A METHOD
FOR
THE IDENTIFICATION OF PURE ORGANIC COMPOUNDS

BY A SYSTEMATIC ANALYTICAL PROCEDURE BASED
ON PHYSICAL PROPERTIES AND
CHEMICAL REACTIONS

Vol. I

CONTAINING CLASSIFIED DESCRIPTIONS
OF ABOUT 2300 OF THE MORE IMPORTANT COMPOUNDS OF CARBON
WITH HYDROGEN AND WITH HYDROGEN AND OXYGEN

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PREFACE.

AT the time of writing the only general and fairly systematic procedure for the identification of previously described organic compounds of all classes is that which may be conveniently designated the Method of the Empirical Formula. In following this procedure a determination of the percentage composition is first made. The molecular weight is next determined or conjectured. From these data an empirical formula is calculated. The properties of the substance are then compared with those of all the known compounds possessing this formula by reference to their scattered literature, for which Richter's "Lexicon der Kohlenstoff-Verbindungen" with its supplements now furnishes a very complete index. Resting, as it chiefly does, on the two fundamental properties, percentage composition and molecular weight—which alone among the chemical constants can be readily calculated for every compound in advance of its discovery—it is probable that this method will long remain the last resort in all earnest attempts to establish the identity of compounds which have been previously undescribed or very imperfectly characterized through their physical and chemical properties. Nevertheless, when we turn to the great body of well-characterized compounds that occur with some frequency in the products of Nature, the useful arts, and the scientific laboratory, there is good reason to raise the question whether the Method of the Empirical Formula is from the practical standpoint a sufficiently satisfactory one. It is evidently not if any substitute can be found that will lead the analyst to the same results with less expenditure of time and effort, and without requiring unusual knowledge or skill on his part; and it is not to be denied that in these respects this method makes a very poor showing. The indispensable key to its use is proficiency in ultimate organic analysis, whose difficult technique is fully mastered only by long practice. The performance of the combustions, which must be made in duplicate to secure certainty, is at best a time-consuming operation; and even after reliable results have been obtained, it is further necessary, in order to fully identify a compound, to resort to a study of its physical properties, chemical behavior, and perhaps to a molecular-weight determination. The consequence of this has been that the identification of organic compounds by this general method has been practically limited to its occasional employment in laboratories devoted to synthetic organic research, and that such identifications when attempted elsewhere are usually accomplished, often with uncertain results, by the use of disconnected desultory tests. Through these considerations, and with the belief that a path of less resistance could be broken out for the analyst, the writer began more than eight years ago the studies whose first results appear in this volume.

The present method, as contrasted with that just described, gives fuller recognition to the important truths that percentage composition and molecular weight are merely two among many highly significant characteristics of every compound; and that without recourse to them, by the use of the more easily determined properties like qualitative elementary composition, color, melting-point, boiling-point, solubility, specific gravity, alkali neutralizing power, and chemical behavior under prescribed conditions, entirely satisfactory identifications may be made —provided a sufficient number of these facts which are at the disposal of the systematist are carefully verified and suitably coördinated in a classified system.

The new method therefore rests, as will be more fully explained in the introductory chapter, upon a classification designed to secure for the carbon compounds those advantages which have been already so long enjoyed in Botany and other branches of Natural History through the use of systematized descriptions of salient characteristics. The compounds, or chemical "species," have been first grouped into "orders" on the basis of their qualitative elementary composition; then into "genera" (aldehydes, acids, phenols, etc.), usually on the basis of behavior in simple chemical tests; and, finally, arranged within each genus according to the increasing value of some readily-determined constant like the melting-point or boiling-point. The name of each species is followed in the tables by a brief specific characterization enumerating some of the simpler properties of the substance that have genuine analytical significance, and then, whenever possible, by detailed directions for preliminary and corroborative chemical tests which can be performed with small quantities of material.

The phrase "More Important Compounds" used in the title is unavoidably indefinite; but the intention has been to admit all substances to the tables for which there is more than a remote chance that they may come into the hands of the analyst as unknown compounds. Such a list naturally includes: first, all compounds that may be isolated in a state of purity and without excessive difficulty from materials used in the arts, or from substances which occur somewhat abundantly in Nature; second, compounds of minor importance which may easily be formed in the laboratory as by-products in reactions between substances of more common occurrence; third, many rare compounds which have acquired a general scientific interest either on account of their properties or as representatives of peculiar types. Very few compounds that could be purchased in the market in a state of purity have been omitted except through oversight. The most important intentional omissions are: substances whose claims to recognition as distinct chemical species are not generally accepted; uncrystallizable syrups that cannot be distilled without decomposition; the oily and fatty glycerides; those glucosides and synthetic sugars of which specimens could not be obtained for examination.

The claims for admission to this volume of every compound of carbon with hydrogen, or with hydrogen and oxygen, that receives mention in the second edition of Beilstein's great "Handbuch der organischen Chemie" and in its supplements issued prior to January, 1902, have been separately passed upon, and about 2300 selected as deserving mention in the tables. All copied data used in the manuscript sent to the publisher have been twice compared with their source by the author and once by Dr. Heyward Scudder.

Obviously the attempt to establish an analytical system of the proposed character on any less secure foundation than an extended first-hand study of a very large number of representative compounds so selected as to cover all important types, would be to invite the fate of "the foolish man which built his house upon the sand"; for existing descriptions of the reactions of even the most familiar compounds very rarely state the experimental conditions and phenomena in terms that are immediately available for the purposes of a systematic analytical classification. The chemical tests that have been relied upon for arranging the chemical species in genera are therefore the result of many hundred original experiments made upon several hundred compounds in the laboratories of the Massachusetts Institute of Technology, the preparations used being supplied for the most part from the valuable Institute collection. Yet in spite of the considerable labor expended in this way, since it has been physically impossible to examine personally every species described, it would be absurd to deny that some may be wrongly located in the classification. To safeguard the analyst as far as possible against errors arising from such imperfect descriptions, every reasonable precaution that has suggested itself has been taken during the construction of the procedures and tables. The names of those compounds whose generic positions have been established by original experiments in the author's laboratory are distinguished from others by being preceded by the mark †, though it is not true that *every property* ascribed to a substance thus marked is necessarily an original or guaranteed datum. Of the "numbered specific tests" it may, however, be said that each one has been performed at least several times in accordance with the directions contained in the manuscript; that they have all been used on more than one occasion; and that they have proved successful in the hands of two or more persons.

The specific characterizations are all quite brief because the work is intended to be used as a compact practical analytical guide and index, and not as a handbook of descriptive Organic Chemistry; and because the value of a specific description to the analyst never increases, beyond a certain point, directly in proportion to the number of properties and tests included—long descriptions often becoming unwieldy and confusing through suggesting too many alternatives of unequal merit.

To obtain all the new material required for these pages single-handed would have proved a disheartening labor. The writer's grateful acknowledgments are therefore due to the many friends (most of whom are or have been connected with the chemical department of the Massachusetts Institute of Technology) who have rendered assistance in the work. Some of the most important contributions from this source are recorded in the unpublished "thesis" investigations of the writer's students. Valuable information has thus been furnished by Messrs. A. P. Norris, C. L. M. Pettee, H. M. Loomis, H. Scudder, B. R. Rickards, A. R. S. Booth, J. W. Brown, J. R. Odell, and Misses E. M. Chandler and A. F. Blood. The writer has also been ably assisted at different times by Dr. Paul Chapin and Messrs. A. C. Davis and Herbert Walker. To his friend, Dr. Heyward Scudder, the author's thanks are however especially due for generous and untiring coöperation during a considerable part of this undertaking. Many of the best methods, particularly among the "specific tests," are the fruits of his research, or have been improved in consequence of his suggestions, while nearly the whole of the manuscript, as well as the proof-sheets, have received the benefit of his criticism. It is regretted that the necessary practice of omitting, for the sake of simplicity and compactness in tabulation, those bibliographical references which, while they have aided the writer, would not be of obvious advantage to the analyst, has prevented that full acknowledgment of aid from many earlier investigators that would otherwise have been gladly rendered.

In closing, a word should be added in regard to the proposed extension of this "Method" to the other organic compounds. It is planned to describe the carbon compounds containing nitrogen, or nitrogen and oxygen—exclusive of the dyestuffs—in Vol. II, as Order II of the analytical system. Although the preparation of material for Vol. II is quite far advanced, it is probable that Vol. III, which is to be devoted to the identification of the organic dyestuffs, will be ready for publication first. The completion of the system will then await the preparation of a fourth volume to include the remaining "orders."

S. P. M.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, December, 1903.

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TABLE OF ABBREVIATIONS.

a. = *above*. Before a melting-point or boiling-point indicates that the change occurs above the temperature given.

abt = *about*. Indicates that the value following is only approximate.

$\bar{A}$ (standing after the symbol for a metal) represents the acid residue of the acid in whose description it occurs; e.g., $Pb\bar{A}_2$ in a description of benzoic acid would represent lead benzoate.

Ac. = *acetic acid* or *acetate*.

ac. = *acid*.

alc. = *alcohol* or *alcoholic*.

ald. = *aldehyde*.

alm. = *almost*.

alk. = *alkaline*.

anhyd. = *anhydride*.

aq. = *water* or *aqueous*.

as. = *asymmetrical*.

b. p. = *boiling-point*.

Bu. = *butyl*, C_4H_9, without regard to structure of the radical.

bz. = *benzene*.

c. = *corrected* (not necessarily correct); also *cold*.

chlf. = *chloroform*.

conc. = *concentrated*.

cryst. = *crystals*, *crystalline*, or *crystallizes*.

d. = *decomposes*. Standing *after* a number indicates the temperature at which a substance melts or boils with decomposition. Standing *before* a number it indicates the temperature at which decomposition occurs without necessarily implying that the substance either melts or boils.
Standing before the name of a compound means dextro-gyratory.

d. a. = *decomposes above*. Is used in the same way as *d.*

d. w. m. = *decomposes without melting*.

deliq. = *deliquescent* or *deliquesces*.

dil. = *dilute*. In expressions like "dil. alc. (3:1)," the first term of the numerical ratio between parentheses always refers to the substance directly mentioned, and the second term to the water used as diluent or solvent.

dif. = *difference*.

dist. = *distils*; also, *may be distilled*, without stating the temperature.

d. s. = *difficultly soluble*. See page 38.

Et. = *ethyl*, C_2H_5.

Eth. = *ether*, (*ethyl oxide*).

e. s. = *easily soluble*. See page 38.

fr. = *from*.

floc. = *flocculent*.

h. = *hot*.

i. = *insoluble*; also, in name of a compound, *optically inactive*.

(*i. v.*) = *in vacuo*.

G. = *specific gravity*.

gran. = *granular*.

l. = *lævo-gyratory*.

liq. = *liquid*.

lgr. = *ligroïn*.

m- = *meta*.

mic. = *microscopic*.

Me. = *methyl*, CH_3.

misc. = *miscible*.

m. p. = *melting-point*.

N. Eq. = "*neutralization equivalent*." (Defined on page 77.)

n. f. = *non-fusible*.

n. v. = *non-volatile*.

o- = *ortho*.

o. p. = *ordinary atmospheric pressure*.

o. t. = *ordinary room temperature*.

oxid. = *oxidize*, *oxidizes*, or *oxidation*.

p- = *para*.

Ph. = *phenyl*, C_6H_5.

Pr. = *propyl*, C_3H_7 (without indicating the structure of the radical).

ppt. = *precipitate* or *precipitates*.

pt. = *part* or *parts*.

pulv. = *pulverulent*.

(*r. h.*) = *rapidly heated*. (See page 220.)

s. = *soluble*. (See page 38.)—Before the name of a compound signifies symmetrical.

sbl. = *sublimes*.

s. d. = *slightly decomposed*. (Signifies that the substances melts or boils with slight decomposition at the temperature given.)

Sap. Eq. = *saponification equivalent*. (Defined on page 113.)

sol. = *solution*.

s. f. = *softens*. Indicates that the substance softens at the temperature stated.

Sbl. w. m. = *sublimes without melting*. (Often followed by specification of the temperature.)

tbl. = *tabular crystals*.

(*Th. i.*) = *thermometer immersed in the vapor*.

u. c. = *uncorrected*.

unsat. = *unsaturated*.

v. = *vicinal* or *adjacent*.

vol. = *volume*.

volat. = *volatile*.

vol. w. st. = *volatile with steam*.

w. = *with*.

x. s. = *excess*.

