30	.31	.31	.32	.33	.34
.0013.....	.20	.21	.22	.22	.23	.24	.25	.26	.27	.27	.28	.29	.30	.31	.31	.32	.33	.34	.35	.36	.36
.0014.....	.21	.22	.23	.24	.25	.26	.27	.28	.29	.29	.30	.31	.32	.33	.34	.35	.36	.37	.37	.38	.39
.0015.....	.23	.24	.25	.26	.27	.28	.29	.30	.31	.32	.32	.33	.34	.35	.36	.37	.38	.39	.40	.41	.42
.0016.....	.24	.25	.27	.28	.28	.30	.31	.31	.33	.34	.35	.36	.37	.38	.39	.40	.41	.42	.43	.44	.45
.0017.....	.26	.27	.28	.29	.30	.31	.32	.33	.35	.36	.37	.38	.39	.40	.41	.42	.43	.44	.45	.47	.48
.0018.....	.28	.29	.30	.31	.32	.33	.34	.35	.37	.38	.39	.40	.41	.42	.44	.45	.46	.47	.48	.49	.50
.0019.....	.29	.30	.32	.33	.34	.35	.36	.37	.39	.40	.41	.42	.44	.45	.46	.47	.48	.50	.51	.52	.53
.0020.....	.31	.32	.33	.34	.36	.37	.38	.39	.41	.42	.43	.45	.46	.47	.48	.50	.51	.52	.53	.55	.56
.0021.....	.32	.33	.35	.36	.37	.39	.40	.41	.43	.44	.45	.47	.48	.50	.51	.52	.54	.55	.56	.58	.59
.0022.....	.34	.35	.37	.38	.39	.41	.42	.43	.45	.46	.48	.49	.50	.52	.53	.55	.56	.57	.59	.60	.62
.0023.....	.35	.37	.38	.40	.41	.43	.44	.45	.47	.48	.50	.51	.53	.54	.56	.57	59	.60	.61	.63	.64
.0024.....	.37	.38	.40	.41	.43	.44	.46	.47	.49	50	.52	.54	.55	.57	.58	.60	.61	.63	.64	.66	.67
.0025.....	.38	.40	.42	.43	.45	.46	.48	.49	.51	.53	.54	.56	.57	.59	.61	.62	.64	.65	.67	.69	.70
.0026.....	.40	.41	.43	.45	.46	.48	.50	.51	.53	.55	.56	.58	.60	.61	.63	.64	.66	.68	.69	.71	.73
.0027.....	.41	.43	.45	.46	.48	.50	.52	.53	.55	.57	.58	.60	.62	.64	.65	.67	.69	.70	.72	.74	.76
.0028.....	.43	.45	.46	.48	.50	.52	.53	.55	.57	.59	.60	.62	.64	.66	.68	.69	.71	.73	.75	.77	.78
.0029.....	.44	.46	.48	.50	.52	.54	.55	.57	.59	.61	.63	.65	.66	.68	.70	.72	.74	.76	.77	.79	.81
.0030.....	.46	.48	.50	.52	.53	.55	.57	.59	.61	.63	.65	.67	.69	.71	.73	.74	.76	.78	.80	.82	.84

[1] Percent oil as determined from table 1.

ml of petroleum ether [1] and filter into a small shallow evaporating dish. Evaporate the bulk of the solvent on a steam bath and then place the dish containing the oil in an air oven at 105° C. for 30 minutes. (c) Use the freshly extracted oil prepared in the determination of oil content. In this case petroleum ether [1] should be used for extraction and the last traces of solvent should be removed from the extract by placing the extraction flask in a vacuum oven at 100° C. for 30 minutes.

(3) Determine the refractive index of the oil at 25.0° C. If the reading is taken at any other temperature, add 0.000357 for each 1.0° above 25.0° and subtract that value for each 1.0° below that temperature. The refractive index should always be determined promptly as soon as the oil sample is prepared.

(4) Convert refractive index value into iodine number (Wijs) by use of table 1.

Table 3. Conversion table for determining Wijs iodine number of freshly prepared flaxseed oil from refractive index

Data calculated from regression equation: $I = -12513.827 + 8584.966\ n_D^{25}$]

n_D^{25}	Iodine number	n_D^{25}	Iodine number	n_D^{25}	Iodine number	n_D^{25}	Iodine number	n_D^{25}	Iodine number
1.4733	134.4	1.4750	149.0	1.4767	163.6	1.4784	178.2	1.4801	192.8
1.4734	135.3	1.4751	149.9	1.4768	164.5	1.4785	179.0	1.4802	193.6
1.4735	136.1	1.4752	150.7	1.4769	165.3	1.4786	179.9	1.4803	194.5
1.4736	137.0	1.4753	151.6	1.4770	166.2	1.4787	180.8	1.4804	195.4
1.4737	137.8	1.4754	152.4	1.4771	167.0	1.4788	181.6	1.4805	196.2
1.4738	138.7	1.4755	153.3	1.4772	167.9	1.4789	182.5	1.4806	197.1
1.4739	139.6	1.4756	154.1	1.4773	168.7	1.4790	183.3	1.4807	197.9
1.4740	140.4	1.4757	155.0	1.4774	169.6	1.4791	184.2	1.4808	198.8
1.4741	141.3	1.4758	155.9	1.4775	170.5	1.4792	185.1	1.4809	199.6
1.4742	142.1	1.4759	156.7	1.4776	171.3	1.4793	185.9	1.4810	200.5
1.4743	143.0	1.4760	157.6	1.4777	172.2	1.4794	186.8	1.4811	201.4
1.4744	143.8	1.4761	158.4	1.4778	173.0	1.4795	187.6	1.4812	202.2
1.4745	144.7	1.4762	159.3	1.4779	173.9	1.4796	188.5	1.4813	203.1
1.4746	145.6	1.4763	160.2	1.4780	174.8	1.4797	189.3	1.4814	203.9
1.4747	146.4	1.4764	161.0	1.4781	175.6	1.4798	190.2	1.4815	204.8
1.4748	147.3	1.4765	161.9	1.4782	176.5	1.4799	191.1	1.4816	205.7
1.4749	148.1	1.4766	162.7	1.4783	177.3	1.4800	191.9	1.4817	206.5

It should be distinctly understood that this method for determining iodine number is meant to apply only to samples of oil prepared from flaxseed in such a way that no significant amount of hydrolysis, oxidation, or polymerization occurs, and no solvent residues remain in the oil. Immaturity, frost damage, or scabbiness of the seed do not appear to affect the reliability of the method. The method is not reliable, however, for oils from flaxseed that have become fermented or musty because of prolonged storage at a high moisture content. Oils from such seed will generally be found to have undergone considerable hydrolysis.

The method may not be used for the direct determination of the iodine number of commercial linseed oils since the processing that the oil undergoes tends to alter its refractive index.

[1] For this purpose a petroleum ether conforming to the specifications of the American Oil Chemists' Society should be used. (*Oil and Fat Ind.*, **8**, 345, 347 (1931).

The principal value of the method is for determining in advance the iodine number of the linseed oil which a given lot of flaxseed will produce. The method is of considerable value to the flaxseed crusher because determinations may be made in a small fraction of the time required for the conventional iodine number determinations, and because the use of high priced chemical reagents is eliminated.

The plant breeder should also find the method helpful when requiring the iodine numbers of the oils from very small samples of seed. The refractometric method requires only a drop of oil which can be prepared from about 0.1 g of flaxseed.

Appendix I

Various Other Seed Oils

In view of the inquiries that are made from time to time in regard to the quantity and character of oils from the seeds of ornamental and other trees and plants, the following information may be found useful. Most of those to be described for one reason or another are of no commercial importance from the standpoint of oil production. In some cases, the seeds contain only a few per cent of oil; in others, although they contain notable quantities of oil, the cost of collecting the seeds together with the small tonnage available in a community makes them of no commercial importance. For some of these oils, only two or three of the characteristics are available.

Bittersweet Seed Oil. The seeds of the vine *Celastrus scandens (Celastraceae)* contain about 36 per cent of oil. C. Barkenbus and C. F. Krewson [*J. Am. Chem. Soc.*, **54**, 3993 (1932)] reported the following characteristics for the oil: Sap. V. 297; Iod. No. 121.5; SCN V. 69.9; Acid V. 3.9; R.M.V. 70.8; Acetyl V. 121.5; Hexabromides 17.6; Sol. acids as butyric 19%; Sat. acids 9.83%; Unsap. 2.96%.

Boysenberry Seed Oil. The plant is probably a cross between the eastern dewberry and the western trailing blackberry. The seeds which were examined contained 14.36 per cent of oil and 9.7 of moisture. Oil characteristics: $N_D^{25°}$ 1.4779; Sap. V. 188.6; Iod. No. (Hanus) 171.5.

Buffalo Nut Oil. The fruits of the shrub *Pyrulia pubera (Santalaceae)* contain 82.8 per cent of "nuts" of which 81.9 per cent is kernel. The kernels contained 58.5 per cent of oil. Oil characteristics: $N_D^{25°}$ 1.4786; Sap. V. 189.6; Iod. No. (Hanus) 104.6.

Bird's Eye Seed Oil. The plant, *Caperonia palustris (Euphorbiaceae)*, is a weed found in American rice fields. The seed contain about 28 per cent of oil, one specimen of which gave an iodine number of 169.

Bind Weed (Field Morning Glory). The seed of *Convolvulus arvensis (Convolulaceae)* which were examined were found to contain 4.7 per cent of oil, giving an iodine number of 103.2.

Chan Seed Oil. The seed of *Hyptis suaveolens (Labiatae)* contain 13 per cent of oil, which gave an iodine number of 140.2.

Daubentonia drummondii **Seed Oil.** The seeds of this shrub, a member of the *Leguminosae* contain 4.3 per cent of oil, which gave an iodine number of 122.

Glottidium vesecarium **Seed Oil.** The plant was formerly classified as *Sesbania vesecarium*, and belongs to the *Leguminosae* family.

The seeds contain 5.3 per cent of oil. The characteristics of the oil are as follows: $N_D^{25°}$ 1.4730; Iod. No. (Hanus) 132.8; Sap. V. 187.5

Hare's Ear Mustard Seed Oil. The seed of *Conringia orientalis* contain from 34 to 36 per cent of oil, a sample of which was examined by R. M. Johnson and J. E. Greaves [*Proc. Utah Acad. Sci.*, **17**, 85 1940); *Chem. Abs.*, **35**, 2740 (1941)] with the following results: $N_D^{24°}$ 1.4716; Sap. V. 165; Iod. No. 99 to 101; R.M.V. 0.96; Pol. No. 0.11.

Lecythis elleptica (Lecythidaceae) **Seed Oil.** The seeds from Colombia obtained 64.4 per cent of kernels. These were found to contain 57.6 of oil giving an iodine number of 114.4 and a thiocyanogen value of 72.7.

Mahogany Seed Oil. The kernels from the seeds of the tree *Swietonia mahogani (Meliaceae)* contained 53 per cent of oil and 3.6 of moisture. The characteristics of the oil were as follows: $N_D^{25°}$ 1.4694; Sap. V. 178.9; Iod. No. (Hanus) 116.2; Unsap. 8.15 per cent.

Milk Weed Seed Oil. The seeds and oil of the *Asclepis syrica (Aschepiadaceae)* were investigated by F. Herhardt [*Ind. Eng. Chem.*, **22**, 160 (1930)]. He estimated an acre planted to this common milk weed would yield 30 bushels of seed, 280 pounds of "floss" and a ton of air dried stems.

The seeds were found to contain the following percentages of constituents: Oil 21.2, proteins 37.5, crude fiber 11.5, and ash 4.1. The floss contained 34.86 and the stems 36.68 per cent of α-cellulose. The characteristics of the oil were as follows: Sp. g. at 15° C. 0.9230; $N_D^{30°}$ 1.4714; Sap. V. 193.6; Iod. No. (Hanus) 128.6; R.M.V. 0.50; Pol. No. 0.30.

Mimosa Seed Oil. The seeds of the ornamental tree *Acacia julibrissin* contain 9.9 per cent of oil which gave an iodine number of 136.4.

Persimmon Seed Oil. The seeds from the fruit of the common American tree *Diospyros virginiana (Ebenaceae)* were found to contain 1.3 per cent of oil. M. J. Lane [*Chem. Rev.*, **12**, 136 (1905)] reported the following characteristics for the oil: Sap. V. 188.0; Iod. No. 116.8; Acetyl V. 7.15; Titer 20.2° C.

Poinsetta Seed Oil. The seed of *Poinsetta pucherrina (Euphorbiaceae)* contained 34.9 per cent of oil which gave an iodine number (Hanus) 209.2 and a saponification value of 194.

Soapberry Kernel Oil. The fruit of *Sapindus marginatus (Sapindaceae)* from North Carolina consisted of 39.03 per cent of seed and 60.97 of pulp, The kernels which amounted to 55.7 per cent of the seeds contained 40.9 per cent of oil. The characteristics of the oil were: $N_D^{25°}$ 1.4709; Sap. V. 197.4; Iod. No. (Hanus) 90.4; Unsap. 0.57 per cent.

The fruit of *Sapindus drummondii* from Oklahoma consisted of 58.2 per cent of pulp and 41.8 of seed. The kernels which amounted to 43 per cent of the seeds contained 43.1 per cent of oil. The following characteristics were determined: $N_D^{25°}$ 1.4686; Sap. V. 192; Iod. No. (Hanus) 89.4; Unsap. 0.89 per cent; Sat. acids 10.9 per cent.

Garcia Nutans Seed Oil. The tree which belongs to the *Euphorbiaceae* family is called Pinonchillo in Mexico. The spherical seeds each of which weighs somewhat more than a gram, consist of 80.5 per cent of kernel and 19.5 of shell. The kernels contained 53.7 per cent of oil and 2.9 of moisture. The characteristics of the oil were as follows: $N_D^{25°}$ 1.5260; Iod. No. (Wijs—1 hr.) 176.7; Diene V. (Ellis-Jones) 81.5; Carbonyl V. 0.0; Sap. V. 192.3; Acid V. 0.6; Unsap. 0.5 per cent; Sat. acids 2.2 per cent; Browne heat test, 7.25 minutes. The oil contains about 91.8 per cent elaeostearic acid.

Appendix II

Table 1. Neutralization Values of Fatty Acids.