SIGNS.

$[\alpha]_D$	Specific rotary power (using monochromatic sodium light). For the carbohydrates the values given are the "permanent" rotations at 20° C. obtained with aqueous solutions.
$[N]_D$	Index of refraction (using monochromatic sodium light).
+	placed after a number in a column of boiling- or melting-points indicates that the substance melts or boils slightly above the temperature given.
[+] or [−]	placed before the name or symbol for a compound indicates that the substance is optically active.
†	placed before the name of a compound indicates that the position of the latter in the analytical system has been experimentally determined in the author's laboratory. The "specific descriptions" for such compounds are also based, for the most part, on experimentally verified data.

BIBLIOGRAPHICAL.

Abbreviation.	Title.
A.	Liebig's Annalen der Chemie.
A. ch.	Annales de chimie et de physique.
A. ch. an.	Annales de chimie analytique.
Allen.	Allen's Commercial Organic Analysis, 3d Edition (Blackiston's Son).
Anl.	The Analyst.
Am.	American Chemical Journal.
Am. Soc.	Journal of the American Chemical Society.
Ar.	Archiv der Pharmacie.
B.	Berichte der deutschen chemischen Gesellschaft.
Bl.	Bulletin de la Société Chimique de Paris.
C.	Chemisches Centralblatt.
C. r.	Comptes rendus de l'Académie des Sciences.
Ch. Ind.	Journal of the Society of Chemical Industry.
Ch. Z.	Chemiker Zeitung (Cöthen).
Ch. N.	Chemical News.
Fr.	(Fresenius') Zeitschrift für analytische Chemie.
G.	Gazzetta Chimica italiana.
H.	(Hoppe-Seyler's) Zeitschrift für physiologische Chemie.
J.	Jahresbericht der Chemie.
J. pr.	Journal fur praktische Chemie.
M.	Monatshefte fur Chemie.
Ph. Ch.	Zeitschrift für physicalische Chemie.
R.	Recueil des travaux chimiques des Pays-Bas.
Soc.	Journal of the Chemical Society of London.

IDENTIFICATION OF ORGANIC COMPOUNDS.

CHAPTER I.

CLASSIFICATION OF COMPOUNDS AND THE GENERAL ANALYTICAL PROCEDURE.

To facilitate their identification, the pure compounds or chemical species described in this work are systematically arranged in genera, orders, and various minor groups. The general analytical procedure can be applied intelligently only after the underlying principles of this classification are clearly understood.

The *order* of any species is determined by its qualitative elementary composition. Compounds made up of the same elements belong to the same order. The compounds of carbon and hydrogen, and of carbon, hydrogen, and oxygen, constitute Order I of the system, and are the only ones described in the present volume. Order I contains two suborders, Suborder I including all colorless, and Suborder II all colored species. Tests having as their object the determination of the order of a species, i.e. tests for the elements, are called *ordinal tests.* They will be fully treated in Chapter II.

A *genus* is a group of species characterized by showing a common behavior in certain prescribed and carefully defined *generic tests.* With few exceptions generic tests are based on chemical reactions rather than differences in physical properties. The experimental details for each generic test are to be found at the beginning of the chapter devoted to the genus whose number it bears. Typographically generic tests are distinguished from other numbered tests by being printed in Roman instead of Arabic numerals. Test III, for instance, means the test prescribed (page 35) for the recognition of species of Genus III (Acids). The genera are so arranged that no species shall give the generic test for any genus preceding it in the same suborder. A concise summary of the generic tests of Suborder I, Order I, is given on page 5.

All genera, including both solid and liquid species, contain two *divisions.* Division A contains the solid, and Division B the fluid species. Gaseous species are so few in number that they are treated in division B with the species that are liquid under the ordinary conditions of temperature and pressure.

The "divisions" of some genera are composed of smaller groups of species called *sections.* The term section is also, though less frequently, applied to small artificial groups of species, like the two sections of Suborder II, when the chemical relationships between the members of the group are not sufficiently intimate to warrant their erection into genera. *Sectional tests* when based upon chemical reactions are referred to by numbers, and described just before the true specific tests, and immediately after the tabulated descriptions of the species of the genus.

The chemical *species* or compounds, the fundamental units in the classification, are, whenever practicable, arranged within their respective genera, divisions, or sections according to the numerical values of their melting-points, if they are solids; or of their boiling-points, under standard conditions, if they are liquids. Genus II of Suborder I, and Supplementary Section 2 of Suborder II, furnish the only examples in this volume, of groups of compounds whose arrangement within their respective sections of the tables is not dependent on the values of these constants.

Specific tests are primarily designed to distinguish a species from others situated near it in the same subdivision of its genus, and in the regular course of analysis should follow the ordinal, generic, and sectional tests. Very few of them have much significance if applied directly to an entirely unknown compound. It is conceivable, for instance, that there may be a number of organic liquids which will give a white crystalline derivative melting at 92°–93° when treated as directed in Specific Test 814; but if it is also shown that the unknown substance is a colorless compound of carbon, hydrogen, and oxygen belonging to Genus VIII, Division 2, and boiling at 78°, the proof that the species is ethyl alcohol is overwhelming. The most satisfactory specific tests are usually those in which a few centigrams of a compound are quickly converted into a well-characterized derivative.

The directions for many specific tests form a part of the specific characterizations of the tables, but some of the more important tests in each genus are described together immediately after the tables of the genus to which they relate, and referred to in the characterization by test numbers. In Order I, one hundred numbers are reserved for the description of the sectional, semi-specific, and specific tests of each genus, the first ten numbers in each hundred being set aside for the sectional and semi-specific,* and the last ninety for the true specific tests. Any numbered test in Order I may be easily found without consulting the index, if it be remembered that the numeral denoting the hundreds in the test number (e.g. 3 in 321) is also the number of the genus to which the compound concerned in the test belongs. The last two numerals in the test number indicate the position of the test among its fellows. Test 302 will accordingly be recognized at a glance as either a sectional or semi-specific test of Genus III (Acids). By turning to page 78 it will be found to be a reaction for the recognition of α-hydroxy acids. In the same way Test 319 will be seen to be a specific test for *some particular* acid. It is actually a description of two reactions for the identification of salicylic acid. The tests connected with the nine genera of Suborder I, Order I, are assigned numbers 100–900. Suborder II, not being divided into genera, has its specific tests numbered as if it were the tenth genus of its order; i.e. they are represented by the numbers 1000 to 1100.

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* By a semi-specific test is meant one employing some general experimental procedure that leads to similar results with a number of compounds, but which enables a partial selection between some of the species situated in the same smallest subdivision of a genus. Tests 301, 302, and 303 are semi-specific tests.

GENERAL DIRECTIONS FOR THE IDENTIFICATION OF AN UNKNOWN COMPOUND.

The numbered paragraphs in heavy type which follow form an analytical key to the use of the "Method". They indicate the successive considerations that should receive the attention of the analyst in the investigation of every unknown compound. With the explanatory remarks in ordinary type which accompany them, they give a comprehensive view of the general analytical procedure disencumbered of detailed descriptions of special operations and tests which can be more advantageously discussed elsewhere. It will be assumed that the reader has already acquainted himself with the classification of the "Method".

I. PURITY.

ESTABLISH A PRESUMPTION THAT THE UNKNOWN SUBSTANCE IS REALLY A PURE COMPOUND BEFORE ATTEMPTING TO IDENTIFY IT. IF IT IS NOT HOMOGENEOUS, PURIFY IT. THE CONSTITUENTS OF AN UNKNOWN ORGANIC MIXTURE CAN NOT BE SATISFACTORILY IDENTIFIED PREVIOUS TO THEIR SEPARATION. THE HOMOGENEITY OF COMPOUNDS WHICH EXIST ONLY IN THE FORM OF UNCRYSTALLIZABLE SYRUPS THAT CAN NOT BE DISTILLED WITHOUT SERIOUS DECOMPOSITION, IS SO DIFFICULT TO ESTABLISH, THAT SUCH SPECIES ARE, AS A RULE, EXCLUDED FROM THE TABLES.

To prove absolutely that a substance is chemically homogeneous, it would have to be shown that the physical and chemical properties of all the parts into which a given mass of it can be separated by methods of fractionation that do not affect it chemically, are identical; or, in other words, that no substance can be thus isolated from it whose melting-point, boiling-point, solubility, specific gravity, crystalline structure, chemical behavior, etc., is different from that of the original body. This absolute proof is of course impossible in practice. But if the properties whose identity in the several fractions has been ascertained are very few in number, they may still afford a presumption in favor of chemical homogeneity so strong as to closely approximate to the absolute proof, provided they are judiciously selected and are of a kind that permit of exact measurement.

The decision of the analyst as to just how many and what purity tests it will be profitable to apply to any particular substance, will be influenced by a variety of circumstances, among which will be included the importance of the identification, the extent of his knowledge of the methods employed in the preparation and purification of the substance, and the quantity of material that is available. If the supply is so small as to barely suffice for the tests of the regular procedure exclusive of special homogeneity tests, there will be no alternative between abandoning the examination altogether, and hazarding the loss of all the substance in what may at the end prove to be fruitless experiments upon a mixture. Whenever it is decided in such a case to proceed with the examination, it must be remembered that the results will be worthless unless the final specific tests are most unequivocal.

Of all the methods affording indications of purity, those which depend upon constancy or sharpness in melting- and boiling-point have been the most widely used. Indeed, it is altogether probable that for a majority of the organic compounds which have been described, the only direct evidence of purity that it has been considered necessary to secure, preliminary to the first ultimate analysis,—aside from that incidentally gained from their general appearance and behavior towards solvents—has been that furnished by these simple thermometric methods. The use and interpretation of these purity tests will be discussed somewhat fully in Chapter XIII (pp. 223–227).

The truth of the proposition that "The constituents of an unknown mixture can not be satisfactorily identified previous to isolation," may, at the first glance, appear to be invalidated by the existence of direct tests for organic adulterants in foods, for abnormal constituents in the urine, and the like. These tests, however, all owe their usefulness to the fact that the mixtures to which they are applied—except as regards the compound sought—are, virtually, known mixtures, in the sense that the combined effect of all their customary constituents—known and unknown—upon the test, has been carefully ascertained by previous investigations. Their value accordingly becomes problematical as soon as any substance not usually present in such a mixture is added to it.

The preliminary treatment of unknown mixtures is, undoubtedly, that part of most organic analyses which makes the greatest demands on the originality and patience of the analyst. While the number and peculiarities in chemical behavior of the organic compounds are so great as to forbid the expectation that a general scheme for their separation comparable in simplicity and comprehensiveness to that used in qualitative analysis for the elements can ever be realized, it is reasonable to anticipate that this important branch of Analytical Chemistry will eventually be so far systematized that much less will be left to chance and individual dexterity than at present. The omission from this volume of suggestions for methods of separation occurs, not because the importance of the matter has been underestimated, but because sufficient data for comprehensive and practical generalizations on the subject have not yet accumulated. It is, however, the author's hope to present such recommendations as can be given for the systematic treatment of mixtures in a later volume.

2. PHYSICAL PROPERTIES.

IF THE SUBSTANCE IS A SOLID, DETERMINE ITS MELTING-POINT; IF A LIQUID, ITS BOILING-POINT AND ITS SPECIFIC GRAVITY AT 20°/4°. IN EITHER CASE NOTE ITS ODOR, COLOR, TASTE, AND OTHER SALIENT PHYSICAL CHARACTERISTICS, AND DETERMINE ITS APPROXIMATE SOLUBILITY IN WATER.

The determination of melting-points is discussed on pages 217–221. Most of the melting-points recorded in the tables are probably "uncorrected." The boiling-points, on the contrary, are in general to be regarded as corrected for stem-exposure, and have been approximately reduced to their values under the standard pressure of 760 millimeters whenever possible. The determination of boiling-points is treated on pages 221–223. Whenever small distilling flasks are employed in making these determinations, the use of the asbestos diaphragm shown in Fig. 6 should never be neglected. The specific gravity of liquids, if the quantity available is very small, is best determined by aid of the capillary pyknometer described on page 228. 0.2 cc. of the liquid will be enough to enable a satisfactory determination in this apparatus. Color comparisons should be expressed in terms of the color standard placed in the back cover of this volume and described on pages 230–234. The determination of solubility in water at the temperature of the laboratory may be quickly made by the approximate method of page 38.