Acid	Formula	Molecular Weight	Neutralization Value
Acetic	$C_2H_4O_2$	60.05	934.28
Butyric	$C_4H_8O_2$	88.10	636.83
Caproic	$C_6H_{12}O_2$	116.15	483.03
Caprylic	$C_8H_{16}O_2$	144.20	389.07
Capric	$C_{10}H_{20}O_2$	172.25	325.71
Lauric	$C_{12}H_{24}O_2$	200.31	280.08
Myristic	$C_{14}H_{28}O_2$	228.35	245.69
Palmitic	$C_{16}H_{32}O_2$	256.41	218.80
Stearic	$C_{18}H_{36}O_2$	284.46	197.23
Arachidic	$C_{20}H_{40}O_2$	312.51	179.52
Behenic	$C_{22}H_{44}O_2$	340.56	164.74
Lignoceric	$C_{24}H_{48}O_2$	368.61	152.22
Melissic	$C_{30}H_{60}O_2$	452.98	123.85
Oleic	$C_{18}H_{34}O_2$	282.44	198.64
Linoleic	$C_{18}H_{32}O_2$	280.43	200.07
Linolenic	$C_{18}H_{30}O_2$	278.40	201.66
Hydnocarpic	$C_{16}H_{28}O_2$	252.38	222.29
Gorlic	$C_{18}H_{30}O_2$	278.40	201.66
Chaulmoogric	$C_{18}H_{32}O_2$	280.43	200.07
Ricinoleic	$C_{18}H_{34}O_3$	298.44	187.99
Erucic	$C_{22}H_{44}O_2$	340.56	164.74
Sativic	$C_{18}H_{36}O_6$	348.46	161.00
Linusic	$C_{18}H_{28}O_8$	380.46	147.46

Table 2. Iodine Numbers of Some Unsaturated Acids.

Acid	Iodine Number
Chaulmoogric	90.52
Elaeostearic	273.53
Erucic	74.54
Gorlic	182.36
Hydnocarpic	100.58
Linoleic	181.04
Linolenic	273.53
Oleic	89.87
Ricinoleic	85.06

Table 3. Methyl Esters.

Ester	Formula	Molecular Weight	Saponification Value
Butyrate	$C_4H_7O.OCH_3$	102.13	595.34
Caproate	$C_6H_{11}O.OCH_3$	130.18	430.97
Caprylate	$C_8H_{15}O.OCH_3$	158.23	354.57
Caprate	$C_{10}H_{19}O.OCH_3$	186.28	301.18
Laurate	$C_{12}H_{23}O.OCH_3$	214.33	261.76
Myristate	$C_{14}H_{27}O.OCH_3$	242.38	231.47
Palmitate	$C_{16}H_{31}O.OCH_3$	270.43	207.46
Stearate	$C_{18}H_{35}O.OCH_3$	298.48	187.96
Arachidate	$C_{20}H_{39}O.OCH_3$	326.53	171.82
Behenate	$C_{22}H_{43}O.OCH_3$	354.58	158.25
Lignocerate	$C_{24}H_{47}O.OCH_3$	382.63	146.63
Oleate	$C_{18}H_{33}O.OCH_3$	296.47	189.24
Linoleate	$C_{18}H_{31}O.OCH_3$	294.45	190.54
Linolenate	$C_{18}H_{29}O.OCH_3$	292.43	191.86

Table 4. Bromides of Unsaturated Fatty Acids.

	Per Cent of Bromine
Oleic dibromide $C_{18}H_{34}O_2Br_2$	36.18
Linoleic tetrabromide, $C_{18}H_{32}O_2Br_4$	53.33
Linolenic hexabromide, $C_{18}H_{30}O_2Br_6$	63.32

Table 5. Factors for Calculation of Acids from Methyl Esters.

Ester	Factor	Log of Factor
Butyrate	0.8627	0.93584
Caproate	0.8924	0.95055
Caprylate	0.9114	0.95970
Caprate	0.9247	0.96600
Laurate	0.9345	0.97060
Myristate	0.9418	0.97397
Palmitate	0.9482	0.97690
Stearate	0.9527	0.97898
Arachidate	0.9567	0.98082
Lignocerate	0.9631	0.92369
Oleate	0.9527	0.97898
Linoleate	0.9522	0.97875

Table 6. Factors for the Calculation of Triglycerides from Acids.

Acids	Triglycerides	Acids	Triglycerides
Caproic × 1.109 =	Triglycerides	Stearic × 1.045 =	Triglycerides
Capryllic × 1.087 =	Triglycerides	Arachidic × 1.030 =	Triglycerides
Capric × 1.073 =	Triglycerides	Lignoceric × 1.030 =	Triglycerides
Lauric × 1.063 =	Triglycerides	Oleic × 1.045 =	Triglycerides
Myristic × 1.056 =	Triglycerides	Linoleic × 1.040 =	Triglycerides
Palmitic × 1.049 =	Triglycerides	Linolenic × 1.038 =	Triglycerides

Table 7.

Triglycerides	Formula	Molecular Weight	Saponification Value
Tributyrin	$C_3H_5(C_3H_7COO)_3$	302.35	556.7
Tricaproin	$C_3H_5(C_5H_{11}COO)_3$	386.5	435.5
Tricaprylin	$C_3H_5(C_7H_{15}COO)_3$	470.7	357.6
Tricaprin	$C_3H_5(C_9H_{19}COO)_3$	554.8	303.4
Trilaurin	$C_3H_5(C_{11}H_{23}COO)_3$	639.0	263.4
Trimyristin	$C_3H_5(C_{13}H_{27}COO)_3$	723.1	232.8
Tripalmitin	$C_3H_5(C_{15}H_{31}COO)_3$	807.3	208.5
Tristearin	$C_3H_5(C_{17}H_{35}COO)_3$	891.5	188.8
Triarachin	$C_3H_5(C_{19}H_{39}COO)_3$	975.6	172.6
Tribehenin	$C_3H_5(C_{21}H_{43}COO)_3$	1059.7	158.8
Trilignocerin	$C_3H_5(C_{23}H_{47}COO)_3$	1143.9	147.2
Triolein	$C_3H_5(C_{17}H_{33}COO)_3$	885.4	190.1
Trilinolein	$C_3H_5(C_{17}H_{31}COO)_3$	879.4	191.4
Trilinolenin	$C_3H_5(C_{17}H_{29}COO)_3$	873.3	192.7
Trierucin	$C_3H_5(C_{21}H_{41}COO)_3$	1053.7	159.7
Triricinolein	$C_3H_5(C_{17}H_{32}OHCOO)_3$	933.4	180.3
Trihydnocarpin	$C_3H_5(C_{15}H_{27}COO)_3$	795.2	211.7
Trichaulmoogrin	$C_3H_5(C_{17}H_{31}COO)_3$	879.3	191.4

Table 8. Thiocyanogen Values.*

Oil	Iodine Number	Thiocyanogen Value
Apricot kernel	102.06	79.36
Coconut	7.60	6.97
Cottonseed	111.88	67.00
Linseed	182.32	109.05
Olive	86.26	79.36
Palm	55.59	46.13
Peanut	85.02	63.02
Perilla	204.48	124.87
Soybean	136.39	79.21
Tung	172.27	81.17

* W. Kimma, *Chem. Umschau*, **36**, 255 (1929).

Table 9. Density, Degrees Baumé, Weight of Gallon and Cubic Foot of Various Oils.

Oil	Density at 60° F.	Degrees Baumé	Lbs. in 1 Gal.	Lbs. in 1 Cubic Ft.
Almond	.918	23	7.65	57.38
Castor	.962	15	8.02	60.20
Cod liver	.927	21	7.72	57.94
Cottonseed	.922	22	7.67	57.53
Hemp	.931	20	7.75	58.17
Lard	.917	23	7.64	57.34
Linseed	.930	21	7.75	58.12
Neatsfoot	.914	23	7.62	57.14
Olive*	.916	23	7.63	57.25
Palm	.905	25	7.54	56.54
Poppy	.924	21	7.70	57.77
Rape	.916	23	7.63	57.22
Whale	.925	21	7.71	57.84

* The U. S. Federal Trade Commission, *Chem. Markets*, **21**, 853 (1927), ruled that a U. S. gallon of olive oil must weigh 7.61 pounds and other edible oils 7.7 pounds.

Table 10. Melting Point of Fats.*

Fat	Melting Point ° C	Fat	Melting Point ° C
Babassu	22-26	*H. venenata*	19.20
Bacury	50-52	*H. wightiana*	22-24
Beef tallow	46-50	Illipé (Bassia)	25-31
Bey bean	40-44	Japan tallow	46-54
Bicuhyba	39-42	Kokerite kernel	26-28
Borneo tallow	36-39	Kokum	40-42
Cacao	30-34	Lard	36-46
Cay-cay	39-40	Lupu seed	40-42
Coconut	23-26	Mafura	39-41
Cohune	21-24	Malabar tallow	30-40
Cupu seed	43-45	Otoba	35-38
Dika	38-40	Palm	20-50
Djave	21-23	Palm kernel	24-28
Gorli seed	40-45	Phulwa	39-50
Hydnocarpus		Sequa	30-34
H. Alcalæ	30-32	Shea	27-42
H. alpina	22-26	Swarri	35-37
H. anthelminthica	24-25	Vegetable (Stillingia)	41-52

* Fats when heated undergo more or less liquefaction depending upon their character, at temperatures below those recorded. The figures given with few exceptions represent the range of melting points noted for different samples of a fat. The higher the fatty acid content, the higher the melting point of the fat; *cf.* palm oil for sample.

Table 11. Smoke, Flash and Fire Points.*

Oil	Smoke Points ° F.	Smoke Points ° C.	Flash Points ° F.	Flash Points ° C.	Fire Points ° F.	Fire Points ° C.
Castor, refined	392	200	568	298	635	335
Castor dehydrated	348	176	570	299	638	337
Corn, crude	352	178	562	294	655	346
Corn, refined	440	227	618	326	678	359
Linseed, raw	325	163	549	287	667	353
Linseed, refined	320	160	588	309	680	360
Olive, virgin	391	199	610	321	682	361
Soybean, expeller, crude	357	181	564	296	664	351
Soybean, extracted, crude	410	210	603	317	670	354
Soybean, refined	492	256	618	326	673	356
Perilla, raw	321	161	575	302	678	359
Perilla, refined	352	178	608	320	685	363
Perilla, refined	408	209	615	324	685	363

* S. B. Detwiler and K. S. Markley, *Oil and Soap*, **17**, 39 (1940).

Smoke, flash and fire points were determined by the Cleveland open cup method Am. Soc. Test. Mat., Part 2, 892 (1936). It should be noted that the smoke, flash and fire points of an oil are subject to considerable variation depending upon the method of extraction, whether or not it is refined, and upon its condition at the time the test is made. Consequently, it is important to give the history of the samples tested along with the results. For the determination of smoke, flash and fire points see American Oil Chemists' Society's Committee Report, Oil and Soap, 17, 127 (1940).

The flash points are subject to considerable variation, depending upon the method employed and the condition of any particular sample of oil. Oils containing notable quantities of free fatty acids would be expected to give lower flash points than those of low acidity.

Table 12. Titers (Maximum Solidification Points of Fatty Acids).

Source of Fatty Acids	Degrees C.	Source of Fatty Acids	Degrees C.
Almond oil	12	Niam fat	42-43
Beef tallow	38-46	Nutmeg butter	35-36
Chaulmoogra oil	39-40	Palm oil	36-45
Crabwood or carapa oil	34-35	Palm kernel oil	20-26
Cacao butter	48-50	Peanut (arachis) oil	28-32
Chinese vegetable tallow	45-53	Pongam oil	44-45
Coconut oil	22-25	Peach kernel oil	13-14
Corn oil	18-20	Poppy seed oil	16-17
Cod liver oil	14-24	Rape oil	13-15
Cottonseed oil	32-36	Safflower oil	15-17
Croton oil	18-20	Sesame oil	23-25
Hempseed oil	15-17	Sawarri butter	46-47
Japanese tallow	58-59	Shea butter	53-54
Lard	38-42	Seal oil	15-16
Linseed oil	14-15	Sunflower seed oil	17-18
Macassar oil	51-53	Tung oil	36-37
Mourah seed oil	40-41	Whale oil	23-25
Mutton tallow	41-48		

Table 13. Weights, Measures, and Equivalents.

1 metric ton (t.)	= 2204.6 avoirdupois pounds
1 metric quintal	= 220.46 avoirdupois
1 hundredweight (cwt.)	= 112 avoirdupois pounds
1 short ton (sh. t.)	= 2000 avoirdupois pounds
1 long ton (l. t.)	= 2240 avoirdupois pounds
1 pound avoirdupois	= 453.5924 grams (0.45359 kilogram)
1 ounce	= 28.3495 grams
1 kilogram	= 2.2046 avoirdupois pounds
1 kin	= 1.3228 avoirdupois pounds
1 picul	= 133⅓ avoirdupois pounds
1 pood	= 1.36 avoirdupois pounds
1 yard	= 0.91437 meter
1 meter	= 39.37 inches
1 acre	= 0.40469 hectare
1 hectare	= 2.471044 acres
1 U. S. gallon	= 231 cubic inches = 4.5435 liters
1 cubic foot	= 7.4805 U. S. gallons
1 liter	= 1.05668 liquid U. S. quarts
1 quart	= 0.94633 liter

Table 13.—*(Continued)*

1 Imperial gallon	=	1.20 U. S. gallons
1 U. S. gallon	=	0.833 Imperial gallons
1 U. S. bushel	=	2150.42 cubic inches
1 U. S. gallon of water at 60° F.	=	8.33 pounds
1 U. S. gallon of water at 20° C.	=	8.321 pounds

Table 14. Standard Volumetric Solutions.

Substance	Formula	Molecular Weight	Normality	Grams in One Liter
Barium hydroxide	$Ba(OH)_2.8H_2O$	315.510	0.1*N*	15.7755
Hydrochloric acid	HCl	36.465	0.1*N*	3.6465
" "			0.4*N*	14.5860
" "			0.5*N*	18.2325
Iodine	I_2	126.92	0.1*N*	12.6920
Potassium hydroxide	KOH	56.104	0.1*N*	5.6104
" "			0.5*N*	28.0520
" iodate	KIO_3	214.02	0.1*N*	3.5670
" permanganate	$KMnO_4$	158.03	0.1*N*	3.1605
Sodium hydroxide	NaOH	40.005	0.1*N*	4.0005
" "			0.5*N*	20.0025
" carbonate	Na_2CO_3	106.00	0.1*N*	5.3302
" thiosulfate	$Na_2S_2O_3.5H_2O$	248.20	0.1*N*	24.8200
Sulfuric acid	H_2SO_4	98.07	0.1*N*	4.9035
" "			0.5*N*	24.5175
Thiocyanogen	SCN	58.078	0.1*N*	5.8078

Table 15. A Partial List of Atomic Weights.

Aluminum	26.97	Molybdenum	95.95
Antimony	121.76	Nickel	58.69
Arsenic	74.91	Nitrogen	14.008
Barium	137.36	Oxygen	16.000
Bromine	79.916	Phosphorus	30.98
Calcium	40.08	Platinum	195.23
Carbon	12.01	Potassium	39.096
Chlorine	35.457	Silicon	28.06
Cobalt	58.94	Silver	107.880
Copper	63.57	Sodium	22.997
Gold	197.2	Strontium	87.63
Hydrogen	1.0081	Sulfur	32.06
Iodine	126.92	Thallium	204.39
Iron	55.84	Tin	118.70
Lead	207.21	Titanium	47.90
Magnesium	24.32	Vanadium	50.95
Manganese	54.93	Zinc	65.38
Mercury	200.61		

Table 16. Some Characteristics of Fats and Oils Described in Chapter II.