These tests are made so early in the procedure, because, unlike most of those which follow, they consume little or no material which can not be recovered, while the information which they furnish is almost certain to be required at some later period in the investigation.

3. ORDER.

DETERMINE THE ORDER OF THE COMPOUND BY APPLYING THE ORDINAL TESTS IN THE SUCCESSION AND MANNER DIRECTED IN CHAPTER II, PAGE 9 ET SEQ. IF THE COMPOUND CONTAINS ANY ELEMENTS OTHER THAN CARBON, HYDROGEN, AND OXYGEN, IT IS NOT DESCRIBED IN THIS VOLUME. IF IT CONTAINS CARBON AND HYDROGEN, OR CARBON, HYDROGEN, AND OXYGEN, AND IS COLORLESS, IT BELONGS TO SUBORDER I, ORDER I. IN THIS CASE TURN TO PARAGRAPH 4 BELOW. IF IT BELONGS TO ORDER I, BUT IS COLORED (I.E., BELONGS TO SUBORDER II), TURN TO PAGE 204.

4. GENUS.

[For Species of Suborder I, Order I.]—APPLY GENERIC TESTS I–IX SUCCESSIVELY UNTIL THE GENUS OF THE COMPOUND IS ASCERTAINED. DO NOT VARY THE ORDER OF THE TESTS, NOR OMIT ANY WHICH ARE NOT KNOWN FROM THE CIRCUMSTANCES TO BE POSITIVELY UNNECESSARY. BEFORE PERFORMING ANY GENERIC TEST FOR THE FIRST TIME, READ CAREFULLY THE "OBSERVATIONS" WHICH FOLLOW THE DIRECTIONS. THE PAGES ON WHICH DIRECTIONS FOR THE SEVERAL GENERIC TESTS ARE TO BE FOUND, ARE GIVEN IN THE "TABULAR SUMMARY OF GENERIC TESTS" BELOW.

When a generic test is subdivided into parts, a statement of the sequence in which they should be applied, or of the circumstances under which certain of them are to be omitted, is always conspicuously placed near the head of the chapter devoted to the genus.

TABULAR SUMMARY OF GENERIC TESTS I–IX IN SUBORDER I, ORDER I.

Test Number and Page.	Condensed Description of Test.
I (p. 15)	**Aldehydes.**—A color reaction with a fuchsine solution decolorized by sulphurous acid. Requires 5 cgr. of substance. Time about 3 minutes.
II (p. 26)	**Carbohydrates.**—The Molisch color reaction with α-naphthol, followed by three short supplementary tests to exclude glucosides in case the proper color is obtained. The Molisch reaction requires 5 mgr. of substance and can be applied in 5 minutes. The supplementary tests, when made, require in all 11 cgr. of substance and can be applied in 5 minutes.
III (p. 35)	**Acids.**—A titration with decinormal sodium hydroxide and phenolphthaleïn. Requires 1 decigr. of substance. Time about 30 minutes when a neutralization equivalent is determined; in other cases (cf. note on p. 35) 5 minutes.
IV (p. 87)	**Phenolic Compounds.**—The test has two parts: (1) a color test with ferric chloride consuming 5 to 10 mgr. of substance, which can be applied in less than 5 minutes; (2) a solubility test with aqueous alkali, which can be made with 10 cgr. of substance in 5 minutes. Part 2 is used only for solids that fail to give part 1.
V and VI (pp. 111–128)	**Esters and Anhydrides.**—A saponification experiment with 10 cgr. of substance, which is heated with 2 cc. of alcoholic potash solution for 30 minutes. (During the heating, preparations for Tests VII and VIII will be made.) [A second longer and more difficult saponification procedure (cf. p. 113) with aqueous potash and a gram or two of substance is required when it is wished to isolate the neutral saponification products from an ester, and thus distinguish certainly between species of Genera V and VI. It is never applied when the first procedure has given a negative result; and its use is generally inadvisable when the total supply of substance does not exceed 2 grams. When omitted, Genera V and VI have to be treated as a single composite genus.]
VII (p. 133)	**Ketones.**—Solid compounds melting above 30° are tested with hot alkaline hydroxylamine solution; all compounds liquid at temperatures below 30°, with phenylhydrazine solution. The test with hydroxylamine requires 10 cgr. of substance; that with phenylhydrazine about 5 cgr. Time in either test about 15 minutes.
VIII (p. 151)	**Alcohols.**—To this genus belong: (A), all species not included in earlier genera that are soluble in less than 30 parts of water at 20°; (B), all compounds liquid below 75° that evolve hydrogen on treatment with sodium; (C), all compounds solid at 75° that are not acetylated by acetic anhydride under certain prescribed conditions. Test A has been already made in the preliminary examination. Tests B and C require about 20 cgr. and 10 cgr. of substance respectively. Test B can be performed in 10 or 15 minutes; C can not be completed in less than about 50 minutes. [In dealing with insoluble solids time will often be saved by referring directly to the appropriate division and section in the tables of both Genus VIII and IX without applying test C.]
IX (p. 173)	**Hydrocarbons, etc.**—Genus IX includes all species not giving Tests I to IX, and hence has no special generic test of its own.

5. GENERIC SUBDIVISIONS.

TURN TO THE PROPER DIVISION (A FOR SOLIDS, AND B FOR LIQUIDS) IN THE TABLES OF THE GENUS. IF THE DIVISION CONTAINS SECTIONS, THE DESCRIPTIVE DIVISIONAL HEADINGS WILL INDICATE WHAT ADDITIONAL TESTS, IF ANY ARE NECESSARY, MUST BE MADE TO ASCERTAIN THE SECTION.

As the divisions in many genera are not subdivided, and as many of the sections are distinguished from one another by differences in solubility or specific gravity which are already known from the preliminary examination of paragraph 2, additional tests at this point are usually unnecessary. The following table gives a general view of the subdivisions of the genera of Suborder I, together with page numbers of each divisional heading.

SUBDIVISIONS OF THE GENERA IN SUBORDER I, ORDER I.

Genus and Divisions.	Page No. of Division Head.	Number of Sections.	Basis of Sectional Distinctions.
I A	17	0	
B	19	0	
II A	29	2	Solubility in water at 20°, with special chemical tests for subsections.
III A	39	2	
B	73	2	
IV A	91	0	
B	104	0	
V A	118	0	
B	120	2	
VI A	129	0	
B	131	0	
VII A	135	0	
B	141	0	
VIII A	155	2	Solubility in water at 20°.
B	160	2	Sp. gr. (20°/4°) greater or less than 0.90.
IX A	174	0	
B	182	3	Sp. gr. (20°/4°) in sections 1 and 2 less than 0.85; in 3 greater than 0.85. Sec. 1 is distinguished from 2 by chemical tests.

6. SPECIES.

COMPARE THE PROPERTIES OF THE SUBSTANCE WITH THE PROPERTIES OF ALL SPECIES THAT MELT OR BOIL WITHIN FIVE OR TEN DEGREES OF ITS MELTING- OR BOILING-POINT AND ARE DESCRIBED IN THE SUBDIVISION OF THE GENUS TO WHICH IT HAS BEEN FOUND TO BELONG.

The published data concerning melting- and boiling-points are, unfortunately, not always based upon exact determinations. (See page 217.) Hence the necessity for extending the inspection of the tables to include species that are described as melting or boiling a number of degrees from the temperature actually observed. The 5° limit is sufficient for most species whose melting- or boiling-points are below 150°; but the limit of 10° is none too large for compounds that melt or boil at 300°. When the recorded and observed temperatures are both "corrected" ones, the limit may be safely much reduced. The mode of procedure in the few sections in which the species are not arranged according to melting- or boiling-points, will always be sufficiently indicated in the sectional headings of the tables.

The specific characteristics most serviceable in making a first partial choice between compounds having nearly the same melting-points or boiling-points are: properties like color, taste, and odor, which are obvious from a casual inspection; properties like specific gravity, solubility, boiling-point (for solids), refractive index, and neutralization equivalent, for which numerical values can be determined quickly, or which are already known in consequence of the preliminary examination and the generic, divisional, and sectional tests that have been made; and, lastly, simple semi-specific tests, such as number 901 with bromine for unsaturation, or 302 with ferric chloride for α-oxyacids. Undue weight should not be attached to statements concerning crystalline form which are unaccompanied by exact crystallographic measurements; the general appearance of crystals of the same compound being often strongly influenced by the solvent, temperature, and other conditions accompanying crystallization.

The final confirmatory specific tests of the tables are not all of equal merit or conclusiveness. Many which have been inserted on the strength of apparently good authority, but not verified by the author, may be deficient in essential details. Those introduced by the words "Apply Test —" or "Identify by Test —" have been carefully studied in the author's laboratory, and may be accepted as thoroughly reliable. The basis for the recommendation of such as begin with the phrase "Gives Test —" or "Gives — in Test —" (e.g. "Gives isophthalic acid in Test 905") is either experiments made in the author's laboratory, or positive published statements that the result specified has been produced under conditions which it is reasonably certain will be supplied by the method of the numbered test cited.

To complete the identification of any compound for which adequate specific confirmatory tests are not suggested in the tables, recourse to the original literature of the body and its derivatives will frequently be necessary. These descriptions have now been made so accessible, and are so well summarized in "Beilstein's Handbuch", that suggestions for the desired tests will often be quite readily found. Some general remarks on the selection of suitable derivatives for use in such impromptu specific tests are given on page 234.

The properties of many of the species whose names appear in the chemical literature have, however, been either so imperfectly determined or described, that their identification by *any* purely analytical method, without some knowledge of the reactions leading to their formation, is an impossibility. All that can be done analytically with such compounds, when the quantity of material is limited, is to ascertain whether their percentage compositions and molecular weights harmonize with any hypothesis that we may be in a position to make concerning them. In such cases it will usually make little difference whether we begin or close the examination of the body with the determination of an empirical formula; for when all has been done that is possible under the circumstances, the labor performed will be the same, whichever procedure is chosen. Substantial justification for the subordination of the method of identification by properties and reactions to that founded on the empirical formula, exists in one case only. This is met with when there are strong reasons for suspecting the unknown substance to be a new compound, or one very unlikely to appear in the tables of this work, and when its quantity is less than about two grams. It would then be unfortunate, in view of the anticipated failure of the attempt at identification by properties and reactions, to forego the possible advantages that might be derived from a knowledge of the empirical formula.

EXAMPLES ILLUSTRATING THE ANALYTICAL PROCEDURE.

The following examples of identifications by the procedure of this "Method" are the records of actual experiments made in a laboratory where the apparatus and reagents required were all in readiness. The contents of each numbered paragraph are a record of the results obtained by following that part of "General Directions for the Identification of an Unknown Compound" summarized in the paragraph in heavy type designated by the same number. The compounds being known to be pure, the description of operations begins with the examination of physical properties referred to in paragraph "(2)," page 4, of the "General Directions".

EXAMPLE 1. (HYDROQUINONE.)

(2).—The compound crystallizes in thin colorless needles melting in a capillary tube at 168°–169° (uncor.). It is odorless; tastes faintly bitter-sweet; and is soluble in approximately 20 parts of cold water. (Time 28 minutes.)

(3).—Ignited on platinum foil it leaves no ash. The tests after ignition with sodium in the iron tube show the absence of sulphur, nitrogen, and the halogens. It is therefore to be considered a species of Order I; and, because colorless, of Suborder I. (Time 20 minutes.)

(4).—It does not give Generic Tests I or II. In the titration of Generic Test III, some alkali is consumed, but the final color transition is not sharp, and the slightly alkaline solution soon acquires a brownish color. The substance is therefore not an acid, but may be a phenol. Test IV-1 gives a yellow-orange coloration. Test IV-2 gives a solution that rapidly turns brown on standing. The compound is hence a phenol. Turn to the analytical tables of Division A, Genus IV. (Time 22 minutes.)

(5 and 6).—Of the ten phenolic species in the tables (p. 99) that melt between 163° and 173°, hydroquinone (m. p. 169°) appears to be the only one easily soluble in cold water. (The solubility given is 17 parts of water at 15°.) The solubility in alcohol and ether, taste, YO coloration with ferric chloride in Test 401, power to reduce silver-nitrate solution on warming, and browning of the alkaline solution in the air, are found to be all properties of the substance which agree with those described for hydroquinone. The final confirmatory Test 411 (cf. p. 108) is next applied, and by oxidation with ferric-chloride solution, quinone is obtained. The quinone is recognized by its odor, and by conversion into quinhydrone, which forms green-black needles melting to a dark-red liquid at about 170°, after previously beginning to soften at about 150°. (Time 40 minutes.)

All the tests in the identification of hydroquinone were completed within 1 hour and 50 minutes, and 0.85 gram of hydroquinone was consumed.

EXAMPLE 2. (MESITYLENE.)

(2).—The compound is a colorless liquid which boils sharply between 163° and 163.5° (uncor.). Its specific gravity (determined in a capillary pyknometer (cf. p. 228) of known capacity, at 25°/4°) is 0.860. Its odor is aromatic; its taste slightly burning. It is insoluble in cold water. (Time 30 minutes.)

(3).—Ash constituents, sulphur, nitrogen, and the halogens are absent. The compound is to be sought among the species of Suborder I, Order I. (Time 18 minutes.)

(4).—Negative results are obtained in Generic Tests I, III, IV-1, VI, VII, and VIII, which are the only ones required for liquids. The compound must therefore be sought in Section 3 of Division B, Genus X (Liquid Hydrocarbons with Specific Gravity greater than 0.85 at 20°/4°). (Time 1 hour and 7 minutes.)

Turning to the sections designated, it is found that of the six species mentioned with boiling-points between 159° and 169°, only two, p-methylethylbenzene, of B. P. 162°, mesitylene of B. P. 164.5° (cor.), and possibly tert. butylbenzene, B. P. 168°–8.5°, have specific gravities approximating that of the unknown compound. Specific Test 914 (cf. p. 201) for mesitylene is therefore applied, and a white crystalline nitro derivative melting at 235° (uncor.) is obtained. The formation of this derivative, trinitromesitylene, proves the unknown substance to be mesitylene. (Time 60 minutes.)

All the tests in this identification of mesitylene were completed in two hours and fifty-five minutes, with an expenditure of 0.87 gram of substance.

CHAPTER II.

ORDINAL TESTS.

DIRECTIONS FOR THE DETECTION OF THE ELEMENTS IN AN ORGANIC COMPOUND.

To determine the Order in which an unknown chemical species belongs usually involves a systematic qualitative examination for its component elements. This examination can be safely omitted only when the analyst's knowledge of the origin of the compound is so complete that it is in itself demonstrative proof that certain elements must be, and alone can be, present.

The qualitative procedure that will be given in this chapter makes provision for the detection of all the elements * that are of common occurrence in pure organic compounds, and will ensure the ready determination of the *order* of all species to be included in the "Method". *Whenever a complete qualitative examination is called for, the several tests should be applied in the order in which they appear in the following lettered paragraphs:*

(a) **Ignition Test for Carbon and Ash Constituents.**—If reducible metals are probably absent, ignite a little of the substance on platinum foil; otherwise in a porcelain crucible. If the substance burns with a flame, or leaves a black carbonaceous residue which gradually burns away, it may be considered organic. Care must, however, be taken not to mistake a permanent black residue consisting of a metallic oxide, like copper oxide, or of a reduced metal, like platinum, for carbon.

If an incombustible ash is formed, incinerate a larger quantity of the substance in a crucible, and make a complete qualitative examination of the ash by the usual analytical methods.

Should the ash contain a metallic element, it is probable that the original compound is a salt of some organic substance of acidic character. Since the "Method" only provides for the identification of metallic salts through the acids from which they are derived, it will be necessary, in dealing with a salt, to isolate its acid in a state of purity, preparatory to the location of the latter in the tables.

(a′) **Ignition Test for Carbon and Hydrogen.**—It is rarely necessary to make any other test for carbon than that already given under (a); but the following more exact method is occasionally required: Place 0.1 gram of the substance mixed with five times its bulk of freshly ignited, dry, powdered copper oxide in an ignition-tube of hard glass, having an internal diameter of about 5 mm., and a length of 12 cm. Fill half the space remaining above the mixture with granulated copper oxide, and connect the open end of the tube with a bent gas-delivery tube leading into a narrow test-tube containing a few cubic

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* Oxygen and hydrogen form important exceptions to this general statement. A simple qualitative test for oxygen in combination, although much to be desired, is at present lacking. A test for hydrogen might always be applied, but the numerical preponderance of the hydrogen-containing species is so great—the present volume being without a single example of a compound in which this element is missing—that its general employment is unnecessary.

centimeters of baryta solution. Support the ignition-tube in a horizontal position, and begin by heating that portion which contains the granulated copper oxide nearly to the temperature at which the glass begins to soften. This may be conveniently accomplished by use of a single Bunsen burner whose flame has been extended by a wing-top spreader. Next heat the mixture of substance and copper oxide by a second burner held in the hand, manipulating the flame so as to decompose the substance very gradually. The condensation of drops of water on the glass at the cold end of the tube indicates the presence of hydrogen in the substance; the precipitation of barium carbonate in the test-tube, the presence of carbon.

The above test, when applied to sulphur compounds, gives a precipitate of barium sulphate. In this case, allow the precipitate to settle without exposing to the air; decant the clear solution; cover the precipitate with a concentrated solution of potassium permanganate; acidify with dilute sulphuric acid; and test the gas evolved for carbon dioxide. (The permanganate serves to oxidize the sulphur dioxide, thus preventing its escape when the solution is acidified.)

SULPHUR, NITROGEN, PHOSPHORUS, CHLORINE, BROMINE, AND IODINE.

Before applying the tests for these elements it is necessary to bring them into inorganic combination by fusing the organic substances containing them with metallic sodium. The analysis is then easily and quickly accomplished with an insignificant expenditure of material, even in the unusual case when all six elements are simultaneously present, and the product of the fusion consists of a mixture of alkaline sulphide, cyanide, (sulphocyanide), phosphide, chloride, bromide, and iodide. The manipulations connected with these tests, when once learned, will be found to offer no difficulties. The reliability of the process has been established by several years' practical trial in the author's laboratory.

(b) Directions for the Ignition with Sodium.—Prepare an ignition-tube 8–10 cm. in length from a piece of hard-glass * combustion tubing. Support it in an

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* The employment of an iron or steel instead of a glass tube is usually permissible and preferable. Fig. 1 represents such a tube in use, suspended by the flange A through the perforated asbestos-board screen B. The dimensions of these tubes should be: length, 9 cm.; internal diameter, 1.3 cm.; thickness of walls, 1.6 mm. They may now be obtained from the firm of Eimer & Amend of New York, by whom they are for sale under the name of "Iron Ignition-tubes for Use in Organic Analysis" Unlike glass tubes they may be used for many successive fusions. After each experiment they should be allowed to stand filled with strong hydrochloric acid for several minutes, and then thoroughly cleaned by use of a test-tube brush and water. The manipulations in the test are the same as with glass tubes, except that an iron tube may be rapidly cooled after the ignition by the application of cold water to its outer surface, as soon as its temperature falls below visible redness. The time required to complete a test is thus materially shortened; and even when the tubes are iron castings, this practice, in the writer's experience, has not been the cause of any accidents. [As the opacity of the iron tube makes it impossible to observe just when the free sodium is completely destroyed after adding alcohol to it, the operator using this method should always be on his guard against the slight explosions that will follow a premature treatment of the residue with water.]

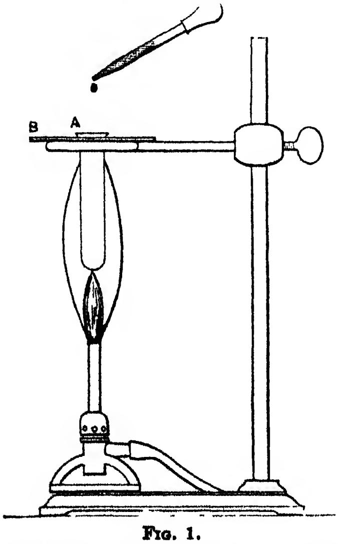

FIG. 1.

Since it is well known that nitrogen is fixed as cyanide when a mixture of sodium, iron powder, and carbonaceous matter is strongly ignited with free access of air, it might be anticipated that iron would exactly vertical position by a narrow metal clamp whose jaws are protected by being wrapped about by one or two layers of asbestos paper permanently wired on. Warm the closed end of the tube gradually before adding the sodium to lessen the danger of cracking the glass. Then drop in the sodium, which should be freshly cut from a large piece that has been wiped free from all adhering oil by filter-paper. The sodium should weigh about a quarter of a gram, and will be of about the size of a pea. Place a burner flame directly underneath the tube and heat its lower end quickly to redness. As soon as the purple vapor of the melted metal is seen to form a layer more than a centimeter in depth, allow five drops of the substance if a liquid, or an equivalent quantity in fragments if a solid, to fall at intervals of one or two seconds directly upon the red-hot bottom of the tube without touching its side walls. The ensuing decomposition is almost instantaneous, and is sometimes accompanied by slight but harmless explosions. The face of the operator should not be brought too close to the mouth of the tube during the reaction.*

When the ignition-tube has become cold, remove the excess of sodium by adding 3 cc. of alcohol. Immediate addition of *water* is liable to cause explosions. As soon as the reaction between alcohol and sodium ceases, stir with a glass rod, and then pour cold water in *cautiously*, in small portions, until the tube is about two-thirds full. Finally stir again with a glass rod and rinse into a test-tube. Boil and filter. Dilute the alkaline filtrate, which will be nearly colorless if the fusion has been satisfactory, to about 20 cc. Separate portions of this filtrate, which will be designated as "S," will be used in making the following tests:

(c) **Tests for Sulphur.**—To 1 cc. of the alkaline "solution S", add two or three drops of a dilute sodium-nitroprusside solution. The presence of sulphur will be indicated by the immediate appearance of an intense, but not very permanent, purple coloration.—[It is best to prepare the reagent at the time when it is to be used, by dissolving a small crystal of nitroprusside in a little distilled water. Nitroprusside solutions do not keep well, though in the dry condition the sodium salt is very stable.]

As an alternative test for sulphur, prepare a clear alkaline solution containing lead, by mixing two or three drops of lead-acetate solution with several cubic

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prove an unsatisfactory substitute for glass in these ignition tests. But experiments have shown that even when the ignition is prolonged (unnecessarily) for five minutes after the addition of the last portion of the organic compound, only a scarcely perceptible blue stain is formed on the filter-paper in test (*d*) for nitrogen. The tests for sulphur and halogens are not interfered with by the iron. *The use of an iron tube is, however, not permissible when the test for phosphorus is to be applied;* for sodium appears always to take up some phosphorus or silicon when ignited in contact with cast iron.

* The preliminary examination and the ignition test (a) will have given warning of danger if the substance under examination is a high explosive. Accidents from other compounds, if ordinary caution is observed, need not be feared.

Liquids are best dropped into the tube from a medicine-dropper or small pipette. If the liquid is very volatile, its introduction will be much facilitated by passing the ignition-tube through a tight-fitting circular hole cut in the middle of a square screen of asbestos-board. This screen, resting on the iron ring of a lamp-stand, shields the hand and dropper from the heat of the flame, and at the same time may be made to serve as a substitute for the clamp which would otherwise be used for holding the ignition-tube in position. The same screen may be used with tubes of smaller diameters if the tube is first fitted with a circular disc or washer cut from heavy asbestos paper. When in use, such a tube will be suspended from a point near the upper end by its washer, which will rest on the upper surface of the asbestos-board screen. By employing such screens, liquids whose boiling-points are very near the temperature of the laboratory may be successfully treated. An improvement in the method for testing for nitrogen in small quantities of volatile or explosive substances in given in Vol. II, p. 3.

centimeters of a solution of sodium hydroxide [1 : 10], and add to 1 cc. of "S." The presence of sulphur will be shown by the appearance of a black precipitate of lead sulphide.