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	M. Pt. ° C.	Titer ° C.
A					
Acorn, see *Quercus Spec.*					
Adenanthera pavonina	181	68	1.4		58.4
Allanblackia fats:					
A. *oleiferae* (kagne)	198	42	1.6	38–40	56.5
A. *stuhlmannii*	187	38		43–46	57.5
A. *floribunda*	191	44	0.4	37–40	57.6
Almond oil	183–196	95–102			
Andiroba (crabwood) oil	195–6	58–78	0.6–2.0		35–37
Andiroba (*Carapa grandiflora*) oil	198–202	73–84	1.6–3.7	23–30	35–39
Aoura, see tucum oil					

Table 16—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	M. Pt. ° C.	Titer ° C.
Apeiba (burillo) oil	235	77	1.2		
Areca (palm) kernel oil	234	12	1.0	36–38	
Astrocaryum aculeatum oil	184			18–23	
A. *aculeatum* kernel oil	211–214	9–10	0.6	32	
A. *tucum* kernel oil	240	12		31	
Atta (owala bean) oil	181	100	0.3–1.4	18–24	52–53
Avocado oil	186–197	71–94	1.6		
Awarra (A. *jauari*) palm oil	195.–8	68	0.5		37
Awarra palm kernel oil	242	13–15	0.5–0.8	31	23.5–27
B					
Babassu palm kernel oil	247–251	14–16.3	0.3–0.7	22–26	22–23
Bacury oil	192	63	4.2		52
Balanites aegyptiaca oil	194–197	92–98	0.6		34–35
B. orbicularis oil	193	76	0.5		39
Baobab (fony) seed oils:					
Adansonia digitata	190–192	76–78			32–34
A. grandidieri	190–193	57–66		21–25	43–45
A. madagascariensis	191	68		22	44
Bassia (*Madhucca*), see illipe tallow					
Bataua (patua) palm oil	190–2	75–80	0.5–1.1		17–18
Batiputa or bati oil	192–212	51–70			
Bayberry (wax) tallow	205–216	1–4	0.8–2.5	40–46	46
Bay oil, see laurel					
Bay tree (Cal.) seed fat	275.1	5.7	2.1	29–30	
Ben or moringa oil	179–187	67–72	0.9–1.5		32–38
Betel nut, see areca kernel oil					
Bey bean butter	180	81	6.2	33–34	
Borneo tallow (green butter)	189–200	29–38	0.4–2	34–39	51–52
Burillo, see apeiba oil					
Butea bonneti kernel oil	260	24			
C					
Cacao butter	192–198	34–40	0.3–0.8	30–34	48–50
Calophyllum oil	188–202	82–98	0.3–1.4		
Calumpang, see sterculia oil					
Canarium, see pili kernel oil					
Carnauba palm kernel oil	221	23	0.8	27	
Carob bean, see locust					
Carapa, see andiroba seed oil					
Carpotroche seed oil	201–203	102–108	0.6		
Cashew kernel oil	187–196	79–85	0.4–1.15		28–30
Castor oil	177–187	82–90	0.3–0.7		
Cay-cay fat	230–237	4–7		38–40	36–37
Chaulmoogra oil	198–208	98–106			
Chile molasses palm kernel oil	273	12	0.2		19
Chinese vegetable tallow	200–207	18–30	1–1.3	50–60	45–53
Chufa tuber oil	191	76	0.6		
Coffee bean oil	160–180	79–98	6–10		
Coconut oil	251–264	8–10	0.2–0.4	23–26	20–23
Cocos pulposa palm kernel oil	260.3	24.6	0.44	17–18	
Cokerite palm kernel oil	242–253	12–13	0.3	27–29	24
Cokerite palm oil	212	51			
Condor, see A. pavonina seed oil					
Coquito oil, see noli palm					
Coyal palm kernel oil	246	25		25	
Crabwood, see andiroba oil					
Crotalaria oil	183	88			
Cupu kernel fat	188	44–45	0.9	32	48
Curua palm kernel oil	260	9	0.4	24–26	25

Table 16—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	M. Pt. °C.	Titer °C.
D					
Da (anbari hemp) seed oil	187–194	90–100	0.4		
Date kernel oil	206–212	50–54.5	0.4–1.98		
Dika butter	241–250	3–5	0.3–0.8	38–41	35–38
Djave (adjab) butter	182–188	56–65	2–3		46–48
Dumoria oil	186–187	43–48	0.9		
E					
Ebor seed butter	181	73	1.6		
Elm seed oils	264–279	15.9–37.9	1–1.4		
Ergot oil	172–197	62–74	1.2–3.3		
F					
Filbert, see hazel nut oil					
G					
Gamboge butter	195–198	54–56		34–37	
Gembok bean oil	190	96	0.8		31
Gorli seed oil	190–194	94–100	1–1.6	42–46	
Guere palm kernel oil	250	9		36	30
H					
Habai, see tangallak butter					
Hazel nut (kernel) oil	193–197	84–90	0.3–0.5		19–20
Hegli, see zachun oil					
Horse chestnut oil	194.5	95–.4	2.5		
Hydnocarpus kernel oils:					
H. alcalae	202	94		32	
H. alpina	201–209	84–96		22–26	
H. anthelminthica	191–226	84–99		20–25	
H. cauliflora	201	84			
H. hutchinsonii	199	84			
H. ilicifolia	213	89		23–28	
H. ovoidea	215	47			
H. subfalcata	206	89			
H. venenata	191–207	84–99		22–26	
H. wightiana	197–208	93–103	0.2	21–24	
H. woodii	192–202	86–89	0.5	29	
Hungay, see pongam seed oil					
I					
Illipe butters	188–207	53–70	0.8–3.5		
Imburano seed oil	198.6	116.6			
Inoy kernel oil	184–193	89–94	0.4		22–25
Irvingia smithii oil	237	2.96		38–39	
I. malayana oil		5.2		39	
J					
Jaboty butters	229–236	5–23	0.5–1.6	40–46	
Japan tallow	208–220	5–17	0.5–1.7	50–54	55–58
Java almond, see C. commune oil					
Jiconga, see koeme oil					
Jojoba seed liquid wax	92.2–95	82–88	48.3		circa 12
K					
Kagne butter, see allanblackia					
Kaloempang, see sterculia oil					
Kanga, see lamy butter					
Kapok (Java) seed oil	189–195	86–98	0.8–1.6		27–32
Kapok (India) seed oil	193–194	74–78	1		38
Koeme seed oil	193–197	89–101	0.3–0.9		39–42
Kokum (goa) butter	187–192	25–36	1.2–2.3	39–43	

Table 16—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	M. Pt. ° C.	Titer ° C.
Kombo butter	255	65.4			37
Krobonko (telfaria) seed oil	262	43.4	0.38		
Kullam, see zachun seed oil					
Kurrajong seed oil	198	101		30	
Kussum, see Macassar seed oil					
L					
Lamy butter	186–189	42–47	0.9–1.7	33–42	51–55
Laurel oil	198–201	75–86	1.0	32–34	15–19
Locust seed oil	198–205	98–99	2.8		25
M					
Macadamia nut (kernel) oil	194–196	74–76	0.1–0.3		
Macassar kernel oil	215–230	48–69	1.5–7		52
Macaúba, see Paraguay palm oils					
Macrocarpa oil	189	83		37–39	
Mafuro oil	195-202	66-70	0.6-0.8		44
Mafuro tallow	201	43-49	1-1.4	33-41	51-52
Mahuba rana fat	245	21	4	40-44	
Malabar tallow	187-192	36-41	1.2-2.5	30-40	53-55
Mammy apple seed oil	190	70	1.4		
Manicaria saccifera palm kernel oil	250	10.7			
Margrosa, see neem oil					
Marmarron kernel oil	251	11	0.4	24	23
Marola kernel oil	194	73-76	0.6		
Maximiliana caribaea kernel oil	236.9	22.7	0.23		
Meni, see niam oil					
Mexican buckeye, see ungnadia oil					
Mowrah, see illipe butter					
Mung bean oil	173.3	81.6	2-3.5		
Murumuru palm kernel oil	237–247	10-13	0.7	32-35	
Myristica carnarica butter	203-206	19-27	2-3.5		34
Myristica malabarica butter	189-192	50-54		41	
Myristica platysperma butter	240	5		42-43	
Myrobalans seed oil	190.2	105.1			
N					
Nasturtium seed oil	172-179	75-78.5	1.14		
Neem oil	186-204	70-73	0.7-7		
Niam kernel oil	182-195	70-73	0.5-9	24	47-49
Noli palm oil	199	84	0.7		
Noli kernel oil	234	28			
Nutmeg butter	168-181	45-50	high	42-45	
O					
Ochna pulchra pulp oil	197.7	58.5			
O. pulchra kernel oil	197	74.3			
Oenocarpus bacaba palm oil	193.4	81.5	0.46		
Ochoco butter	238	2	0.4	45-48	
Okra seed oil	195	93-100			18.25
Olive oil	185-200	74-94	0.6-1.3		
Oliver kernel oil	182-184	86-87			
Oncoba klainii kernel oil		86.3		38-39	
Oncoba spinosa kernel oil	192	177	1.3		23-24
Oncoba welvitschii kernel oil	184	84		38-40	
Otoba butter	185-198	54	20		37
Ouricury (licury) kernel oil	257	14.7	0.27		
Owala bean, see atta oil					

Table 16—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	M. Pt. ° C.	Titer ° C.
P					
Palm oil	196-206	48-58	0.3	27-50	38-47
Palm kernel oil	240-250	16-23	0.2-0.8	21-29	20-28
Palma real (Ecuador) kernel oil	253.4	16.4			
Papaya seed oil	189	72.6	1.32		
Paraguay palm oil	190	77			
Paraguay palm kernel oil	237-246	16-28	0.3		21
Parkia seed oil	189.5	80.9	1.11		
Pataua palm oil	190-192	75-80	0.5-1.1		17-18
Peanut oil	185-192	83-95	0.2-0.8		23-32
Pecan kernel oil	190	100	0.4		
Picramnia fats	186-194	56-83	1.-1.7	40-52	
Pili nut (kernel) oils	187-197	56-74	0.2-0.6		37-41
Piney, see Malabar tallow					
Piririna palm kernel oil	252	13-17		22-26	
Pistacia lentiscus kernel oil	209	81.6	0.96		
Piqui pulp fat	204.9	47-49	0.7-0.8	27-28	
Piqui kernel fat	202.9	52	1.3-1.7	31-32	
Pitjong (samaun) oil	196-200	79-108	0.6		20.4
Plumy coconut kernel oil	239.5	28.4	0.41		
Pongam seed oil	177-189	83-94	2-9		
Pracaxy kernel oil	175-180	67-70			
Pulasan tallow	199	42	0.5	40-42	51
Q					
Queensland, see macadamia oil					
R					
Rambutan tallow	193-194	39-44	0.5	40-46	51-57
Royal palm kernel oil	226.5	39.8	0.5		20.5
S					
Samaun, see pitjong oil					
Sawarri fat	197-200	41-50			46-47
Segeu palm oil	187-191	73-74			
Sequa oil	192	52	0.7	34	
Shea butter	178-189	56-65	2.2-11	33-42	52-53
Siak tallows	182-187	38-51	1.2-8	31-39	
Siene bean oil	177.5	97.3	3.0		38.8
Sierre Leone, see lamy butter					
Soap tree kernel oil	194	58	1.2		
Sterculia kernel oil	187-199	75-83	5.6		
Sterculia pulp oil	192-194	56-59			43
Sterculia bequaerti oil	207.3	80.6	0.2		
Sugar apple seed oil	181-188	85-88	0.2		
Sumach seed oil	192	97.5	1.63		
T					
Talisay kernel oil	186-193	75-77	0.5-1.9		
Tangallak butter	257	8.5	1.5	above 40	
Tea seed oils	190-196	78-93	0.2		13-15
Tiger apple (yellow oleander) seed oil	194	68-76	1.4		
Tsubaki (*Thea japonica*) seed oil	187-193	78-82	0.2		
Tucum (aoura) palm oil	220	46	0.7	27-30	
Tucum palm kernel oil	240-249	11-14	0.3	30-32	26-27
U					
Ucuhuba butter	218-228	10-18	1.1-3.2	40-47	
Ungnadia (Mexican buckeye) oil	192-302	82-84	0.8		

Table 16—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	M. Pt. ° C.	Titer ° C.
V					
Vegetable tallow, see Chinese tallow					
Virola guatamalensis butter	223-230	11-18		41	
Virola surinannensis butter	244	14	1.0		37
W					
Wrightia annamensis oil	184	85	1.0		
X					
Ximenia seed oil	155-183	81-95	0.6-1.7		
Y					
Yellow oleander, see tiger apple oil					
Z					
Zachun (hegli) seed oil	191-197	92-98	0.6		34-35

Table 17. Some Characteristics of Fats and Oils Described in Chapter III

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	Titer ° C.
A				
Ajowan seed oil	177	109	1.1	
Anise seed oil	178	109	0.9	
Apple seed oil	187.7	122.4	1.1	
Apricot kernel oil	188-193	100-108		
Argemone seed oil	190-193	124-128	1.1-1.4	
B				
Bael seed oil	193.6	108	1.6	
Beech nut (kernel) oil	191-196	111-120	0.27	
Benne, see sesame oil				
Brazil nut (kernel) oil	192-200	98-106	0.5-0.7	29-32
Bryony seed oil	193	135		
C				
Cantaloupe seed oil	192	125	1.1	
Cape chestnut seed oil	193	109	0.5	*27*
Caraway seed oil	178		2.7	
Carrot seed oil	179	105	1.5	
Cayeté seed oil	192	116	0.5	
Celery seed oil	178	95	0.8	
Charlock seed oil	181-182	119-121		
Cherry kernel oil	192-198	111-122	0.3-0.5	13-15
Chinese colza seed oil	173	100		
Colocynth seed oil	178-203	120-129		27-29
Commiphora kernel oil	189	107	1.3	
Commiphora pulp oil	201	57	0.6	
Coriander seed oil	182-190	93-100	2.3	
Corn oil	188-193	116-130	1.3-2	18-20
Cottonseed, crude oil	192-200	100-115	0.9-2	
Cottonseed, refined oil	191-196	103-115	0.7-1.5	32-38
Croton seed oil	200-215	102-108	0.6	19
Cucumber, see sativus seed oil				
Cumin seed oil	179	92	2	
Curcus seed oil	189-193	93-107	0.4-1.1	27.5-29
D				
Datura seed oil	186-202	113-126	1-2.6	
Devil claws, see unicorn oil				
Dill seed oil	178	120	1.1	