✓ **(d) Test for Nitrogen.**—Boil 2 cc. of solution "S" for a minute or two with five drops of sodium-hydroxide solution and five drops of ferrous-sulphate solution. Then add just enough dilute hydrochloric acid to dissolve the precipitate of iron hydrates, and finally, a slight excess of ferric-chloride solution. A single drop of the last-named reagent will be enough, unless the solution should happen to contain much sodium sulphide, which would act on the ferric salt as a reducing agent. If no blue precipitate appears at once, allow the mixture to stand for a few minutes; then throw on a filter and wash with water. Presence of nitrogen will be indicated by a precipitate of Prussian blue. This precipitate, if scanty, may remain for some time in suspension, giving a turbid greenish appearance to the solution, which, in the absence of nitrogen, should merely show a pale yellow color due to the iron salts that have been added. After filtration, the Prussian blue in such a mixture will appear as a precipitate, or a very pronounced blue stain on the filter-paper.

Test (d), so far as known, is universally applicable to all nitrogenous compounds except the diazo salts. These bodies when heated lose their nitrogen as a gas at such a low temperature that none of it reaches the sodium in a form that is convertible into cyanide. Diazo salts are, however, so well characterized by their physical and chemical properties, that they are not likely to be mistaken for species of the non-nitrogenous orders.

(e) Test for Nitrogen and Sulphur when Present together.—Faintly acidify 1 cc. of "S" with hydrochloric acid, and add two or three drops of ferric-chloride solution. A red coloration (ferric sulphocyanide) indicates the presence of sulphur *and* nitrogen. This test may be omitted when (c) and (d) have both given a positive result.

When a sufficient excess of sodium is used * for the fusion, no sulphocyanide will ever be met with at this point, as, at the temperature of the fusion, sulphocyanides are decomposed by the alkali metal to form sulphide and cyanide. It therefore rarely happens that sulphur and nitrogen are not detected by tests (c) and (d).

(f) Test for Phosphorus.—Boil 1 cc. of solution "S" with 3 cc. of concentrated nitric acid. Cool; mix with two volumes of the ordinary acid ammonium-molybdate reagent; warm to 50°; and allow to stand for ten or fifteen minutes. A pulverulent yellow precipitate indicates phosphorus—(in the absence of arsenic).

A portion of the phosphorus originally combined as sodium phosphide is lost as phosphoretted hydrogen when the solution "S" is prepared from the fused mass. Enough, however, remains to give a satisfactory phosphomolybdate precipitate in test (f).

(g) Tests for Halogens.—Two cases are to be distinguished:—

(1) *When sulphur and nitrogen are both absent,* acidify 1 cc. of solution "S" with nitric acid and add silver nitrate. If a precipitate of silver halide appears,

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* Cf. Tauber, Ber. 32, 3150.

place the remainder of "S" in a very small porcelain dish; add dilute sulphuric acid to faint acid reaction; and boil down to one third of the initial volume. The boiling is to remove alcohol, which may interfere with test (i), in which chromic acid is employed. Dilute the concentrated solution to 20 cc. Under the name of solution "H" it will be used for tests (h), (i), and (j).

(2) *If either sulphur or nitrogen has been found,* prepare solution "H" first, and use 1 cc. of it instead of "S" in making test (1) with silver nitrate. In the preparation of "H" the sulphur will usually have been completely expelled as hydrogen sulphide, and the nitrogen as hydrocyanic acid, so that if no precipitate is obtained, it will be safe to conclude that the halogens are all absent.

To detect several halogens in presence of one another, the following analytical scheme, based on the principles used in Carnot's method for their quantitative separation, is recommended as direct and reliable. The complications and mistakes which are liable to occur in using other procedures when a solution contains sulphocyanide, or when all hydrocyanic acid and sulphuretted hydrogen have not been removed in the preparation of "solution H," are here rendered impossible in consequence of the complete oxidation or expulsion of the disturbing compounds that occurs during the operations in the test for bromine in (i).

(h) **Test for Iodine.**—Place "solution H" in a 50-cc. separatory funnel, add 3 drops of the nitrosyl-sulphate solution whose preparation is described in the footnote,* and shake out thoroughly with 5 cc. of carbon disulphide. If iodine is present it will be liberated and taken up by the disulphide, which will acquire an amethystine purple color. Shake out with fresh portions of the disulphide until the last portion added is removed colorless. Then add two or three more drops of the nitrosyl-sulphate solution, and repeat the operations described until it is certain that all the iodine has been removed.

(i) **Test for Bromine.**—After the separation of iodine by the method described in the last paragraph, filter the solution through a wet filter to remove the last of the carbon disulphide and transfer to a 75- or 100-cc. round-bottomed flask. Support the latter in a slightly inclined position by means of a clamp, and add to its contents 0.7 grm. of powdered potassium dichromate (free from chloride) and 6 cc. of dilute sulphuric acid. Rinse out the neck of the flask with a little distilled water. Drop in an ebullator tube (cf. p. 223), and then boil the solution briskly over a free flame. Just before boiling begins, insert a short roll of fluoresceïn

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* **Nitrosy[illegible] Acid Solution**—Grind together in a mortar 15 grms of starch and an equal weight o[illegible] Pour the thick cream into a 300-cc distilling-flask, heated by a boiling water-bath, and [illegible] to it 30 cc. of pure nitric acid (sp. gr. 1.35). The flask is to be provided with a dropp[illegible]el, and with a delivery-tube for conveying the oxides of nitrogen that will be evolved. [illegible] cc. of concentrated sulphuric acid, in which they are to be absorbed. The sulphuric acid shou[illegible] placed in a small flask surrounded by cold water. A small empty bottle should be interposed between the distilling-flask and the sulphuric acid to condense most of the water and nitric acid that pass over with the gases. Heat the mixture in the flask until a vigorous evolution of gas sets in. When this begins to slacken, gradually admit into the flask through the dropping-funnel 60 cc. more of the nitric acid of 1.35 specific gravity, and continue the heating as long as the oxides of nitrogen are given off freely. The product is a nearly saturated solution of nitrosyl-sulphuric acid in sulphuric acid. In a closed bottle it keeps indefinitely.

$$2H_2SO_4+N_2O_3=H_2O+2NO.O.SO_2.OH.$$

paper * for half its length into the mouth of the flask. If the solution contains bromide, bromine vapors will be liberated. These vapors mixed with the hot steam change the lemon-yellow color of the test-paper to a rose-pink. Chlorine is not set free. The test with fluoresceïn must be repeated at intervals of two minutes, using fresh portions of the test-paper each time, until it is certain that the last trace of bromine has been expelled.

(j) **Test for Chlorine.**—Dilute "H," after the removal of iodine and bromine, to at least 50 cc.; add 2 or 3 cc. of dilute nitric acid; bring to a boil and test for chlorine with silver nitrate. If a precipitate which remains reddish after washing is formed, it is probably colored by silver chromate. In such a case it should be redissolved in a little warm ammonia, and after dilution reprecipitated by nitric acid. The precipitate, if silver chloride, will now be white.

DETERMINATION OF THE SUBORDER.

The colorless species of every order form its first suborder, and its colored species its second suborder. The position in the classification of compounds that are only very slightly colored is fixed by rules stated on page 204.

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* **Fluoresceïn Paper.**—This is prepared by soaking filter-paper in a filtered solution containing one part of fluoresceïn in two hundred parts of 50 per cent acetic acid. The paper, which should then have a clear lemon-yellow color, is quickly air-dried, cut in strips, and preserved in stoppered bottles. It keeps well when not exposed to bright sunlight. The change in color produced in this paper in test (i) by the mixture of bromine vapor and dry steam is due to the formation of eosine (tetrabromfluoresceïn).

CHAPTER III.

GENUS I. ALDEHYDES

OF

SUBORDER I, ORDER I.

(Colorless Compounds of Carbon, Hydrogen, and Oxygen.)

This genus is by definition made to include all species of the suborder which give Generic Test I. The definition admits to the group in addition to the true aldehydes those acetals that are partially hydrolyzed to aldehydes under the conditions of the test, but excludes the aldose carbohydrates.

GENERIC TEST I.

ADD 0.05 GRM. OF THE FINELY POWDERED SUBSTANCE, IF IT IS A SOLID, OR ONE DROP, IF IT IS A LIQUID, TO 5 CC. OF A FUCHSINE ALDEHYDE REAGENT * THAT HAS BEEN PREPARED BY THE METHOD DESCRIBED BELOW. IF THE SUBSTANCE DISSOLVES, ALLOW THE SOLUTION TO STAND *TWO MINUTES* AND THEN OBSERVE THE COLOR. IF THE SUBSTANCE DOES NOT DISSOLVE, SHAKE THE TEST-TUBE CONTAINING IT GENTLY FOR TWO MINUTES AND THEN OBSERVE THE COLOR. NEVER APPLY HEAT.

THE APPEARANCE OF A DISTINCT PINK, RED, PURPLE, OR BLUE COLORATION IN THE SOLUTION WITHIN THE TIME LIMIT INDICATES THAT THE COMPOUND TESTED SHOULD BE SOUGHT FOR IN THE TABLES OF THIS GENUS. IF THE SUBSTANCE IS A SOLID, AND NO COLORATION IS OBTAINED, PASS ON TO GENERIC TEST II; IF A LIQUID, TO GENERIC TEST III.

Observations on Generic Test I.

Soluble aldehydes usually color the fuchsine reagent within a few seconds; those which are difficultly soluble and of high molecular weight sometimes require the full two minutes. Solid substances which for any reason are suspected to be polymerized aldehydes should be boiled with 5 cc. of water containing a drop of strong hydrochloric acid, if no color appears within the time limit, and a few drops of the cooled solution then added to the reagent. Enough of the compound (e.g. metaldehyde) may thus be depolymerized to give a good reaction.

Ordinary acetone and some other soluble ketones prepared by destructive distillation gradually redden the reagent if added to it in large quantity, or allowed

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* [**The Fuchsine Aldehyde Reagent.**—Dissolve 0.2 grm. of rosaniline, or, if the free base can not be obtained, of the hydrochloride or acetate, in 10 cc. of a freshly prepared, cold, *saturated* aqueous solution of sulphur dioxide. Allow the solution to stand until all signs of pink disappear and it becomes colorless or pale yellow. This will require several hours. Then dilute with water to 200 cc. and preserve for use in a tightly stoppered bottle.

This reagent keeps well if not unnecessarily exposed to air and light, and should always be kept on hand. The directions for its preparation should be followed with care, since any large increase of sulphurous acid above the quantity specified diminishes its sensitiveness so much as to render it unserviceable in testing for the less reactive aromatic aldehydes like salicylic aldehyde, vanilline, etc. A reagent that has been in use many months and is found to have lost sensitiveness may be re-sensitized by the cautious addition of sodium acetate, stopping at the moment when a faint pink coloration begins to appear, and then discharging this color by a few drops of the oxidized solution held in reserve for the purpose. In this connection it should be stated, by way of caution, that free alkali, or the alkali salts of any weak acid, organic or inorganic, will redden the reagent like an aldehyde. It is also reddened by heat or when exposed in small quantities to the air for some hours at the ordinary temperature. Mineral acids greatly diminish its sensitiveness.]

to remain in contact with it for a number of minutes; but the color is due chiefly, if not wholly, to the presence of traces of aldehydes or acetals. The limits set upon the quantity of material used, and the time allowed for the development of a distinct coloration, are, therefore, both conditions that must not be disregarded. The reaction is so delicate that the traces of aldehydes occurring as impurities in many commercial preparations may make trouble if their preliminary purification is neglected. But if the conditions prescribed for the test are carefully observed, the best commercial preparations of bodies belonging to other genera rarely give any color within two minutes.*

General Physical and Chemical Characteristics of the Aldehydes.

Nearly all aldehydes of the liquid division are distinguished by characteristic odors, which, for the more volatile species, may be described as ethereal and at the same time irritating or pungent; and for the higher boiling ones, as aromatic, fragrant, or spicy. The solid aldehydes are either odorless or have odors similar to those of the higher boiling liquid aldehydes, though as a rule less intense.

Genus I is notable chemically for the great reactivity of its species. Brief contact with small quantities of concentrated mineral acids, alkalies, or certain metallic salts often causes gradual or sudden polymerization of aldehydes to more stable "para" or "meta" modifications, which would entirely fail to give aldehydic reactions were it not for their tendency to dissociate to some slight extent, under the influence of reagents, to the parent compounds.

Since the liquid aldehydes are gradually oxidized to acids by exposure to the air, commercial preparations of the species of Division 2 will often be found to react acid towards litmus or phenolphthaleïn. Aldehydes are readily oxidized by alkaline permanganate in Test 304, and by ammoniacal silver nitrate in Test 101. The latter reaction, which is accompanied by the formation of a silver mirror, or a precipitate of finely divided metallic silver, is a simple and valuable test.