Table 17—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	Titer °C.
E				
Egyptian lettuce seed oil	190	122-136		
Eruca sativa seed oil	169-171	97-100		
F				
Fennel seed oil	181	99		
G				
Garden chervil seed oil	183	110	1.5	
German sesame oil	185-188	127-150		13-14
Gingili, see sesame oil				
Grapefruit seed oil	194	106	0.7	
H				
Hodgsonia seed oil	201.2	65.5-67	0.3-0.4	42
Hollyhock seed oil		119		
Hubbard squash seed oil	192	121	1	
I				
Ivory wood seed oil	207	113	0.6	
J				
Jamba seed oil	171-175	91	0.4-0.7	11-16
Jute seed oil	185	103	2.3	
L				
Lemon seed oil	188-196	103-109		32-38
Lime seed oil	198	110	0.4	35
M				
Madia seed oil	193-195	117-129	0.8	20-22
Maize, see corn oil				
Mexican prickly poppy, see argemone seed oil				
Millet seed oil	182-184	92-114	2.5-5.0	25-26
Mlenda seed oil	182	118		
Mustard (alba) seed oil	171-177	94-106		9-10
Mustard (nigra) seed oil	178-184	114-124	1.2	6-8
N				
Narras seed oil	181	117		26
O				
Oat oil	185-199	100-116	1.3-2.6	
Orange seed oil	194-197	98-104		34-35
P				
Papaw seed oil	194	111.3	0.8	
Parsley seed oil	177	110	2.2	
Peach kernel oil	189-192	96-110		13-14
Pinus gerardiana seed oil	182	121	0.5	
Pinus monophylla seed oil	184-189	102-109	1.95	
Pinus pinea seed oil	193	118	1.98	
Pinus pumila seed oil	191.3	161		
Pinus sabiniana oil	189.2	120		
Plum kernel oil	188-196	100-105	0.4	12-15
Prickly poppy, see argemone seed oil				
Princeps seed oil	192-207	119-123		1-1.98
Pumpkin seed oil	185-198	120-130		
Purge (physic) nut, see curcus oil				

Table 17—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	Titer ° C.
R				
Radish seed oil	180-182	90-104		
Rape (colza) seed oil	168-180	98-106	0.5-1.5	
Ravision oil	173-181	109-122	1.4-1.8	
Rice oil	183-194	92-109	3.5	27
Rose mallow seed oil	185.5	107.8	1.34	
Rye oil	175-196	110-140	7-11	
S				
Sativus (cucumber) seed oil	195-197	118		35
Senat seed oil	187-192	117-128		30
Sesame oil	188-193	103-115	0.7-1.2	21-24
Spurge nettle seed oil	187	125-129		
Sunflower seed oil	189-194	120-130	0.8-1.8	17-20
T				
Teel, see sesame oil				
Tomato seed oil	184-192	118-125		
U				
Unicorn seed oil	197	123		
W				
Watermelon seed oil	190-198	115-125	0.7-1.3	29-35
Watermelon (Cuban Queen) seed oil	197.4	133.6	1.2	
Wheat oil	180-189	115-126	3.5-4.7	
X				
Xanthocarpum (bkatkayta) oil	182.5	124.3	1.2	

Table 18. Some Characteristics of Oils Described in Chapter IV

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	Titer ° C.
A				
Afzelia seed oil	184	142-144		
Alfalfa seed oil	172-185	142-148	3-4.4	
Akaritton kernel oil	187	214	1.15	
Arara kernel oil	189-192	130	0.5	
B				
Bagilumbang (banncalag) oil	190-200	127-160	0.5	
Belladonna seed oil	191.2	145-147	2-5	
Black walnut kernel oil	191-193	135-140	0.4	
Butternut kernel oil	191.7	163		
C				
Candlenut, see lumbang kernel oil				
Carthamus oxyacantha, see poli oil				
Ceara rubber, see manihot seed oil				
Cedar (Siberian) nut oil	188-192	150-160	1-1.6	11-12
Chia seed oil	195	190-200	0.7	
Cockle burr seed oil	190	141		
Croton ("Elliott") seed oil	192	147		
E				
Elderberry (European) seed oil	187-198	161-177	0.6-1.1	
Elderberry (American) seed oil	180	171	1.48	
Euphorbia amygaloides seed oil	194	192	0.8	
E. cyparissias seed oil	196	205	0.9	
E. esculа seed oil	196	207	0.9	

Table 18—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	Titer ° C.
E. exigua seed oil	191.5	212.5	0.94	
E. helioscopia seed oil	191	204	0.8	
E. paralias seed oil	194	196	1.5	
E. platyphylla seed oil	191	212	0.7	
E. verrucosa seed oil	190	209	1	
F				
Fig seed oil	190	169.4	1.07	
Funtumia seed oil	180-185	131-138		
G				
Grape seed oils	181-206	94–143	0.7-1.4	
Gynocardia oil	197-199	153-160		
H				
Hackberry tree seed oil	191	150	1.35	
Hempseed oil	190-193	150-166	1-1.3	15-17
Hickory nut (kernel) oil	190	107		
Hickory (swamp) kernel oil	190	105		
Hyoscyamus seed oil	171-188	131-143	0.7-1.9	
I				
Isano (boleko) seed oil	191.4	143	3.27	
J				
Japanese wood (kernel) oil	189-196	148-160	0.4-0.8	22
Japanese walnut kernel oil	191	150	0.55	
K				
Kentucky coffee tree kernel oil	191	138	1.3	
Kicksia seed oil	180	131		23
L				
Lallemantia seed oil	181-195	162-197		11
Linseed oil	189-196	175-204	0.5-1.6	19-21
Lumbang kernel oil	190-193	140-160	0.9	13-16
M				
Manihot seed oils	189-193	130-142	0.5-0.9	20-23
Manshurian walnut oil	188	158	0.53	
Manketti kernel oil	192–195	129–137	0.9	35–39
Mercuriales annua seed oil	190–193	206–216	0.5–0.9	22
M. perennis seed oil	190–192	203–204	0.7–1.7	22
M. tomentosa seed oil	191–194	201–208	0.8	21
Mexican rubber seed oil	195	110		
N				
Neasana oil	185–192	147		34–36
Neon kernel oil	190	135	0.9	
N'Gart oil	190–192	198–204	0.2	24–25
Niger seed oil	189–193	125–134	0.5–3.6	
Nsa-sana (essang) kernel oil	185–194	146–148	0.5–1.2	34–36
O				
Oiticica oil	186–195	140–152	0.4–0.9	
Osage orange seed oil	192	134–136		
P				
Paprica seed oil	185–195	133–144		
Para rubber seed oil	186–195	133–145	0.5–0.8	
Passion fruit seed oil	190.4	140–.4	0.62	
Perilla oil	188–197	185–208	0.6–1.3	

Table 18—(*Continued*)

Name or Source	Sap. V.	Iod. No.	Unsap. Per Cent	Titer ° C.
Pimento seed oil	171	134		21
Poli seed oil	174–189	136–167		
Poppy seed oil	189–196	132–140	0.5	16–19
Po-yoak seed oil	189–193	140–160	0.3–1	
R				
Rabbit's fruit kernel oil	188	140	2.1	
S				
Safflower seed oil	188–194	140–150	0.5–1.3	16–17
Salvia sclarea seed oil	193	141		
S. spinosa seed oil	193	159		
Sandal tree seed oil	185–197	138–153	8.8–19	
Siberian cedar, see cedar nut oil				
Soybean oil	189–194	124–136	0.5–1.8	20–21
Stillingia (kernel) oil	203–210	170–187	0.4–1.5	12–13
T				
Tall oil	145–175	120–188	6–20	
Thistle (cardo) seed oil	188	133.4	0.63	
Tobacco seed oil	186–197	131–147	1–1.4	18
Tung (China wood)oil	189–195	160–170	0.4–0.8	37–38
W				
Walnut (Persian or English) oil	189–197	132–153	0.5	14–15
Walnut, see black walnut kernel oil				
Z				
Zeylanicum seed oil	192	161	0.5	22

Table. 19. Botanical Families with Species

Botanical Names	Common Names
Anacardiaceae	
Anacardium occidentale	Cashew
Pistacia lenticus	Pistach
Pistacia vera	"
Rhus coriara	Sumach
" *acuminata*	" (Oriental)
" *succedanea*	" "
" *sylvestris*	" "
" *vernicifera*	Lack or varnish tree
Anonaceae	
Anona squamosa	Sugar apple or bottle tree
Asimina triloba	Papaw (N. America)
Apocynaceae	
Funtumia elastica	Funtumia
Kickxia elastica	Kickxia
Thevetia nerufolia	Tiger apple or yellow oleander
Wrightia annamensis	Wrightia
Asclepiadaceae	
Asclepis syriaca	Milkweed
Asteraceae (Compositae)	
Carthamus tinctorius	Safflower
Carthamus oxyacantha	Poli
Cynaria cardunculus	Cardo (thistle)
Guizota abyssinica	Niger
Helianthus annuus	Sunflower
Lactuca scariola	Egyptian lettuce
Madia sativa	Madia, tar weed
Xanthium echinatum	Cockle burr

Table 19—(*Continued*)

Botanical Names	Common Names
Betulaceae	
Corylus avellana	Hazel or filbert
Bombacaceae	
Adansonia digitata	Baobab or Fony
Adansonia grandidieri	" " "
Adansonia madagscariensis	" " "
Bombax ceiba	Kapok (S. America)
Bombax malabaricum	" (Indian)
Ceiba pentandra	" (Java)
Boraginaceae	
Trichodesma zeylanicum	
Burseraceae	
Canarium commune	Java almond tree
" *luzonicum*	Pili nut tree
" *oleosum*	
" *ovatum*	
" *polyphyllum*	
Commiphora zanzibarica	
Buxaceae	
Simmondsia californica	Jojoba, goat, or sheep nut shrub
Caesalpiniaceae	
Afzelia africana	
Caricaceae	
Carica papaya	Papaya
Caprifoliaceae	
Sambucus canadensis	Elderberry (American)
Caryocaraceae	
Caryocar amygdaliferum	Sawarri or Swari
Caryocar brasiliense	" " "
Caryocar butyrospermum	" " "
Caryocar tomentosum	" " "
Caryocar villosum	Piquia
Celastraceae	
Celastrus scandens	Bittersweet
Combretaceae	
Terminalia chebula	Myrobalans
Terminalia catappa	Talisay, badam, catappa or tropical almond
Compositae see *Asteraceae*	
Convolulaceae	
Convalvulus arvensis	Field bind weed
Cruciferae	
Brassica arvensis	Charlock
Brassica besseriana	
Brassica campestris	Rape (Ravison)
Brassica chinoleifera	Chinese colza
Brassica glauca	
Brassica juncea	Indian mustard
Brassica napus	Rape
Brassica nigra	Black mustard
Brassica oleifera	Rape
Brassica rapa	Rape
Camelina sativa	Dodder or German sesame
Conringia orientalis	Hare's ear mustard
Eruca sativa	Yamba, Cawnpore, or Rochet
Raphanus spec.	Radish
Sinapis alba	White mustard
Cucurbitaceae	
Acanthosicyos horrida	Narras
Bryonia dioica	Bryony
Citrullus colocynthis	Colocynth
Citrullus naudinianus	
Citrullus vulgaris	Watermelon

Table 19—(*Continued*)

Botanical Names	Common Names
Cucumis chate	Senat
Cucumis melo	Cantaloupe
Cucumis sativus	Sativus
Cucurbito maxima	Hubbard squash
Cucurbito pepo	Pumpkin
Fevillea cordifolia	Sequa
Hodgsonia capiocarpa	Hodgsonia
Telfairia occidentales	Krobonko
Telfairia pedata	Koeme or Jiconga
Cyperaceae	
Cyperus esculentus	Chufa
Dipterocarpaceae	
Shorea aptera	Borneo tallow tree
" *gysbertiana*	" " "
" *seminis*	" " "
" *stenoptera*	" " "
Hopea aspera	" " "
Pentacme siamensis	
Vateria indica	Dhupta (Malabar or Piney)
Ebenaceae	
Diospyros virgineana	Persimmon
Euphorbiaceae	
Aleurites cordata	Japanese tung
Aleurites fordii	Tung or Chinese wood
Aleurites moluccana	Lumbang, Candlenut, kekune or ignape
Aleurites montana	Abrasin, Mu, or Tung
Aleurites trisperma	Bagilumbang
Caperonia palustris	Birds' eye (seed)
Croton elliotianus	Elliot Croton
Croton tiglium	Croton
Euphorbia amygdaloides	
Euphorbia cyparissias	
Euphorbia elastica	Mexican rubber
Euphorbia esula	
Euphorbia exigua	
Euphorbia helioscopia	
Euphorbia paralias	
Euphorbia platyphylla	
Euphorbia verrucosa	
Fumtumia elastica	
Hevea brasiliensis	Para rubber
Jatropha curcas	Physic or Purge nut
Jatropha stimulosa	Spurge nettle
Joannesia heveoides	Arara nut
Joannesia princeps	Anda-assu or Joanesia
Manihot dichotoma	
Manihot glaziovia	Ceara rubber or Manihot
Manihot piauhyensis	
Mercurialis annus	Bingel
Mercurialis perennis	Forest Bingel
Mercurialis tomentosa	
Omphalea megacarpa	Cayete
Plukenetia conophora	N'Gart
Poinsetta pulcherrina	Poinsetta
Ricinus communis	Castor
Ricinus zanzibarinus	Castor
Ricinodendron africanum	Nsasana
Ricinodendron rautanenii	Manketti
Stillingia sebifera	Stillingia
Fabaceae, see *Leguminosae*	
Fagaceae	
Fagus sylvatica	Beech

Table 19—(*Continued*)

Botanical Names	Common Names
Quercus dilatata	Oak (India)
" *ilex*	" "
" *incana*	" "
" *palustris*	Pin oak (U. S.)
" *ruba*	Red oak (U. S.)
Flacourtiaceae	
Asteriostiama macrocarpa	Inacrocarpa
Carpotroche amazonica	
Carpotroche brasiliensis	Carpotroche
Carpotroche crassiramea	
Carpotroche denticula	
Carpotroche glaucescens	
Carpotroche grandiflora	
Carpotroche intergrifolia	
Carpotroche laxiflora	
Carpotroche longifolia	
Carpotroche platyptera	
Carpotroche paludosa	
Carpotroche surinamensis	
Carpotroche sulsava	
Gynocardia odorata	Gynocardia
Hydnocarpus alcalae	
Hydnocarpus alpina	
Hydnocarpus anthelminthica	Hydnocarpus or Lukrabo
Hydnocarpus castanea	
Hydnocarpus curtisii	
Hydnocarpus hutchinsonii	
Hydnocarpus ilicifolia	
Hydnocarpus ovoidea	
Hydnocarpus subfalcata	
Hydnocarpus venenata	
Hydnocarpus wightiana	Hydnocarpus
Hydnocarpus woodii	
Lindackeria latifolia	
Lindackeria maynensis	
Lindackeria paraensis	
Lindackeria paucifolia	
Mayna echinata	
Oncoba echinata	Gorli
Oncoba klainii	
Oncoba spinosa	
Oncoba (caloncoba) welwitschii	
Panguim edule	Pitjoeng or Samoun
Taraktogenos kurzii	Chaulmoogra
Gramineae	
Avena sativa	Oats
Oryza sativa	Rice
Panicum miliaceum	Millet
Secale cereale	Rye
Triticum sativum, etc.	Wheat
Zea mays	Corn or Maize
Guttiferace	
Allanblackia floribunda	Bouandjo
" *oleifera*	Kagne
" *parviflora*	
" *stuhlmannii*	Mkanyi
Calophyllum inophyllum	Calophyllum
Garcinia indica	Kokum or Goa
" *babansae*	
Garcinia cambogea	
Garcinia morella	Gamboge, Gurgi or Murga