Aldehydes usually dissolve in concentrated sulphuric acid with decomposition. Hot solutions of caustic alkali attack them with greater or less ease, according to the species, forming salts of organic acids that are sometimes accompanied by other products. Bromine reacts with them readily, hydrobromic acid being evolved. Metallic sodium attacks them much as it does alcohols or phenols, hydrogen being sometimes liberated. Phenylhydrazine, hydroxylamine, and aniline condense with them to hydrazones, oximes, and anils, compounds which often crystallize well and are very valuable in the identification of individual species. Phenylhydrazine, applied in the manner directed in generic Test VII-2 for ketones, is also a very sensitive general reagent for the detection of the carbonyl radical in aldehydes; but many species in the genera intervening between I and VII likewise react with it.

Towards certain reagents like sodium bisulphite, many aldehydes, as well as ketones, act like unsaturated compounds. A concentrated bisulphite solution, when vigorously shaken in a test-tube with an equal volume of a liquid aldehyde, or with a concentrated ethereal solution of a solid aldehyde, frequently evolves heat and solidifies, either at once, or after being cooled and shaken, to a thick crystalline magma of the composition $R.C.H(OH)(SO_3Na)$, from which the original aldehyde may be recovered by treatment with an alkali or an acid. A negative result from this test does not prove that a substance is not an aldehyde, for many bisulphite addition-products are too soluble in water to appear as precipitates, while others do not combine readily with the reagent. Many ketones, moreover, show the same behavior with the reagent as aldehydes.

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* Thus, among the alcohols prepared by Kahlbaum, benzyl and allyl alcohols were the only ones which were found to be sufficiently contaminated with an aldehyde to give this test.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I.

GENUS I, ALDEHYDES.

DIVISION A,—SOLID ALDEHYDES.

Melting-point (C.°).	**ALDEHYDES.**—Colorless and Solid.
35	**o-Methoxybenzoic Ald., $MeO.C_6H_4.CHO$.**—After fusion remelts at 3°.—I. aq.; e. s. eth.; s. alc. B. p. 243°–4° C.
37	**Acetylsalicylic Ald., o-$C_2H_3O.O.C_6H_4.CHO$.**—B. p. 253° (sl. dec.). Cryst. mass v. s. alc. or eth.
37	† **Piperonal (Heliotropine), $CH_2.O_2.C_6H_3.CHO$.**—B. p. 263°. Odor of heliotrope! Ndl. fr. h. aq.; s. 500–600 pts. c. aq.; e. s. alc. or eth.—† Warm 0.1 grm. gently with nitric acid (sp. gr. 1·40); precipitate nitro comp. with cold water; cryst. fr. h. aq.; m. p. of dry, pale-yellow silky ndl. 95·5°.
40	**Propionylpropionic Ald., $Et. CO.CHMe.CHO$.**—B. p. 164–6°. Tbl. s. aq.; v. s. alc. Alc. sol. dark violet w. $FeCl_3$.
44·5	**Lauric Ald., $C_{11}H_{23}.CHO$.**—Cryst. mass.
45–6	† **Metacroleïn, $(C_3H_4O)_3$.**—Cryst.; odor spicy.—Distill. Pass irritating acrolein vapors liberated into 2 cc. aq., and apply Test 112.
51	**Furfuracroleïn, $C_6H_5O.CHO$.**—B. p. a. 200° w. dec.—Cinnamon odor.—D. s. aq.; e. s. alc. or eth.; s. glacial $\bar{A}$c. containing aniline w. green color!
52	**1, 2, 3-Trimethylbenzoic Ald., $Me_3.C_6H_2.CHO$.**—Ndl. fr. dil. alc.
52·5	**Myristic Ald., $C_{13}H_{27}.CHO$.**—B. p. 168°–169° (22 mm.).
52–53	**Polyœnanthylic Ald., $(C_7H_{14}O)_x$.**—I. aq.; v. s. alc. or eth. Dist. gives œnanthylic aldehyde.
54	**o-Oxy-p-toluic Ald., $Me.C_6H_3(OH)CHO$.**—B. p. 222°–3°.—Violet w. $FeCl_3$.—Sol. in ammonia w. deep-yellow color.
56	**o-Oxy-m-toluic Ald., $Me.C_6H_3(OH)CHO$.**—B. p. 217°–8°.—Deep-blue color w. $FeCl_3$.—Ammon. sol. deep yellow.
58·5	† **Palmitic Ald., $C_{15}H_{31}.CHO$.**—B. p. 192°–3° (22 mm.). Pearly scales d. s. c. eth.
59–60	**Paraisobutyric Ald., $(C_4H_8O)_3$.**—B. p. 195° C. Ndl. fr. aq. or alc. Heated w. H_2SO_4 gives isobutyric aldehyde.
61	**β-Naphthoic Ald., $C_{10}H_7.CHO$.**—Lfts. fr. h. aq.; v. s. alc. or eth.
63·5	**Stearic Ald., $C_{17}H_{35}.CHO$.**—B. p. 212°–3° (22 mm.). Scales fr. eth.
80–81	† **Vanilline, $C_6H_3.(MeO)(OH)(CHO)(3 : 4 : 1)$.**—Slender ndl. fr. h. aq.; s. in 20 pt. h. aq. or in 90–100 pt. c. aq ; e. s. alc., eth., or $CHCl_3$. Strong vanilla odor! Taste at first burning, then like vanilla! Aq. sol. (1 : 200) gives immediate blue coloration w $FeCl_3$ in Test 401.—Dissolve 0.05 grm. in 10 cc. aq. Add 2 drops conc HCl and 2 drops $FeCl_3$ sol. (1 : 10). Boil one minute. Filter hot. Wash. Boil residue w. 5 cc strong alcohol. Filter; dry at 100° and determine melting-point The product, dehydrodivanilline, forms slender, nearly colorless, silky microcrystalline ndl. melting w. dec. at abt 304° (uncor.).
97·2	**o-Aldehydobenzoic Ac., $CO_2H.C_6H_4.CHO$.**—Lfts. v. s. aq., alc. or eth. Ag salt cryst. in ndl. fr. h. aq —NH_3 gas passed into alc. sol. gives cryst. comp. m p. 187°. [Gives Test I w. the fuchsine reagent, (A. 239, 82)]
104	**m-Oxybenzoic Ald., $HO.C_6H_4.CHO$.**—B. p. 240° Ndl. fr. h. aq.—Sol. violet w. $FeCl_3$; gives ppt. w. $Pb.\bar{A}c_2$. Heating w. X's acetic anhydride gives diacetate, m. p. 76°.
105–6	**Trimethyl-o-oxybenzoic Ald., $Me_3.C_6H(OH).CHO$.**—Pale-yellow ndl.; i. aq. or KOH; s. alc. or eth. Sublimes.

(ORDER I, SUBORDER I.)

Melting-point (C.°).	**ALDEHYDES.**—Colorless and Solid.
110	**p-Oxy-o-toluic Ald., Me.C_6H_3OH.CHO.**—Tbl. s. h. aq.; e. s. alc., or eth. Rose red w. $FeCl_3$. Ammonia sol. colorless.
Sbl. 112–15	† **Metaldehyde, $(C_2H_4O_2)_x$.**—I. aq.; d. s. eth., alc. Dist. w. dil. H_2SO_4 gives acetaldehyde (Test 111). For behavior toward reagents cf. remark on page 15.
115	**p-Oxy-m-toluic Ald., Me.C_6H_3(OH)CHO.**—Pr. fr. aq.—Blue-violet color w. $FeCl_3$.
115–16	**p-Oxybenzoic Ald., HO.C_6H_4.CHO.**—Sbl. undec. D. s. c. aq.; e. s. alc., eth. Pale-violet color w. $FeCl_3$.—For derivative cf. Paal, Ber. 28, 2409.
Sbl. abt. 120	† **Paraformaldehyde** (commercial), **$(CH_2O)_x$.**—Odor and reactions like formaldehyde. White amorphous powder.—Apply Test 114–1.
128	**Disalicylic Ald., $C_{14}H_{10}O_3$.**—Sbl. undec. Almost i. aq. or KOH; e. s. alc., eth. Cold conc. H_2SO_4 gives salicylic ald.
130	**Dialdane, $C_8H_{14}O_3$.**—Cryst. v. d. s. aq., eth.; e. s. h. alc.
164–6	**m-Aldehydobenzoic Ac., $CO_2H.C_6H_4$.CHO.**—Cu salt green-blue ndl. Oxime m. p. 165°d.
175	**Helicine, $C_{13}H_{16}O_7$.**—(Cryst. w. $\frac{3}{4}H_2O$, which is lost at 100°.) Small ndl. s. 64 pt. aq. at 8°; i. eth.—No color w. $FeCl_3$. Dil. min. acids hydrolyze to dextrose and salicylic aldehyde. Opt. act.
179	**(v-)m-Aldehydosalicylic Ac., (HO)(CO_2H).C_6H_3.CHO.**—Sbl. S. h. aq.; s. w. yellow color in NaOH.—Sol. red w. $FeCl_3$.
180	**Metapropionic Ald., $(C_3H_6O)_x$.**—Sbl. fr. 160°. I. aq.; v. d. s. alc.
221–2	**Aldehydovanillic Ac., MeO.C_6H_2.(OH)(CO_2H)(CHO).**—Silky ndl. v. d. s. c. aq.; s. eth.—Yellow sol. in NaOH. Dingy-violet color w. $FeCl_3$.
234	**p-Aldehydo-m-oxybenzoic Ac., CHO.C_6H_3(OH)CO_2H.**—Ndl. d. s. h. aq.; e. s. alc. or eth.—Sol. in NaOH is deep yellow.—Gives violet color w. $FeCl_3$.
237–8d.	**Aldehydo-(v)-oxyisophthalic Ac., CHO.C_6H_2.(OH)$(CO_2H)_2$.**—S. h. aq.; e. s. eth.—Sol. cherry-red w. $FeCl_3$.NaOH sol. colorless!
243–4	**m-Aldehydo-p-oxybenzoic Ac., CHO.C_6H_3(OH)CO_2H.**—D. s. aq.; e. s. eth. Aq. sol. brick-red w. $FeCl_3$. NaOH sol. deep yellow!
247	**p-Aldehydocinnamic Ac., CHO.$C_6H_4.C_2H_2.CO_2H$.**—Sbl. in lfts. D. s. eth.
248–9	**(a-)m-Aldehydosalicylic Ac., CHO.C_6H_3(OH)CO_2H.**—D. s. h. aq.; e. s. eth. NaOH sol. colorless. $FeCl_3$ gives red color to aq. sol.
260d.	**Aldehydo-(a)-oxyisophthalic Ac., CHO.C_6H_2OH.$(CO_2H)_2$.**—Ndl. fr. h. aq., e. s. eth. Does not sublime. Blood-red color w. $FeCl_3$. Alkali solutions are yellow w. green fluorescence.
285	**p-Aldehydobenzoic Ac., CHO.$C_6H_4.CO_2H$.**—Sbl. in small ndl. D. s. eth. or h. aq.—Ndl. fr. aq.

GENUS I, ALDEHYDES.

DIVISION B,—LIQUID ALDEHYDES.