Table 19—(*Continued*)

Botanical Names	Common Names
Pentadisma butyracea	Lamy or Kanga
Platonia insignis	Bacury
Hippocastanaceae	
Aesculus hippocastanum	Horse chestnut
Hypocreaceae	
Claviceps purpurea	Ergot
Juglandaceae	
Carya ovata	Hickory nut
Hicoria pecan	Pecan
Juglans cinera	American butternut
" *manshuria*	Manchurian walnut
" *nigra*	Black walnut
" *regia*	English (Persian) walnut
" *suboldiana*	Japanese walnut
Labiatae	
Hyptis suaveolins	Chan
Lallemantia iberica	Lallemantia
Perilla frutescens (ocymoides)	Perilla
Perilla frutescens nankinensis	"
Salvia hispanica	Chia
Salvia sclarea	Muskatell
Salvia spinosa	
Lauraceae	
Laurus nobilis	Laurel or Bay tree
Litsoca sebifera	Tangallak or Habai tree
Persea americana	Avocado tree
Umbellularia californica	Bay tree (California)
Acrodiclidium spec.	Mahuna Rana
Lecythidaceae	
Bertholletia excelsa	Brazil nut tree
Lecythis ellcptica	
Leguminosae	
Acacia julibrissin	Mimosa
Adenanthera pavonina	Corall or Condor tree
Afzelia brieyi	
Afzelia africana	
Arachis hypogaea	Peanut, Groundnut or Arachis
Bauhinia esculenta	Gemsbok
Ceratonia siliqua	Locust or Carob Bean
Crotalaria valentonii	Crotalaria
Daubentonio longifolia	Rattlebox or Siene
Daubentonio drummondii	
Dipteryx odorata	Tonka Bean
Dipteryx oleifera	Ebor
Glottidium vesecarium	
Glycine max (Soja max)	Soy Bean
Gymnocladus dioica	Kentucky Coffee Bean
Medicago sativa	Alfalfa or Lucerne
Pentaclethra filamentosa	Pracaxy
Pentaclethra macrophylla	Atta or Owala Bean
Pongamia glabra	Hongay or Pongam
Pongamia pinnata	
Torresea cearensis	Imburana
Linaceae	
Linum usitatissimum	Flax (Linseed)
Malvaceae	
Althaea rosea	Hollyhock
Gossypium arboreum	Cotton
Gossypium barbadense	"
Gossypium hirsutum	"
Gossypium herbaceum	"
Gossypium indicum	"
Gossypium neglectum	"

Table 19—(*Continued*)

Botanical Names	Common Names
Hibiscus cannabiums	Da or Kenoph
Hibiscus esculentus	Okra
Hibiscus moschentos	Rose Mallow
Martyniaceae	
Martynia louisiana	Devil's claws or unicorn
Meliaceae	
Carapa grandiflora	Crabwood or Andiroba
Carapa procera	" " "
Carapa touloucouma	" " "
Mafouriera oleifera	Mafura
Melia azadirachta	Neem or Margosa
Swietonia mahogani	Mahogany
Minosaceae	
Parkia biglandulosa	Inga
Moraceae	
Cannabis sativa	Hemp
Ficus carica	
Toxylon pomiferum	Osage orange
Moringaceae	
Moringa aptera	
Moringa oleifera	Ben or Moringa tree
Myricaceae	
Myrica carolinensis	Bayberry or myrtle
Myrica cerifera	" " "
Myrica mexicana	" " "
Myristicaceae	
Myristica canarica	Mangalore or Pindi
Myristica fragrans	Nutmeg
Myristica malabarica	
Myristica platysperma	
Pycnanthus kombo	Kombo
Scyphocephalium ochocoa	Ochoco
Virola guatamalensis	
Virola otoba	Otoba (Amer. nutmeg)
Virola sebifera	
Virola surinamensis	Ucuhubo
Virola venezuelensis	Cuojo
Ochnaceae	
Lophira alata	Niam or Meni
Ouratea parviflora	Batiputa
Ochua pulchra	
Olacaceae	
Ongokea klaineana	Isano or Boleko
Ximenia americana	Ximenia or Wild Olive
Oleaceae	
Olea europa	Olive
Opiliaceae	
Agonandra brasiliensis	Ivory wood tree (Pao Mafi)
Palmae	
Acrocomia sclerocarpa	Paraguay palm, Macaúba.
Acrocomia vinifera	Coyal
Areca catechu	Areca or Betel
Arecastum romanzoffianum	Plumy coconut
Astrocaryum jauari	Awarra
Astrocaryum murumuru	Murumuru
Astrocaryum aculeatum	Marajo
Astrocaryum tucuma	Gru-gru, Guere or Tucum
Astrocaryum vulgare	Tucan
Attalea cohune	Cohune
Attalea gomphococca	Coquito
Attalea spectabilis	
Butea bonneti	Bonneti
Cocos nucifera	Coconut

Table 19—(*Continued*)

Botanical Names	Common Names
Cocos pulposa	
Cocos syagrus	Pirivima
Copernica cerifera	Carnauba
Diplothemium sp.	
Elaeis guineensis	African Oil palm, Dende in Brazil
Elaeis melanococca	Noli or Cayané
Eurterpe spec.	
Jessenica polycarpa	Segen or Unania
Jaboea spectabilis	Chile molasses or honey palm
Maximiliana caribaes	
Maximiliana regia	Cokerite or Marupa
Maxicaria saccifera	Sugar palm
Oenocarpus bataua	Bataua Pataua, or Coumou
Oenocarpus bacaba	
Oenocarpus distichus	
Orbignya speciosa	Babassu
Phoenix dactylifera	Date
Roystonea regia	Royal palm of Cuba
Scheelea excelsa ?	Mamarron
Scheelea regia ?	"
Syagruss coronata	Ouricury (Uricury)
Ynesia colenda	Palma real of Ecuador
Papaveraceae	
Argemone mexicana	Prickly or Mexican poppy
Papaver somniferum	Poppy
Passifloraceae	
Passiflora edulis	Passion flower
Pedaliaceae	
Sesamum augustifolium	Mlenda
Sesamum indicum	Sesame
Ceratotheca sesamoides	Bungu
Pinaceae	
Pinus cembra	Cedar nut or Swiss pine
Pinus gerardiana	Nejan pine
Pinus monophylla	" " (California)
Pinus pinea	Stone pine (S. Europe)
Pinus pumila	
Pinus sabiniana	Digger pine
Proteaceae	
Macadamia ternifolia	Macadamia or Queensland nut
Punicaceae	
Punica granatum	Pomegranate
Rhizophoraceae	
Poga oleosa	Inoy or Poga
Rosaceae	
Afrolicania elaeosperma	Po-yoak
Licania rigida	Oiticica
Parinarium laurinum	Akaritton
Parinarium macrophyllum	Neow
Prunus amygdalus	Almond
Prunus armeniaca	Apricot
Prunus cerasus	Cherry
Prunus domestica	Plum
Prunus persica	Peach
Pyrus malus	Apple
Pyrus communus	Pear
Rubiaceae	
Coffee arabica	Coffee
Rutaceae	
Aegle marmelos	Bael
Calodendrum capense	Cape chestnut

Table 19—(*Continued*)

Botanical Names	Common Names
Citrus aurantium	Orange
" *decumana*	Grapefruit
" *limetta*	Lime
" *limonum*	Lemon
Santalaceae	
Pyrulia pubera	Buffalo nut
Santalum album	White sandalwood tree
Sapindaceae	
Nephelium lappaceum	Rambutan
Nephelium mutabile	Pulasan
Sapindus drummondii	Soap berry
Sapindus marginatus	
Sapinus trifoliatus	Soap nut tree
Schleichera trijuga	Macasser or Kussum
Ungnadia speciosa	Mexican Buckeye
Sapotaceae	
Baillonella spec.	Bey Bean trees
Butyrospermum parkii	Karite, Galam, or Shea
Calocarpum mammosum	Mammy apple, Zapote
Dumoria africana	Dumoria
Madhuca butyraceae	Phulwa
" *latifolia*	Illipe or Mowrah
" *longifolia*	" " "
" *mottleyana*	Katio or Kachian
Minusops djave	Djave or Adjab
Palaquium oleosum	Siak (Large nut)
" *oblongifolium*	" (small nut)
Simarubaceae	
Irvingia barteri	
" *gabonensis*	Dika or Oba
" *malayana*	
" *oliveri*	Cay-cay
" *smithii*	
Picramnia camboita	
" *carpinterae*	
" *lindeniana*	
" *tariri*	
Simaruba glauca	
Solanaceae	
Atropa belladonna	Belladonna
Capsicum annum	Pimento
Datura stramonium	Datura
Hyoscyamus niger	Henbane
Nicotiana tabacum	Tobacco
Solanacee capsicum	Paprika
Solanum esculentum	Tomato
Solanum xanthocarpum	Bkatkayta
Sterculiaceae	
Brachychiton populneum	Kurrajoung
Sterculia appendiculata	
Sterculia foetida	Java olive
Theobroma bicolor	Lupu
Theobroma cacao	Cacao
Theobroma grandiflora	Cupu
Theaceae	
Camellia japonica	Tsubaki
Thea japonica	Tea
" *sasangua*	"
" *sinensis*	"
Tiliaceae	
Apeiba timbourbou	Burillo
Corchorus capsularis	Jute

Table 19—(*Continued*)

Botanical Names	Common Names
Tropaeolaceae	
Tropaeolum majus	Nasturtium
" *minus*	"
Ulmaceae	
Ulmus americana	American elm
Umbelliferae	
Anethum graveolens	Dill
Anthriscus cerefolium	Garden chevril
Apium graveolens	Celery
Carum carvi	Caraway
Coriandum sativum	Coriander
Cuminum cyminum	Cumin
Daucus carota	Carrot
Foeniculum officinale	Fennel
Petroselinum sativum	Parsley
Pimpinella anisum	Anise
Ptychotis ajowan	Ajowan
Urticaceae	
Celtis occidentalis	Hackberry
Vitaceae	
Vitis vinifera	Grape
Vochysiaceae	
Erisma calcaratum	Jaboty
Erisma uncinatum	"
Zygophyllaceae	
Balanites aegyptiaca	Zachum, Hegli, Betu
" *maughamii*	" " "
" *orbicularis*	" " "

Index of Botanical Names

A

Acacia julibrissin, 470
Acanthosicyos horrida, 250
Acrocomia sclerocarpa, 130
Acrocomia vinifera, 130
Acrodiclidium species, 93
Adansonia digitata, 36
Adansonia grandidieri, 36
Adansonia madagascariensis, 36
Adenanthera pavonina, 30
Aegle marmelos, 321
Aesculus hippocastanum, 79
Afrolicania alaeosperma, 293
Afzelia africana, 253
Afzelia brieyi, 253
Agonandra brasiliensis, 233
Aleurites cordata, 328
Aleurites fordii, 314
Aleurites moluccana, 330
Aleurites montana, 315, 327
Aleurites trisperma, 329
Allanblackia floribunda, 31
Allanblackia oleifera, 31
Allanblackia parviflora, 31
Allanblackia stuhlmannii, 31
Althaea rosea, 233
Anacardium occidentale, 46
Anethum graveolens, 247
Anona squamosa, 166
Anthriscus cerefolium, 247
Apeiba timbourbon, 34
Apium graveolens, 246
Arachis hypogea, 151
Areca catechu, 130
Arecastrum romanzoffianum, 136
Argemone mexicana, 234
Asclepis syrica, 470
Asiminatriloba, 235
Asteriastigma macrocarpa, 76
Astrocaryum aculeatum, 132
Astrocaryum jauari, 133
Astrocaryum murumuru, 133
Astrocaryum tucuma, 133
Astrocaryum vulgare, 132
Atrope belladonna, 312
Attalea cohune, 135
Attalea gomphococca, 137
Attalea spectabilis, 137
Avena sativa, 181

B

Baillonella species, 39
Balanites aegyptiaca, 170
Balanites maughamii, 170
Balanites orbicularis, 170
Bassia species, see Madhuca.
Bauhinia esculenta, 77
Bertholletia excelsa, 174
Bombax ceiba, 84
Bombax malabaricum, 86
Bombax species, 84
Brachychiton populneum, 89
Brassica arvenis, 224
Brassica besseriana, 226
Brassica campestris, 226
Brassica chinoleifera, 225
Brassica glauca, 226
Brassica juncea, 226
Brassica napus, 226
Brassica nigra, 225
Brassica oleifera, 226
Brassica rapa, 226
Bryonia dioica, 250
Butia bonneti, 137
Butyrospermum parkii, 63

C

Calocarpum mammosum, 93
Calodendrum capense, 175
Calophyllum inophyllum, 45
Camelina sativa, 241
Camellia japonica, 168
Canarium colophania, 160
Canarium commune, 160
Canarium oleosum, 160
Canarium ovatum (luzonicum), 159
Canarium polyphyllum, 160
Canarium rufum, 160
Cannabis sativa, 260
Caperonia palustris, 469
Capsicum annum, 291
Carapa grandiflora, 34
Carapa grandiflora, 34
Carapa touloucouna, 33
Carica papaya, 150
Carpotroche amazonica, 68
Carpotroche brasiliensis, 68
Carpotroche crassiramea, 68
Carpotroche denticula, 68
Carpotroche glaucescens, 68
Carpotroche grandiflora, 68
Carpotroche integrifolia, 68
Carpotroche laxiflora, 68
Carpotroche longifolia, 68
Carpotroche paludosa, 68
Carpotroche platyptera, 68
Carpotroche sulsava, 68
Carpotroche surinamensis, 68
Carthamus oxyacantha, 291
Carthamus tinctorius, 297
Carum carvi, 247
Carya amara, 334

Carya ovata, 334
Caryocar amygdaliferum, 164
Caryocar brasiliense, 164
Caryocar butyrospermum, 164
Caryocar tomentosum, 164
Caryocar villosum, 162
Ceiba pentandra, 84
Celastrus scandens, 469
Celtis occidentalis, 260
Ceratonia siliqua, 91
Ceratotheca sesamoides, 241
Citrullus colocynthis, 250
Citrullus naudinianum, 250
Citrullus vulgaris, 249
Citrus aurantium, 233
Citrus decumana, 232
Citrus limetta, 232
Citrus limonum, 232
Claviceps purpurea, 66
Cocos nucifera, 142
Cocus pulposa, 134
Cocus syagrus, 132
Coffea arabica, 58
Coffea liberica, 58
Commiphora zanzibarica, 251
Conringia orientalis, 470
Convalvulus arvensis, 469
Copernica cerifera, 138
Corchorus capsularis, 233
Coriandum sativum, 247
Corylus avellana, 79
Crotalaria valentonii, 59
Croton elliotianus, 255
Croton tiglium, 223
Cucumis chate, 251
Cucumis melo, 175
Cucumis sativus, 251
Cucurbita maxima, 248
Cucurbita pepo, 249
Cumimum cyminum, 247
Cynaria cardunculus, 313
Cyperus esculentus, 57

D

Datura strammonium, 245
Daubentonia drummondii, 469
Daubentonia longifolia, 165
Daucus carota, 247
Diospyros virgineana, 470
Diplothemium species, 138
Dipteryx odorata, 65
Dipteryx oleifera, 65
Dumoria africana, 65

E

Elaeis guineensis, 118, 119
Elaeis melanococca, 130
Erisma calcaratum, 82
Eruca sativa, 226
Euphorbia amygdaloides, 282
Euphorbia cyparissias, 283
Euphorbia elastica, 296
Euphorbia esula, 282
Euphorbia exigua, 283
Euphorbia helioscopia, 282
Euphorbia paralias, 283
Euphorbia platyphylla, 282
Euphorbia verrucosa, 283
Euterpe species, 140

F

Fagus sylvatica, 174
Fevillea corifolia, 165
Ficus carica, 256
Foeniculum officinale, 247
Funtumia elastica, 296

G

Garcia nutans, 471
Garcinia balansae, 88
Garcinia cambogia, 88
Garcinia indica, 87
Garcinia morella, 87
Glottidium vesecarium, 469
Glycine (Soja) max, 300
Gossypium arboreum, 186
Gossypium barbadense, 185
Gossypium herbaceum, 186
Gossypium hirsutum, 186
Gossypium indicum, 186
Gossypium neglectum, 186
Guizota abyssinica, 285
Gymnocladus dioica, 261
Gynocardia odorata, 260

H

Heistera species, 295
Helianthus annuus, 241
Hevea brasiliensis, 295
Hibiscus cannabinus, 59
Hibiscus esculentus, 102
Hibiscus moschentos, 236
Hicoria pecan, 159
Hodgsonia capiocarpa, 251
Hopea aspera, 39
Hydnocarpus alcalae, 73
Hydnocarpus alpina, 73
Hydnocarpus anthelminthica, 74
Hydnocarpus castanea, 68
Hydnocarpus cauliflora, 68
Hydnocarpus curtisii, 68
Hydnocarpus heterophylla, 75
Hydnocarpus hutchinsonii, 73
Hydnocarpus ilicifolia, 74
Hydnocarpus ovoidea, 68
Hydnocarpus subfalcata, 74
Hydnocarpus venenata, 75
Hydnocarpus wightiana, 75
Hydnocarpus woodii, 76
Hyoscyamus niger, 313
Hyptis suaveolins, 469

I

Irvingia barteri, 60
Irvingia gabonensis, 60
Irvingia malayana, 56
Irvingia oliveri, 55
Irvingia smithii, 56

J

Jatropha curcas, 224
Jatropha stimulosa, 241

Jessenica polycarpa, 140
Joannesia heveoides, 254
Joannesia princeps, 236
Juboea spectabilis, 138
Juglans cinera, 333
Juglans manshuria, 333
Juglans nigra, 333
Juglans regia, 332
Juglans sieboldiana, 333

K

Kickxia elastica, 296

L

Lactuca scariola, 231
Lallemantia iberica, 261
Laurus nobilis, 90
Lecythis elleptica, 470
Licania aborea, 471
Licania rigida, 286
Lindackeria latifolia, 68
Lindackeria maynensis, 68
Lindackeria paraensis, 68
Lindackeria paucifolia, 68
Linum usitatissimum, 262
Litsea sebifera, 166
Lophia alata, 100

M

Macadamia termifolia, 91
Madhuca butyraceae, 62
Madhuca latifolia, 79
Madhuca longifolia, 79
Madhuca mottleyana, 62
Madia sativa, 234
Manicaria saccifera, 131
Manihot dichotoma, 281
Manihot glaziovii, 280
Manihot piauhyensis, 281
Martynia louisiana, 248
Maximiliana caribaea, 137
Maximiliana regia, 141
Mayna echinata, 68
Medicago sativa, 253
Melia azadirachta, 99
Mercurialis annua, 281
Mercurialis perennis, 281
Mercurialis tomentosa, 281
Minusops d'jave, 61
Moringa aptera, 39
Moringa oleifera, 38
Myrica carolinensis, 37
Myrica cerifera, 37
Myrica mexicana, 37
Myristica canarica, 97
Myristica fragrans, 95
Myristica malabarica, 98
Myristica platysperma, 97

N

Nephelium lappaceum, 163
Nephelium mutabile, 164
Nicotiana tabacum, 313

O

Ochna pulchra, 101
Oenocarpus bacaba, 139
Oenocarpus bataua, 139
Oenocarpus distichus, 139
Olea europaea, 102
Omphalea megacarpa, 175
Oncoba echinata, 71
Oncoba klainii, 72
Oncoba spinosa, 72
Oncoba welwitschii, 72
Ongokea klaineana, 261
Orbignya speciosa, 140
Oryza sativa, 182
Ouratea pariflora, 37

P

Palaquium oblongifolium, 81
Palaquium oleosum, 81
Pangium edule, 77
Panicum miliaceum, 181
Papaver somniferum, 292
Papaya carica, 150
Parinarium laurinum, 293
Parinarium macrophyllum, 294
Parkia biglandulosa, 151
Passiflora edulis, 296
Pentaclethra filamentosa, 34
Pentaclethra macrophylla, 34
Pentadesma butyracea, 89
Perilla frutescens nankinensis, 288
Perilla frutescens (ocymoides), 288
Persea americana, 35
Petroselinum sativum, 245
Phaseolus mungo, 94
Phoenix dactylifera, 138
Picramnia camboita, 161
Picramnia carpinterae, 161
Picramnia lindeniana, 162
Picramnia tariri, 161
Pimpinella anisum, 247
Pinus cembra, 254
Pinus gerardiana, 235
Pinus monophylla, 235
Pinus pinea, 235
Pinus pumila, 235
Pinus sabiniana, 235
Pistacia lenticus, 161
Pistacia vera, 160
Platonia insignis, 36
Plukenetia conophora, 284
Poga oleosa, 82
Poinsetta pucherrina, 470
Pongamia glabra, 162
Pongamia pinnata, 163
Prunus amygdalus, 32
Prunus armeniaca, 171
Prunus cerasus, 172
Prunus domestica, 173
Prunus persica, 173
Ptychotis ajowan, 248
Punica granatum, 292
Pycnanthus kombo, 98
Pyrulia pubera, 469
Pyrus communis, 171
Pyrus malus, 171

Q

Quercus dilatata, 30
Quercus ilex, 30

Quercus incana, 30
Quercus palustris, 30
Quercus ruba, 30

R

Raphanus species, 226
Rhus acuminata, 83
Rhus coriara, 166
Rhus succedanea, 83
Rhus sylvestris, 83
Rhus vernicifera, 83
Ricinus communis, 47
Ricinus zanzibarinus, 55
Ricinodendron africannum, 284
Ricinodendron rautanenii, 283
Roystonia regia, 142

S

Salvia hispanica, 254
Salvia sclarea, 299
Salvia spinosa, 299
Sambucus canadensis, 256
Sambucus racemose, 256
Santalum album, 299
Sapindus drummondii, 470
Sapindus marginatus, 470
Sapindus trifoliatus, 165
Scheelea excelsa, 142
Schleichera trijuga, 92
Sclerocarya caffra, 94
Scyphocephalium ochocoa, 97
Secele cereale, 183
Sesamum augustifolium, 234
Sesamum indicum, 236
Shorea aptera, 39
Shorea ghysbertiana, 39
Shorea robusta, 39
Shorea stenoptera, 39
Simmondsia californica, 88
Sinapis alba, 225
Soja max, 300
Solanaceae capsicum, 313
Solanum esculentum, 244
Solanum xanthocarpum, 245
Sterculia appendiculata, 166
Sterculia bequaerti, 166
Sterculia foetida, 165
Stillingia sebifera, 56, 311
Swietonia mahogani, 470
Syagrus coronata, 134

T

Taraktogenos kurzii, 70
Telfairia occidentales, 87
Telfairia pedata, 86
Terminalia catappa, 167
Terminalia chebula, 99
Thea japonica, 168
Thea sasangua, 167
Thea sinensis, 168
Theobroma bicolor, 45
Theobroma cacao, 41
Theobroma grandiflora, 44
Thevetia nerufolia, 167
Torresea cearensis, 82
Toxylon pomiferum, 286
Trichilia emetica, 92
Trichodesma zeylanicum, 334
Triticum species, 184
Tropaeolum majus, 101
Tropaeolum minus, 101

U

Ulmus americana, 61
Umbellularia californica, 38
Ungnadia speciosa, 168

V

Vateria indica, 93
Virolla guatamalensis, 97
Virola otoba, 98
Virola sebifera, 96, 97
Virola surinamensis, 96
Virola venezuelensis, 97
Vitis vinifera, 257

W

Wrightia annamensis, 168

X

Xanthium echinatum, 255
Ximenia americana, 169

Y

Ynesia colenda, 142

Z

Zea mays, 176

Subject Index

A

Abeku (Adjab) butter, 61
Abrasin (mu) tung oil, 327
Acapulco process, 106
Acetyl and hydroxyl values, 403
  determination, 403
Acid value, 387
Acids (esters, salts, etc.)
  acetic, 337
  aleprestic, 76
  alepric, 353
  aleproclic, 76
  aleprylic, 353
  arachidic, 343
  azelaic, 345
  behenic, 343
  brassidic, 351
  butyric, 337
  capric, 338
  caproic, 337
  caprylic, 338
  cerotic, 344
  cetoleic, 351
  chaulmoogric, 352
  di-hydroxystearic, 355
  eicosanic, *see* arachidic
  elaeostearic, 353
  elaidic, 346
  erucic, 351
  erythrogenic, *see* Isano oil, 261
  gorlic, 352
  hexadecenoic, 354
  hexa-hydroxystearic, 356
  hydnocarpic, 352
  isolinolenic, 350
  iso-oleic, 347
  lauric, 338
  licanic, 354
  lignoceric, 344
  linoleic, 348
  linolenic, 349
  linusic, *see* Hexahydroxystearic, 356
  lumequeic, *see* Ximenia oil, 169
  melissic, 344
  montanic, 344
  myristic, 339
  myristoleic, 354
  non-existent, 336
  nonoic, *see* Pelargonic, 345
  oleic, 345
  palmitic, 340
  palmitoleic, 354
  parinaric, 355
  pelargonic, 345
  petroselinic, 348
Acids (esters, salts, etc.) (*continued*)
  punicic, 355
  ricinoleic, 350
  sativic, *see* tetra-hydroxystearic, 355
  sebacic, 345
  soluble and insoluble acids,
    determination of, 386
  stearic, 341
  suberic, 345
  tariric, 349
  tetradecenoic, 354
  tetra-hydroxystearic, 355
  tiglic, 345
  tri-hydroxystearic, 355
  ximenic, *see* Ximenia oil, 169
Acids, formic to caproic, determination
    by steam distillation, 336
Acorn (oak) kernel oils, 30
Adenanthera seed oil, 30
Adjab butter, 61
Afridiwax, *see* Safflower oil, 297
Afzelia seed oil, 253
Ajowan seed oil, 247
Akaritton kernel oil, 293
Alcohols,
  di-glycerine, 358
  glycerine, 356
  trimenthylene glycol, 359
Alfalfa seed oil, 253
Allanblackia seed fats, 30
Almond oil, 32
Ambari hempseed oil, 59
Amburana oil, 82
American nutmeg butter, *see* Otoba, 98
Analysis of cake and meal, 458
Acanthosicyos horrida seed oil, 250
Anda-assu (princeps) oil, 236
Andiroba oil, 33
Anise seed oil, 247
Áouara palm oil, 132
  kernel oil, 132
Apeiba oil, 34
Apple seed oil, 171
Apricot kernel oil, 171
Arachis oil, *see* Peanut, 151
Arara nut oil, 254
Areca palm kernel oil, 130
Argemone seed oil, 234
Ash, determination, 411
Astrocaryum tucuma, 133
Atta seed oil, 34
Attalea gomphococca kernel oil, 137
Avocado pulp oil, 35
Awarra palm oil, 133

B

Babassu kernel oil, 140
Bacury kernel oil, 36
Bael seed oil, 231
Bagilumbang oil, 329
Baka butter, *see* D'jave, 61
Bambuk butter, *see* Shea nut, 63
Banucalag oil, *see* Bagilumbang, 329
Baobab seed oil, 36
Bassia tallow, see Illipé, 79
Bataua (Pataua) Palm oil, 139
Batiputa or bati oil, 37
Batu oil, *see* Zachun, 170
Baudouin text, 240
Bay (Laurel) fats, 90
Bayberry tallow, 37
Bay tree (California) seed fat, 38
Beechnut oil, 174
Belladonna seed oil, 312
Ben oil, 38
Beni seed oil, *see* Sesame, 238
Bertram modified method for saturated acids, 414
Betel nut fat, 130
Bey bean butter, 39
Bind weed seed oil, 469
Bird's eye seed oil, 469
Bittersweet vine seed oil, 469
Black walnut oil, 333
Bleach test for oils, 452
Boiled oil test, 411
Boleko (Isano) seed oil, 261
Borneo tallow, 39
Botanical families with species, 486
Boysenberry seed oil, 469
Brassicasterol, 365
Brazil nut oil, 174
Brown heat test, 322
Bryony seed oil, 250
Buffalo nut oil, 469
Bungu oil, *see C. sesamoides*, 241
Burillo seed oil, *see* Apeiba, 34
Butea palm kernel oil, 137
Butternut (*Juglans cinera*) oil, 333

C

Cacahuananche, *see Licania arborea* oil, 335
Cacao butter, 41
  adulterants, 42
  examination, 42
Caerá rubber seed oil, 280
Cajuile kernel oil, see Cashew, 46
Cake and meal, analysis, 458
Cake sampling, 457
Calophyllum kernel oil, 45
Calorific value, fats and oils, 23
Calumpang oil, *see* Sterculia, 165
Cameline seed oil, 241
Canarium commune nut (kernel) oils, 160
Candlenut oil, *see* Lumbang, 330
Cantaloupe seed oil, 175
Cape chestnut seed oil, 175
Carapa kernel fat, *see* Andiroba, 33
Caraway seed oil, 247
Cardo, thistle seed oil, 313
Carnauba palm kernel oil, 138
Carob bean oil, *see* Locust, 91
Carpotroche seed oil, 68
  species, 68
Carrot seed oil, 247
Cashew nut (kernel) oil, 46
  shell oils, 46
Castanha de cotia seed oil, 294
Castor oil, 47
  dehydrated, 51
  hydrogenated, 48
  tests, 49
  uses, 51
Cathamus oil, *see* Safflower, 297
Cayeté seed oil, 175
Cay-cay fat, 55
Cedar nut oil, 254
Celery seed oil, 246
Cephalins, 369
Ceratotheca sesamoides oil, 241
Chambira kernel oil, *see* Tucum, 132
Chan seed oil, 469
Characteristics, chaulmoogra and related oils, 78
Characteristics of fats and oils, 477
Charlock seed oil, 224
Chaulmoogra and related plants, 68
Chaulmoogra oil, 70
Cherry kernel oil, 172
Chia seed oil, 254
Chicalote oil, *see* Argemone, 234
Chile molasses palm kernel oil, 138
China wood oil, *see* Tung, 314
Chinese colza seed oil, 225
Chinese vegetable tallow, 56
Cholesterol, 364
  detection of, 417
Chufa tuber oil, 57
Cockle burr seed oil, 255
Coffee "bean" oil, 58
Coconut oil, 142, 145
  characteristics, 147
  composition, 148
  grades, 147
  hydrogenated, 149
  oleine and stearine, 146
  refining, 146
  refining tests, 450
  tests, 149
Coconut palms, 143
Cocos pulposa palm kernel oil, 134
Cohune palm kernel oil, 135
Cokerite palm oils, *see M. regia*, 141
Cold pressed (expeller) oils, 19
Cold test, 454
Colocynth seed oil, 250
Coloncoba oils, *see* Oncoba, 71, 72
Color, cake and meal measurement, 458
  measurements of oils, 452
  of oils, 16
  test, sterols, 363
  tests, oils, 419
Colza oil, *see* Rape, 226
Commiphora, fruit and seed oils, 251