Boiling-point (C.°).	**ALDEHYDES.**—Colorless and Liquid.
20·8	† **Acetic Ald., Me.CHO.**—G. 0·8056$^{0}/_{4}$. Odor pungent-ethereal, stifling! Misc. w. aq., alc., or eth.—Apply Test 111!
45·5	† **Methylal, $CH_2.(OMe)_2$.**— G. 0·872$^{15}/_{4}$. Odor alcoholic.—E. s. aq.—Apply formic aldehyde Test 114–1 to dil. aq. sol.
48·8c.	† **Propionic Ald., Et.CHO.**—G. 0·8066$^{20}/_{3}$. S. in 5 pts. aq. at 20°. Odor pungent.—Warm w. 2 pts. phenylhydrazine; wash hydrazone w. dil. acetic acid; then heat w. an equal wt. $ZnCl_2$ at 180°. Disgusting skatol odor is produced.
52·4	† **Acroleïn, CH_2:CH.CHO.**—G. 0·84. Vapor excessively irritating; in traces provokes flow of tears. E. s. aq.—Polymerizes to i. solid so readily that it can not long be preserved liquid.—Apply Test 112!
59–61	**Propargyl Ald., CH⋮C.CHO.**—E. s. aq. Very irritating to mucous membranes. Gives orange ppt. with ammon. Cu_2Cl_2 sol!
63–4	† **Isobutyric Ald., C_3H_7.CHO.**—G. 0·7938$^{20}/_{4}$. S. in 9 vol. aq.—$NaHSO_3$ comp. pearly lfts. rather d. s. aq.
64	**Dimethylacetal, Me.CH.$(OMe)_2$.**—G. 0·866 at 22°.
73–4	**n-Butyric Ald., Pr.CHO.**—G. 0·8170$^{20}/_{4}$. S. in 27 pt. aq.—$NaHSO_3$ comp. *e. s. aq. or alc.*
74·5	**Trimethylacetic Ald., Me_3.C.CHO.**—G. 0·7927 (18°).
89c.	**Methylene-diethyl Ether, $CH_2.(OEt)_2$.**—G. 0·851 (0°). S. in 11 vol. aq.—Not acted on by h. KOH.
92·5	† **Isovalerianic Ald., C_4H_9.CHO.**—G. 0·82 (0°). Odor when free fr. valerianic ac. sweet and aromatic. Shaken w. conc. ammonia solidifies to cryst. comp. (m. p. 56°–8°).
97–8	† **Formic Ald.,** (commercial "40 per cent solution" in water). Distillation leaves white residue of "paraformaldehyde" in flask. Odor pungent. Apply Test 114!
103·4	**n-Valerianic Ald., C_4H_9.CHO.**—G. 0·82 (11.2°).
104	† **Acetal, Me.CH.$(OEt)_2$.**—G. 0·8314$^{20}/_{4}$. Odor agreeable and refreshing—not irritating.—S. in 18 vol. c. aq. The dil. aq. sol. if first mixed with a few drops of HCl gives acetaldehyde (Test 111). (Boiling with NaOH gives no acetaldehyde.)
104–5	**α-Crotonic Ald., Me.CH:CH.CHO.**—G. 1·033$^{0}/_{0}$. Odor fruity, then irritating. Absorbs O, and adds Br_2 easily.
115–17	**Tetramethylene Ald., C_4H_7.CHO.**
116·6c.	**Tiglic Ald., Me.CH:CMe.CHO.**—G 0·87 (15°). Odor like bitter almonds. S. in 40–50 pt. aq. Air oxid. easily.
121·7	**Isobutylacetic Ald., $C_4H_9.CH_2$.CHO.**—Odor aromatic.
124c.	† **Paraldehyde, $(C_2H_4O)_3$.**—G. 0·9992 at 15°. M. p. 10°.5. Odor ethereal, agreeable. S. in 10 pt. aq. Heated with a *very little* conc. H_2SO_4 gives off acetic aldehyde freely. Pure, does not give acetic aldehyde (Test 111) distinctly. Solidified by freezing mixture. M. p. +12.5°
129c.	**n-Caproic Ald., C_5H_{11}.CHO.**—G. 0·8498 at 0°.
137·3c.	**Methylethylacroleïn, Et.CH:CMe.CHO.**—G. 0·8577 at 20°. Almost i. aq. Odor penetrating.

Boiling-point (C.°).	**ALDEHYDES.**—Colorless and Liquid.
146·8	**Ethylidenedipropyl Ether, $CH_3.CH.(OPr)_2$.**—G. 0·825 at 22°. I. aq.; s. conc. HCl. Reduces ammon. $AgNO_3$ sol.—Not attacked by hot KOH.
155	† **Œnanthic Ald., $C_6H_{13}.CHO$.**—G. 0·8495$^{20}/_{3}$. Odor aromatic.
160–2	**Ethyl Methylformylacetate, $CO_2Et.CH.Me.CHO$.**—Gives intense red-violet coloration w. $FeCl_3$.
161	† **Furfurol, $C_4H_3O.CHO$.**—G. 1·1594$^{20}/_{4}$. Darkens on exposure to light. Odor remotely resembles that of bitter almonds and cinnamon.—Apply Test 115.
161·2d.	**[Glycid,** cf. Genus VIII.**]**—Dist. w. dec. giving acroleïn (Test 112).
166·2c.	**Propylidinedipropyl Ether, $Et.CH.(OPr)_2$.**—G. 0·8495 at 0°.
169·6	**Isocapric Ald., $C_9H_{19}.CHO$.**—G. 0·828 at 0°. $NaHSO_3$ gives no comp.
169–70	**Parapropionic Ald., $(C_3H_6O)_3$.**—I. aq. Dist. w. a drop or two of conc. H_2SO_4 gives much propionic ald.
170–1d.	**$\Delta^{4,6}$-Dihydrobenzaldehyde, C_7H_8O.**—G. 1·0327 at 0°. Oil w. penetrating odor.
179·5	† **Benzaldehyde, Ph.CHO.**—G. 1·0504.$^{15}/_{4}$. Bitter-almond odor. S. in abt. 300 pt. aq.—Apply Test 113.
186–8d.	**Lævulinic Ald., $Me.CO.(CH_2)_2.CHO$.**—G. 1·0156 at 16° "Odor aldehydic." Misc. w. aq.—Reduces Fehling's sol. in the cold. Colored red by conc. H_2SO_4.
186–8	**Tetrahydrobenzaldehyde, $C_7H_{10}O$.**—G. 1·0091 at 0°. I. aq. Odor like acetone and bitter almonds. Reduces Fehling's sol. in cold.
187 (th. i.)	**Methylfurfurol, $Me.C_4H_2O.CHO$.**—G. 1·1087 at 18°. S. in 30 pt. aq.—1 drop in 5 cc. alc. + 1 cc. conc. sulphuric acid gives green color. Conc. ammonia gives the furfuramide (m. p. 86–7°, ndl. fr. dil. alc.).
188–92	**Diisovalerianic Ald., $C_{10}H_{18}O$.**—G. 0·861 at 0°. I. aq.; e. s. alc. Odor aromatic.
193–4	**Phenylacetic Ald., $Ph.CH_2.CHO$.**—G. 1·085. Phenylhydrazone ndl. fr. lgr. m. p. 58°.
196·5c	† **Salicylic Ald., o-$HO.C_6H_4.CHO$.**—G. 1·173 at 13°. Odor faint aromatic. D. s. aq.; v. s. alc. or eth. Aq. sol. gives w. $FeCl_3$ intense violet color.—Convert into the phenylhydrazone.
199	**m-Toluic Ald.. $Me.C_6H_4.CHO$.**—G. 1·037 at 0°. Bitter-almond odor. Prepare corresponding phenylhydrazone, m. p. abt. 90°.
200	**o-Toluic Ald., $Me.C_6H_4.CHO$.**—M. p. of oxime 48°–49°.
204	**p-Toluic Ald., $Me.C_6H_4.CHO$.**—Odor pepper-like.—M. p. of oximes 79°–80°, and 108°–110°
205–8	† **Citronellal, $C_9H_{17}.CHO$.**—G. 0·8538 at 17.5°. Strong geranium-like odor! Opt. active. Identify by conversion into its semicarbazide of m. p. 84°. (Cf. Ber. 31, 3307.)
208	**Hydrocinnamic Ald., $Ph.C_2H_4.CHO$.**
208–9	**(v)-o-Oxy-m-toluic Ald., $Me.C_6H_3OH.CHO$.**—M. p. 17°. D. s. aq.; e. s. eth.—Sol in ammonia yellow. Sol. in $FeCl_3$ bluish.
210·8c.	**Ethylidene-diisoamyl Ether, $Me.CH.(OC_5H_{11})_2$.**—G. 0·8347 at 15°.
228–9	† **Citral, $C_9H_{15}.CHO$.**—G. 0·8972 at 15°. Odor of oil of lemon! Opt. active.—Identify by converting into the semicarbazide of m. p. 164° (cf. Ber. 31, 3331).
230	**m-Oxybenzoicaldehydemethylether, $MeO.C_6H_4.CHO$.**—G. 1·1187$^{20}/_{4}$. Forms a d s. $NaHSO_3$ comp.
230	**β-Diisobutylene Ald., $C_8H_{14}O$.**—G. 0·9575 at 0°. Thick oil of agreeable odor. Resinified by h. NaOH sol.
235	† **Cuminic Ald., p-$Me_2.CH.C_6H_4.CHO$.**—G. 0·9832 at 0°. Odor aromatic and characteristic. Gives terephthalic ac.(cf. Test 318).—Color reaction with H_2SO_4 (A. 137, 104). † Phenylhydrazone deriv. white but unstable (m. p. 127°–129°).
235–40	**1, 3, 5-Trimethylbenzoic Ald., $Me_3.C_6H_2.CHO$.**

Boiling-point (C.°).	**ALDEHYDES.**—Colorless and Liquid.
245	**m-Oxybenzoicaldehyde-ethylether, EtO.C_6H_4.CHO.**—G. 1·0768$^{20}/_4$. Yellow oil.
248c.	† **Anisic Ald., p-MeO.C_6H_4.CHO.**—G. 1·1228 at 18°. M. p. 0°. Odor aromatic. Hot alc. KOH gives anisic ac. and anisic alcohol.—† Prepare the phenylhydrazone, a pearly-white ppt., m. p. 120° (uncor.). Procedure exactly as in Test 113-1, except that only half the quantity of dilute alcohol there prescribed should be used in each operation.
279	**Diœnanthylic Ald., $C_{14}H_{26}O$.**—G. 0·8494 at 15°. Oil with faint odor.
	[Important aldehydes that can be distilled only under reduced pressure.]
128–30 (20 mm.)	† **Cinnamic Ald., Ph.C_2H_2.CHO.**—G. 1·0497$^{24}/_4$. Odor like cinnamon, changed by shaking w. excess of permanganate sol. [1 : 10] to odor of benzaldehyde.—† Prepare the phenylhydrazone by method given in Test 113-1, except that the product should be boiled up three times with 15 cc. of 50 per cent alcohol, instead of twice with 12 cc. This hydrazone is yellow (YT1–YT2), and melts at 168° (uncor.).

NUMBERED SPECIFIC AND SEMI-SPECIFIC ALDEHYDE TESTS.

[TESTS 101-200.]

101. Compounds Reducing Silver from Tollen's Reagent.

Place 1-2 drops, or about 0.05 grm., of the finely powdered substance in a test-tube with 2-3 cc. of the reagent (whose preparation is described below *). Shake and allow to stand *without warming* for about five minutes.

A black or brownish-black precipitate of metallic silver, or a silver mirror adhering to the walls of the tube, shows that the compound has silver-reducing power and may be an aldehyde. Outside of Order I, Genus I, many scattered species reduce silver from Tollen's reagent. Representative bodies of this description are glucose among the carbohydrates, and hydroquinone among the polyacidic phenols. So far as it is known, this reaction fails among the aldehydes only in the case of a few aromatic oxy-aldehydes like salicylic aldehyde and vanilline. It is generally a very delicate and satisfactory reaction.

111. Acetaldehyde. (Properties tabulated on p. 19.)

1. Boil 1 cc. of a clear aqueous solution of the aldehyde that is concentrated enough to have a distinctly pungent odor with 5 cc. of sodium hydroxide solution (1:10) for a minute or two. The solution, which at first assumes a clear-yellow color, soon becomes turbid, opaque, and yellow orange (YOSI) from separation of finely divided acetaldehyde resin. At the same time a peculiar, penetrating and rather persistent odor is given off. Although many other aldehydes give colorations to boiling soda solution, and emit odors during treatment, this reaction when applied comparatively, or when the odor and color are both familiar from earlier experience, is a delicate and characteristic preliminary test.

Propionic aldehyde, which resembles acetaldehyde more closely in its physical properties than any other species in its genus, gives a somewhat similar odor and turbidity; but the turbidity is less conspicuous in dilute solutions, is nearly white instead of yellow-orange and entirely disappears if the boiling is long continued. Half a drop of acetaldehyde, for instance, when boiled with 5 cc. of the soda solution is enough to give the test as described; while three drops of propionic aldehyde under the same circumstances give only a milky-white precipitate which disappears on continued boiling with emission of a strong lemon-like odor. The lemon odor is usually noticeable in testing acetaldehyde, but is not the dominant odor.