Composition of fats, effect of climate, 15
Composition of fats in relation to plant classification, 15
Condor seed oil, *see* Adenanthera, 30
Conjugated double bonds, test for, 420
Copra oil, *see* Coconut, 145
Copra, preparation, storage, 143
Corall seed oil, *see* Adenanthera, 30
Coriander seed oil, 247
Corn, degermination, dry process, 176
  wet process, 176
Corn oil, 176
  characteristics, 178
  composition, 179
  expression, 177
  refining, 177
  refining tests, 452
  uses, 178
  wax, 180
Coquito palm oils, *see* Attalea gompho-cocca, 137
  noli, 130
Cotton, 185
  Asiatic, 186
  belt in United States, 187
  communities, one variety, 186
  Egyptian, 185
  general classes, 185
  lint, 185, 186
  Sea Island, 185
  species, 185, 186
  tree seed oil, *see* Kapok, 84
  upland, 186
Cotton and cottonseed oil in
  Africa, 192
  Anglo-Egyptian Sudan, 193
  Argentina, 190
  Australia, 193
  Brazil, 190
  Central America, 189
  Chile, 191
  Chosen (Korea), 191
  Colombia, 191
  Ecuador, 191
  Egypt, 192
  Europe, 194
  Guiana, 191
  India, 191
  Japan, 192
  Mexico, 189
  Nigeria, 193
  Paraguay, 191
  Peru, 190
  Uganda, 193
  United States, 187
  U.S.S.R. (Russia) 191
  Venezuela, 191
  West Indies, 190
Cottonseed
  analysis, 434
  cake and meal analysis, 458
  cleaning, 200
  color, 456
  composition, 195
  cooking, 202
Cottonseed (*continued*)
  damaged, 195
  decortication, 201
  expeller oil mill, 201
  free fatty acids, determination, 437
  gossypol, 197
  hulls, 201
  hydraulic press oil mill, 202
  lint determination, 442
  linters, 201
  manufacture of oil and cake, 200
  meats, 201
    cooking, 202
    pressing, 203
    rolling, 202
  mills and equipment, 199
  moisture, determination, 435
  oil, determination, 435
  pressing, 201, 202
  products, yield, 199
  proteins, 197
    determination, 436
    sampling, 434
    storage, 194
  sampling, 433
  sampling slab press cake, 457
Cottonseed oil
  acetyl value, 219
  bleach test, 452
  bleaching, 208
  characteristics, 218
  cold test, 454
  color test, 419
  composition, 220
  crude, 205
    refining, 206, 207
    refining tests, 444
    storage of, 205
  deodorization, 210
  determination of, in seed, 435
  determination of acidity, 444
  distilled fatty acids, 207
  examination of, 223, 443
  expression, 201, 202
  hydrogenated, 213
  composition, 215
  meal and other insoluble matter, 443
  pitch, 207
  refined, 218, 220
    color measurement, 452
    fluorescence, 212
    free fatty acids, determination, 456
    grades, 222
  salad oil, 213
  sampling, 442
  shortening, 216
  smoking temperature, 218
  soap stock, 206
    acidulated, 207
    analysis, 459
  sterols, 220
  tests, 223
  uses, 222
  wintering, 213
Coumou palm oil, *see* Bataua, 139
Country walnut oil, *see* Lumbang, 330

Coyal palm kernel oil, *see A. vinifera*, 130
Crabwood fat, *see* Andiroba, 33
Crismer test, modified, 384
  values, 386
Critical temperature of dissolution, 383
Crotalaria oil, 59
Croton, Oleum Elliot, 255
Croton seed oil, 223
Crude cottonseed oil
  analysis, 443
  characteristics, 218
  constituents, 220
  determination, free fatty acids, 444
  filtration, 205
  grades, 222
  manufacture, 201, 202
  neutral oil, total, 454
  phytosterolines, 220
  refining, 206, 207
  refining test, 444
  sampling, 372
  settling, 203
  settlings, not meal, 221
  storage, 205
Crude oils, neutral oil determination, 454
Crushing and rolling seeds, 17
Cuban queen, melon seed oil, 250
Cumin seed oil, 247
Cupu seed oil, 44
Curcas oil, 224
Curua palm kernel oil, 137

D

Da seed oil, 59
Date kernel oil, 138
Datura seed oil, 245
Daubentonia drummondii oil, 469
Deccan hemp oil, *see* Da seed, 59
Decortication (hulling) seed, 17, 201
Deep (fat) frying temperatures, 218
Dehydrated castor oil, 51
Dende oils, *see* Elaeis guinensis, 119, 124
Deodorization, *see* Cottonseed oil, 210
Deodorizer, continuous, 211
Determination, oil in seeds, etc., 374
Devil's claw seed oil, *see* Unicorn, 248
D'hupa fat, *see* Malabar tallow, 93
Diene value, method, 398
Digitonin, test for sterols, 363
Di-glycerine, preparation, uses, 358
Dihydroergosterol, 367
Dihydrositosterol, 365
Dika butter, 60
Dill seed oil, 247
Diplothemium palms, oils, 138
D'jave butter, 61
Dodder seed oil, *see* German sesame, 241
Domba (dilo) oil, *see* Calophyllum, 45
Dumoria seed oil, 65

E

Earth almond oil, *see* Chufa, 57
Ebor seed butter, 65
Egyptian lettuce seed oil, 231
Elderberry fruit and seed oils, 256
Elm tree seed oil, 61
Emulsions, 27
Ergosterol, and vitamin D, 366
Ergot oil, 66
Essang oil, 284
Ester value, 390
Euphorbia amygdaloides oil, 282
Euphorbia cyparissias oil, 282
Euphorbia esula oil, 282
Euphorbia exigua oil, 283
Euphorbia helioscopia oil, 282
Euphorbia paralias oil, 283
Euphorbia platyphylla oil, 282
Euphorbia verrucosa oil, 283
Euterpe species, palm oils, 140
Expression, fats and oils, 16
Extraction (solvent) fats and oils, 16, 20

F

Families botanical, with species, 486
Fats and oils,
  calorific value, 23
  characteristics, *see* Tables 16-18
  color and measurement, 454
  color of, 16
  color tests, 419
  constituents, 15
  definitions, 13
  determination, 374
  distribution, 14
  effect of germination, 14
  emulsions, 27
  expression, 16
    in laboratory, 372
  formation, 14
  glycerides, 14
  in seeds, 14
  laboratory extraction, 371
  melting point, determination, 379, 475
  neutral oil, determination, 454
  nutritive value, 23
  rancidity, 24
  refining, 22, 206
  samples, 372
  sampling, 372
  solvent extraction, 19
  sources, 14
  stabilization, 26
  synthesis by plants, 14
  terms, use of, 13
  utilization by growing plants, 14
  vitamin content, 23
Fatty acids, 336
  formulas, 473
  free fatty acids, determination, 437
  molecular weights, 473
  neutralization values, 473
  solid, determination of, 415
  soluble and insoluble, 386
Fennel seed oil, 247
Fig seed oil, 256
Filbert nut oil, *see* Hazel, 79
Fire point of oils, 475
Fish oils, detection of, 411

Flacourtiaceae, and oils, 68
optical rotation of oils, 379
Flash point of oils, 475
Flaxseed, *see* Linseed, 262
Fony seed oil, *see* Baobab, 36
Foreign matter, removal from seeds, 16
Free fatty acids, determination, 437
in refined oils, 456
Fuller's earth, 209
Funtumia seed oil, 296

G

Galam butter, *see* Shea nut, 63
Gamboge (Gurgi) butter, 87
Garcia nutans oil, 471
Garcinia fats, 87
Garden chervil seed oil, 247
Gemsbok bean oil, 77
German sesame (cameline) oil, 241
Gingelli seed oil, *see* Sesame, 238
Glothium vesecarium seed oil, 469
Glycerides, 360
constitution, 360
synthesis by plants, 14
synthetic, 360
Glycerine, 356
acetin method, 426
analysis, 359, 424
bichromate method, 429
discovery, 356
fermentation, 358
grades, 358
manufacture, 357
sampling, 424, 430
sources, 357
tests, 359
uses, 359
Goa butter, *see* Kokum, 87
Gomphococca kernel oil, 137
Gorli seed oil, 71
Gossypol, in cottonseed, 197
Grape fruit seed oil, *232*
Grape seed oils, 257
Green butter, *see* Borneo tallow, 39
Gru-gru palm, oils, 131
Guere palm kernel oil, 133
Gurgi butter, see Gamboge, 87
Gynocardia seed oil, 260

H

Habai butter, *see* Tangallak, 160
Hackberry tree seed oil, 260
Halphen test, 419
Hanus iodine number method, 393
Hazel (Filbert) nut oil, 79
Hegli oil, *see* Zachun, 170
Hempseed oil, 260
Hexabromides, determination, 408
Hickory (Walnut) oils, 334
Hodgsonia seed oil, 251
Hollyhock seed oil, 233
Horse chestnut oil, 79
Hubbard squash seed oil, 248
Hydnocarpus oils, 68, 73-76
Hydrocarbons, 368
Hydrogenation, oils, 213
continuous, 215
melting points, 218
reactions, 216
Hyoscyamus seed oils, 313

I

Iguape, *see* Lumbang oil, 330
Illipé tallow, 79
Illipene, 368
Imburana oil, 82
Index of refraction, 377
Indian almond oil, 167
Indian butter, 62
Indian kapok, 86
Inosite phosphates, 370
Inoy oil, 82
Iodine number determination, 391
of unsaturated acids, 473
Irvingia fat, *see* Cay-cay, 55
dika, 60
Isano seed oil, 261
Ivory wood tree seed oil, 233

J

Jaboty butter or tallow, 82
Jamba seed oil, 226
Japan (wax) tallow, 83
Japanese tung or wood oil, 328
Japanese walnut oil, 333
Java almond oil, *see Canarium commune*, 160
Java olive oils, *see* Sterculia, 165
Jiconga seed oil, *see* Koeme, 86
Joannesia seed oil, *see* Princeps, 236
Jojoba seed (liquid wax) oil, 88
Juboea palm kernel oil, 138
Jute seed oil, 233

K

Kagné butter, *see* Allanblackia, 30
Kaloepang oils, *see* Sterculia, 165
Kangna butter, *see* Lamy, 89
Kapok seed oil, 84
Indian, seed oil, 86
tests, 85
Karité (Shea) butter, 63
Katio seed oil, 62
Kaufmann, iodine number method, 395
Kekune kernel oil, *see* Lumbang, 330
Kenaph seed oil, *see* Da. 59
Kentucky coffee nut tree oil, 261
Kerr test, peanut oil, 158, 422
Kickxia seed oil, 296
Koeme (jiconga) seed oil, 86
Koettstorfer number, 388
Kokerite palm oils, *see* Cokerite, 141
Kokum butter, 87
Kombo butter, 98
Korung (honge) oil, *see* Pongam, 162
Kreis test, rancidity, 423
Krobonko seed oil, 87
Kullen nut oil, *see* Zachun, 170
Kurdee seed oil, *see* Safflower, 297
Kurrajong seed oil, 89
Kussum kernel oil, *see* Macassar, 92

L

Laboratory extraction, fats and oils, 371
Lallemantia seed oil, 261
Lamy butter, 89
Laurel (Bay) berry fats, 90
Laurel nut oil, *see* Calophyllum, 45
Laurel wax *see* Bayberry tallow, 37
Lead salt-ether method, 405
Lecithins, 369
Lecithins, soy bean, 303
Lecythis elleptica seed oil, 470
Lemon seed oil, 232
Licania arborea, 471
Licania rigida, 286
Licuri kernel oil, *see* Ouricury, 134
Liebermann-Storch test, 412
Lime seed oil, 232
Linseed, 262
  oil and cake yields, 266
  oil content, 263
  oil, refractometric determination, 461
  preparation of seed for pressing, 264
Linseed oil, 262
  adulterants, 275
  bleaching, 267
  blown, 268
  boiled, 268
  break, 271
  British specifications, 280
  characteristics, 270
  composition, 269
  drying of oil, 271
  expression, 264
  foots, 271
  Iodine number, refracto-metric, determination, 464
  polymerization, 272
  properties, 271
  refining, 266
  refining test, 451
  sampling, 277
  specifications, 276
    methods for testing, 277
  stand oil, 268
  top fired oil, 269
  uses, 275
Lipids, *see* Phosphatides, 368
Lipins, *see* Phosphatides, 368
Lipoids, *see* Phosphatides, 368
Locust (Carob bean) seed oil, 91
Lucerne seed oil, *see* Alfalfa, 253
Lukrabo oil, *see Hydnocarpus anthelminthica*, 74
Lumbang oil, 330
Lumegue nut, *see* Ximenia oil, 169
Lupu seed oil, 45

M

Macadamia nut (kernel) oil, 91
Macasser (Kussum) kernel oil, 92
Macaúba (*A. Sclerocarpa*) oils, 131
Macrocarpa oil, 76
Madia (tar weed) seed oil, 234
Mafura oil and tallow, 92
Mahogany nut butter, *see* D'jave, 61
Mahogany tree seed oil, 470
Mahuba rana fat, 93
Maize oil, *see* Corn, 176
Malabar tallow, 93
Mallow seed oil, *see* Rose mallow, 236
Mamarron nut (palm kernel) oil, 142
Mammy apple (sapote) seed oil, 93
Manchurian walnut oil, 333
Manicaria saccifera kernel oil, 131
Manihot dichotoma oil, 281
Manihot piauhyensis oil, 281
Manihot seed oil, 280
Manketti nut oil, 283
Maraja (*A. aculestum*) palm oil, 132
  kernel oil, 132
Mareepia (*M. regia*) palm oil, 141
  kernel oil, 141
Margarine, references, 28
Margosa oil, 99
Maroola nut oil, 94
Maximiliana caribaea kernel oil, 138
Meal, etc., determination, crude oil, 443
Meal and cake analysis, 458
Melon seed oils, 250
Melting point, determination, 379
Meni oil, *see* Niam, 100
Mercuriales annua seed oil, 281
Mercuriales perennis seed oil, 281
Mercuriales tomentosa seed oil, 281
Methods, 371
Methyl esters, 473
  acids from, 474
Mexican buckeye oil, *see* Ungnadia, 168
Mexican poppy oil, *see* Argemone, 234
Milkweed seed oil, 470
Millet seed oil, 181
Milling seeds, 17
Mimosa seed oil, 470
Mineral oil, test for, 412
Minusops butter *see* D'jave, 61
Mlenda seed oil, 234
Mocaya oil, *see* Gru-gru kernel oil, 131
Moisture, determination, crude oil, 443
Moisture, volatile matter, determination, 374
Moringa seed oil, 38
Mowrah tallow, *see* Illipé, 79
Mu (abrasin) tung oil, 327
Mung bean oil, 94
Murga fat, *see* Gamboge butter, 87
Murumuru palm kernel oil, 133
Mustard seed oils, 225
Myristica butters or fats, 97, 98
Myrobalans seed oil, 99
Myrtle wax, *see* Bayberry tallow, 37

N

Narras seed oil, 250
Nasturtium seed oil, 101
Neem oil, *see* Margosa, 99
Neou oil, 294
Neutral oil, determination, 454
Neutralized olive oil, 107
N'Gart oil, 284
Niam (Meni) oil, 100

Nickel, in hydrogenated fats, 431
catalysts, 213
Niger seed oil, 285
Njato fat, 81
Njave butter, *see* D'jave, 61
Noguera oil, *see* Lumbang, 330
Noli palm, kernel oil, 130
pulp oil, 130
Nsasana kernel oil, 284
Nutmeg butter, 95
Nutritive value of fats and oils, 23

O

Oak kernel oils, *see* Acorn, 30
Oat oil, 181
Oba butter, *see* Dika, 60
Ochna pulchora, kernel oil, 101
Ochoco butter, 97
pulp oil, 101
Oenocarpus oils, 139
Oil, extractors, continuous, 20
Oil, hydrogenation, 213
determination, seeds, etc., 374
labelling of, 372
laboratory extraction, 371
samples, keeping of, 372
sampling, 372
Oiticica oil, 286
characteristics, 286
composition, 287
production, 288
uses, 288
Okra seed oil, 102
Olive oil, 102
Acapulco extraction process, 106
adulterants, 110
blending, 107
characteristics, 108
clarification, 106
composition, 108
detection of rape oil, 112
detection of refined oil, 115
expression, continuous, 106
filtration, 107
flash and smoke points, 475
foots, 106
Leon process of extraction, 106
neutralized, 107
refining, 107
Tea seed oil test, 111
tests for other oils, 110
tests for solvent extracted oil, 114
uses, 108
Olive kernel oil, 118
Olives, crushing and pressing, 105
harvesting, 104
storage, 105
Olives and oil in
Algeria, 103
Argentina, 104
California, 104
France, 104
Greece, 103
Italy, 103
Portugal, 103
Olives and oil in (*continued*)
Spain, 102
Syria, 104
Tunisia, 103
Turkey, 104
Olives and oil, effect of climate, 102
Oncoba kernel oils, 71, 72
Optical method, oil in linseed, 461
Optical rotation, 378
determination, 378
Orange seed oil, 233
Osage orange seed oil, 286
Otoba butter, 98
Ouricury palm kernel oil, 134
Owala bean oil, *see* Atta seed, 34

P

Palms, classification, 118
pulp and kernel oils, 118
African palms, 118, 119
fruit sterilization, 122
in Brazil, 119, 124
East Africa, 119
Liberia, 119
Malaya, 118
Sumatra, 119
West Africa, 119
light, moisture and soil requirements, 119
varieties, 120
Palm oil, bleaching, 126
centrifugal extractions, 122, 123
characteristics, 124
composition, 124
extraction, 121
extraction in Sumatra, 123
glycerides, 124
industry in
Malaya, 118
Sumatra, 120
mill equipment, 123
native method of extraction, 121
properties, 126
refined, in margarin, 126
refining, 124
uses, 126
Palm kernel oil, 127
expression, 127
glycerides, 128
properties and tests, 129
refining, 129
stearine, 129
uses, 129
Palm kernels, separation, 123, 127
Palma real (Ecuador) kernel oil, 142
Pao marfin oil, 233
Papaw seed oil, 234
Papaya seed oil, 150
Paprica seed oil, 313
Para rubber seed oil, 295
Paraguay palmoil, 130
kernel oil, 131
Parinarium oil, *see* Akaritton, 293
Parkia seed oil, 151
Parsley seed oil, 245
Passion fruit seed oil, 296

Pataua oil, *see* Bataua, 139
Peach kernel oil, 173
Peanut (Arachis, ground nut) oil, 151
  adulteration, 157
  bleach test, 452
  characteristics, 156
  composition, 156
  crude, grades, 154
  expression of, 152
  free fatty acids, composition, 155
  Kerr test, 158
  neutral oil content, 155
  refining tests, 450
  tests, 158
  uses, 153
Peanuts, producing countries, 151
  composition, 152
  oil content, 152
  shells, uses, 154
  yield of oil and cake, 152
Pear seed oil, 171
Pecan nut (kernel) oil, 159
Perilla (seed) oil, 288
  characteristics, 289
  composition, 289
  smoke, flash, and fire points, 475
  specifications, 289
  uses, 291
Persimmon seed oil, 470
Phosphatides, 368
Phospholipides, *see* Phosphatides, 368
Phulwa (Indian) butter, 62
Physic (Curcas) nut oil, 224
Phytosterolines, 367
Phytosterols, detection of mixtures of fats, 365
Picramnia fats or butters, 161
Pili nut (kernel) oil, 159
Pimento seed oil, 291
Pine seed oils, 235
Piney tallow, *see* Malabar, 93
Pinnay, *see* Calophyllum oil, 45
Pinonchillo oil, *see Garcia nutans* oil, 471
Piquia fats, 162
Pirirma palm kernel oil, 132
Pistachio nut (kernel) oil, 160
Pitjoeng seed oil, 77
Plant families with species, 486
Plant species, *see* Index to Botanical names.
Plukenetia kernel oil, *see* N'Gart, 284
Plum (pit) kernel oil, 173
Plumy coconut kernel oil, 136
Poga kernel oil, *see* Inoy, 82
Poinsettia seed oil, 470
Polenske number, 400
  determination, 400
Poli seed oil, 291
Pomegranate seed oil, 292
Pongam seed oil, 162
Pontianak Illipé tallow, *see* Borneo, 39
Pontianak tallow, *see* Borneo, 39
Poonseed (Pinnay) oil, *see* Calophyllum, 45
Poppy seed oil, 292
Po-yoak seed oil, 293
Pracaxy seed oil, 34
Prickly poppy oil, *see* Argemone, 234
Princeps seed oil, 236
  laxative action, 236
Pulasan fat, 164
Pumpkin seed oil, 249
Purge nut oil, *see* Physic nut, 224

Q

Queensland nut oil, *see* Macadamia, 91

R

Rabbit's fruit (nut) oil, 295
Radish seed oil, 226
Raisin seed oil, 258
Rambutan tallow, 163
Rancidity, 24
  tests, 24, 423
Rape (Colza) oil, 226
  adulterants, 230
  blown, 229
  characteristics, 228
  composition, 227
  detection, 230, 412
  phosphatides, 228
  properties, 229
  refined, 229
  tests, 230
  uses, 230
Rattle box seed oil, *see* Sicne bean, 165
Ravision oils, 22, 206
Red oil, uses, 346
Refining loss, determination, 444
Refining oils, 22, 206
  continous, 207
Refining under vacuum, 212
Refractive index, determination, 377
Reichert-Meissel value, 400
  determination, 400
Renard peanut oil test, 421
Reniala oil, *see* Baobab, 36
Rice oil, 182
Ricinus zanzibarinus seed oil, 55
Rose mallow seed oil, 236
Rosin and mineral oil test, 412
Royal palm of Cuba oils, 142
Rubber seed oil, 295
  see also
    Ceará rubber, 280
    Mexican rubber, 296
Rye oil, 183

S

Safflower seed, cultivation in the United States, 297
Safflower seed oil, 297
  composition, 298
  uses, 298
St. John's bread, *see* Locust seed oil, 91
Salvia sclarea seed oil, 299
Samaun seed oil, *see* Pitjoenig, 77
Samples, oil, keeping 372
  labelling, 372
Sampling, cottonseed, 433
  cake, 457

Sampling, cottonseed (*continued*)
fats and oils, 372
glycerin, 424, 430
soapstock, 459
Sandal seed oil, 299
Saponification equivalent, 389
Saponification value, determination, 388
Sapote seed oil, *see* Mammy apple, 93
Sapucainha oil, *see* Carpotroche, 68
Sapuyul seed oil, *see* Mammy apple, 93
Sarawak Illipé butter, *see* Borneo tallow, 39
Sativus seed oil, 251
Saturated acids, *see*
Bertram method, 414
Kaufmann method, 395
lead salt-ether method, 405
modified Twitchell method, 415
Sawarri fat or tallow, 164
Secale oil, *see* Ergot, 66
Sedge (Chufa tuber) oil, 57
Segen palm oil, 140
Senat seed oil, 251
Sequa seed oil, 165
Sesame oil, 238
adulteration, 239
composition, 238
expression, 238
refining test, 451
tests, 240
uses, 238
Sesame seed, 236
trade classification, 237
Sesamin, 239
Settling tanks, *see* Storage tanks, 18
Settlings, not meal, 221, 222
Shea nut (kernel) oil or butter, 63
composition, 64
refining, 63
Shortening, *etc.*, smoking temperature, 272
determination of solid acids, 415
Siak fat or tallow, 81
Siene (Rattle box) bean oil, 165
Sierra Leone butter, *see* Lamy, 89
Sitosterols, 365
Slab press cake, sampling, 457
Slipping point, determination, 381
Smoking temperatures of oils, 475
Soap, in refined oil, 456
Soapberry kernel oil, 470
Soapstock analysis, 459
Soaptree kernel oil, 165
Softening points, determination, 380
Solid fatty acids, determination, 415
Solstein's sesame oil test, 240
Soluble and insoluble acids, determination, 386
Solvent extraction, 19
equipment, 19
Solvents, for extraction, 20
Soybean oil, 300
characteristics, 305
composition, 307
flash, smoke and fire points, 475
measurement, color of oil, 452
Soybean oil (*continued*)
neutral glycerides, 306
refining, *see* Cottonseed oil, 206
refining test, 450
specifications, 306
uses, 308
Soybeans, 300, 305
analysis, 432
harvesting, storage, 302
in the United States, 301
manufacture of oil and meal, 302
Specific gravity, determination, 376
Specific heat, determination, 218
Specific rotation, determination, 378
Spinosa seed oil, 72
Spurge nettle seed oil, 241
Stabilization of fats and oils, 26
Stand oil, *see* Linseed oil, 268
Stearates, metallic salts, uses, 341
Stearic acid, grades, 341
uses, 341
Stearine pitch, *see* Cottonseed oil, 207
Sterculia or calumpang oil, 165
Sterols, 362
calciferol, *see* Brassicasterol, 365
cholesterol, 364
color test, 363
dihydroergosterol, 367
dihydrositosterol, 365
ergosterol, 366
phytosterolines, 367
phytosterols, 365
sitosterols, 365
stigmasterol, 366
tests, 363
zymosterol, 367
Stock's method, *see* Castor oil tests, 49
Storage tanks, 18
Suari fat, *see* Sawarri, 164
Sugar apple seed oil, 166
Sulfocyanogen value, 395
Sulfonated oil, *see* Castor, 47
Sulfur olive oil, 106
Summach seed oil, 166
Sump oil, *see* Zachun, 170
Sunflower seed oil, 241
characteristics, 242
press cake, 242
uses, 242
Swiss pine nut oil, *see* Cedar nut, 254

T

Tabanmerak fat, 81
Talisay (tropical almond) oil, 167
Tall oil, 334
Tangallak butter, 166
Tangare kernel oil, *see* Andiroba, 33
Tar weed seed oil, *see* Madia, 234
Tariri fat, *see* Picramnia, 161
Tea seed oil, 167
test, *see* Olive oil, 111
Teng kawang, *see* Borneo tallow, 39
Test, for boiled oil, 411
for fish, oil, 411
Thiocyanogen value, determination, 395, 474

Thistle seed oil, 313
Tiger apple seed oil, 167
Titer, determination, 381, 476
Tobacco seed oil, 313
Tomato seed oil, 244
Tonka bean oil, 65
Top-fired oil, *see* Linseed, 269
Toulouconna fat, *see* Andiroba, 33
Trichodesma zeylanicum, 334
Trienol, 52
Triglycerides, fats and oils, 360
  acids from, 474
  calculation factors, 474
Trimethylene glycol, 359
Tsubaki seed oil, 168
Tucum, kernel oil, 132
  palm oil, 132
Tung (Chinese wood) oil, 314
  adulteration, 319
A.S.T.M. quality tests, 321
  Brown heat test, 322
  characteristics, 320
  composition, 322
  determination, Goldsmith method, 324
  drying of, 325
  expression of, in China, 318
  modified Worstall's test, 323
  properties, 324
  specifications, 320
  uses, 320
Tung trees, in
  China, 317
  United States, 315
  other countries, 318
Types of solvent extractors, 19
Twitchell modified method, solid acids, 415

U

Ucuhuba butter, 96
Unania, *see* Segen palm oil, 140
Ungnadia seed oil, 168
Unicorn seed oil, 248
Unsaponifiable matter, determination, 390
Unsaturated acids, determination, 405
  bromides, 474

V

Vacuum refining method, 212
Vegetable fats, *see* Fats and oils
Vegetable (oil) shortening, 216
Villavecchia test for sesame oil, 240, 420
Virola fat or butter, *see* Ucuhuba, 96
  other virola fats, 97
Viscosity, 387
Volatile fatty acids, 400
Volatile matter and moisture determination, 374
Volumetric solutions, standard, 477

W

Walnut (Black) oil, 333
Walnut (English or Persian) oil, 332
Walnut oils, *see*
  Hickory nuts, 334
  Japanese, 333
  Manchurian, 333
Watermelon seed oil, 249
  see also Cuban Queen seed oil, 250
Weights, atomic, 477
Weights, measures, equivalents, 476
Wheat oil, 184
Wijs iodine number method, 392
Wild olive seed oil, *see*
  Ximenia, 169
Worstalls' modified test,
  tung oil, 323
Wrightia annamensis seed oil, 168

X

Xanthocarpum seed oil, 245
Ximenia (Wild olive) seed oil, 169

Y

Yellow oleander (Tiger apple) seed oil, 167

Z

Zachun seed oil, 170
Zanzibarica pulp and seed oils, 251
Zapote oil, *see* Mammy apple, 63
Zeylanicum seed oil, 334
Zymosterol, 367

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