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* **Tollen's Ammoniacal Silver Nitrate Reagent.**—This reagent is prepared by mixing equal volumes of a 10 per cent solution of silver nitrate in ammonia, and of a 10 per cent aqueous sodium hydroxide solution. The ammonia solution used for dissolving the silver nitrate should be a mixture of one volume of the most concentrated aqua ammonia of commerce (sp. gr. 0.90) with one volume of water. The solution of silver nitrate in the diluted ammonia should always be kept in stock, but must not be mixed with the caustic soda until it is needed for an experiment, since the mixture on *long standing* deposits a highly explosive black precipitate. It also gives a black precipitate *immediately*, and without the addition of any reducing compound, *when heated to boiling*. It is a much more senstive reagent for aldehydes than a simple solution of silver nitrate in ammonia.

2. Shake in a three-inch test-tube 0.18–0.25 grm. of β-naphthol, 2 drops of concentrated hydrochloric acid, and about 2.0 cc. of glacial acetic acid, until the naphthol is nearly all dissolved. Add one drop of the aldehyde and shake again. Heat at 50°–60° for about five minutes. Then boil for one minute. Cool and shake vigorously until a crystalline precipitate separates. Because of its tendency to form supersaturated solutions, this precipitate sometimes comes down slowly. Allow to stand until the precipitate has begun to settle. Filter through a small filter wet with glacial acetic acid. Wash with 1 cc. of cold glacial acetic acid. Boil with a mixture of 3 cc. alcohol and 1 cc. of water for half a minute or so. Most of the precipitate will remain undissolved. Cool thoroughly and shake. Filter. Wash with 1 cc. of cold dilute alcohol (1 : 1). Dry 15–30 minutes at 100°.

The product in this test—which is *not* directly applicable to very dilute solutions of acetaldehyde—is ethylidene-β-dinaphthyl oxide, melting at 172.5°–173.5°.

112. Acroleïn. (Properties tabulated on p. 19.)

The following tests for acroleïn are to be applied to dilute aqueous solutions strong enough to possess a distinctly irritating odor. (Such a solution, for instance, as is obtained from the distillation of one drop of glycerine with acid potassium sulphate in Test 816–2.)

1. Add 2 cc. of the acroleïn solution to 5 cc. of the fuchsine aldehyde reagent prepared as described under Test I. (Addition of sodium acetate will never be necessary.) Allow the mixture to stand overnight at the ordinary temperature. It will then appear opaque by reflected light with a deep violet-blue color like cobalt glass. In very thin layers the color will be approximately VR. Add to the blue solution an equal volume of hydrochloric acid, sp. gr. 1.2. Within half a minute the color will change to an impure OYS2. Gradually dilute 2 cc. of this solution to 30 cc. with water. The color on dilution will change, passing through yellow-green and blue-green to about VB of the color standard (the comparison being made against a white background in a test-tube about 2 cm. in diameter).

These color changes, collectively, distinguish acroleïn from all other common volatile aldehydes, although the *initial coloration alone* is *not characteristic*. A dilute acetaldehyde solution, such as would be obtained in applying the distillation test for glycerine (Test 816) to a drop of ethylene glycol, gives a quite similar coloration at the beginning of the test, but this fades, sometimes almost to colorlessness, on standing overnight, while the surface of the solution becomes covered with a thin cantharides-green scum. At the end of the experiment when an acetaldehyde solution is used, after the treatment with acid and dilution with water, the final color will be an exceedingly pale tint of VR, having an intensity about half or one third of the VRT2 of the standard.

2. Mix one drop of the acroleïn solution with six drops of a cold saturated alcoholic solution of gallic acid, and dilute with water to 2 cc. Pour the mixture gently down the side of an inclined test-tube containing 3 cc. of pure concentrated sulphuric acid, in such a manner that the two liquids shall not mix. Allow to stand for some minutes. A very distinct red-orange (RO) ring will appear at the plane of contact between the liquids.

113. Benzaldehyde. (Properties tabulated on p. 20.)

1. Dissolve one drop of the aldehyde in 12 cc. of 50% alcohol. Add one drop of pure phenylhydrazine and boil for half a minute. Cool. Shake well, and collect the bulky precipitate on a small filter. Wash with 5 cc. of cold 50% alcohol. Redissolve the washed precipitate in 12 cc. of boiling 50% alcohol. Cool. Filter, and again wash with 5 cc. of cold 50% alcohol. Dry the well-drained precipitate on the opened filter for fifteen minutes in an oven at 100°. Determine its melting-point.

The precipitate, benzalphenylhydrazone, is a crystalline white or faintly yellowish compound melting at 156° (uncor.) and changing in color to OT2→ after exposure for one hour to diffuse daylight from a clear sky. The yield is very good.

2. In a small dry test-tube mix, in the order given, one drop each of melted phenol, the aldehyde, and concentrated sulphuric acid. Dissolve as much as possible of the colored product in 2–3 cc. of 10% sodium hydroxide solution by stirring with a glass rod. Benzaldehyde gives immediately a beautiful, intensely violet-red (VR) solution.

3. Prepare a cold saturated aqueous solution of the aldehyde and β-naphthol by shaking together one drop of the aldehyde, a pinch of β-naphthol and 10 cc. of water. Filter, and pour 2–3 cc. of the clear solution down the side of an inclined test-tube containing 3 cc. of concentrated sulphuric acid. A violet-red (VRT1) colored zone will appear at the plane of contact between the acid and aqueous layers.

114. Formic Aldehyde. (Properties tabulated on p. 19.)

1. Mix one drop of a one-half per cent aqueous solution of resorcine with 1 cc. of a dilute aqueous solution of the aldehyde of such a concentration (about 1:500) that the irritating odor of the aldehyde is just barely perceptible in the cold, though rather unpleasantly strong when the solution is heated to 100°. Allow the mixture to flow gently down the side of an inclined test-tube containing 3–5 cc. of pure concentrated sulphuric acid. Impart a gentle rotary motion to the liquids by cautiously swaying the lower end of the tube through a circle about a decimeter in diameter in such a manner as not to cause the disappearance of the two layers.

If formic aldehyde is present a red (R) ring, slightly tinged with violet, will soon appear. Above this ring a light flocculent precipitate, at first nearly white on its upper surface, and red-violet beneath, but soon changing to flocks that are red (R) throughout, will be seen suspended in the aqueous upper layer.

2. Repeat part I of the test, substituting six drops of a cold saturated alcoholic solution of gallic acid for the resorcine. A pure blue (B) ring will be formed.

[In either of the preceding color tests it would be a serious mistake to employ too concentrated aldehyde solutions. Such solutions yield deep-colored precipitates that obscure the purer and more characteristic hues that it is desired to produce.]

3. (Applicable to concentrated aqueous solutions like the commercial "formalin".) Place in a test-tube three drops of the solution, 3 cc. of dilute alcohol (1:2), 0.04–0.06 gram of β-naphthol, and three to five drops of concentrated hydrochloric acid. Boil gently until the liquid fills with an abundant precipitate of small white needles. Filter while hot. Wash with 1 cc. of dilute alcohol (1:2). Boil the precipitate with 4 cc. of dilute alcohol (1:1). (It is not necessary that all should dissolve.) Cool, and filter off the precipitate. Wash with 1 cc. of dilute alcohol (1:1). Dry on porous tile in a warm place and determine the melting-point.

Methylene-di-β-naphthol, the product, forms white needles, which, when the temperature in the neighborhood of its melting-point is raised at the rate of 1° in 15 seconds, begins to turn brown at 180°. It melts with decomposition to a brown-red liquid at 189°–192° (uncor.).

The directions for part (3) of this test are specially intended for use with solutions containing 30–40% of formic aldehyde, but they become applicable to much weaker solutions, if the quantity of the aldehyde solution taken in such cases is proportionately increased. In working with a 10% solution, for example, ten drops instead of three should be used. A moderate excess of the aldehyde produces no injurious results.

4. The *p*-nitrophenylhydrazone of melting-point 181–2° is recommended by Bamberger (Ber., 32, 1807) as an excellent derivative for formic aldehyde.

115. Furfurol. (Properties tabulated on p. 20.)

1. Mix in a dry test-tube one drop of the aldehyde and two drops of phenylhydrazine. Dissolve the pasty reaction product in 3 cc. of boiling 50% alcohol. Cool well in running water, and shake until the precipitate, which often appears at first in an amorphous condition, separates in pearly crystalline scales. Collect on a small filter. Wash with 5 cc.

of a cold mixture of two volumes of water and one of strong alcohol. Transfer the precipitate to a test-tube and redissolve in 5 cc. of a boiling mixture of one volume of strong alcohol and two of water. If a few dark-colored droplets should separate at this point, allow them to settle, and decant the clear hot solution into another tube. Cool and shake the solution until pearly scales are again separated. Collect on a small filter and wash with 5 cc. of a cold mixture of two parts of water and one of strong alcohol. Drain. Dry in an oven at 85°, and then determine the melting-point.

Furfurolphenylhydrazone, the product of this test, melts at 97° (uncor.). The crystals have a pale-yellow color and a conspicuously pearly lustre.

2. Boil in a test-tube a mixture of one drop of the aldehyde and 2–3 cc. of water. Moisten a strip of paper with a mixture of equal parts of aniline and glacial acetic acid, removing any excess of the mixture with blotting-paper. Hold a roll of test-paper in the steam issuing from the tube. If the furfurol is present, the paper will be immediately colored a bright light red (RTI). The test is simple and delicate.

CHAPTER IV.

GENUS II. CARBOHYDRATES

OF

SUBORDER I, ORDER I.

(Colorless Compounds of Carbon, Hydrogen, and Oxygen.)

This genus includes all the carbohydrates treated in the work, but no glucosides. The species described when pure are all solid at the ordinary temperature.

GENERIC TEST II.

THIS TEST CONSISTS OF TWO PARTS, THE MOLISCH CARBOHYDRATE REACTION, AND THREE SUPPLEMENTARY TESTS. APPLY THE MOLISCH REACTION FIRST; THEN, IF THE RESULT SHOULD BE NEGATIVE, OMIT THE SUPPLEMENTARY TESTS. THE REASON FOR APPLYING THE LATTER, WHEN THEY ARE REQUIRED, IS TO EXCLUDE CERTAIN SPECIES OF OTHER GENERA WHICH GIVE COLORATIONS IN THE MOLISCH REACTION, AND MIGHT CONSEQUENTLY BE MISTAKEN FOR CARBOHYDRATES.

The Molisch Carbohydrate Reaction.*—Place about 5 mgr. of the substance with 10 drops of water in a small narrow test-tube, and mix with 2 drops of a 10 per cent chloroform solution of α-naphthol. Allow 1 cc. of pure concentrated sulphuric acid to flow slowly from a pipette down the lower inclined side of the tube, so that the acid may form a layer beneath the aqueous solution without mixing with it. If a carbohydrate is present, a red ring will appear within a few seconds at the line of separation between the two layers. The color soon changes on standing or shaking, a very dark-purple solution being formed. Shake, and allow to stand for one or two minutes; then dilute with 5 cc. of cold water. In presence of a carbohydrate, a dull-violet precipitate will immediately appear. Addition of an excess of strong ammonia will change the color to a rusty-yellowish brown. Any substance that gives the dull-violet and rusty-brown precipitate, as well as the purple coloration, under the circumstances described, may be assumed to be a carbohydrate.

Observations.—On account of the delicacy of the Molisch Reaction it is very essential that the substance examined shall be entirely free from all traces of filter-paper, particles of woody fibre, or dust. The purity of the reagents employed should also be placed beyond question. The presence of nitrous acid in the sulphuric acid is specially objectionable. The reagents may be tested by shaking one drop of α-naphthol solution with ten drops of water and 1 cc. of concentrated sulphuric acid. The mixture should be of a golden-yellow color. If dark green, the reagents are not sufficiently pure. The naphthol solution does not keep well, and so should not be prepared in large quantities.

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* Modified from Molisch, M. 7, 198 (1888).

The immediate cause of the colorations observed in the Molisch Reaction is supposed to be the formation of an unstable condensation product of furfurol and α-naphthol.

The Supplementary Tests.—(1) Test the reaction of a little of the substance, which has been dissolved or suspended in powdered form in a few drops of water, with litmus. If the reaction is distinctly acid, the compound is not a carbohydrate.

(2) Place about 5 mgr. of the substance in a small test-tube, cover with 10 drops of water, and then mix with 1 cc. of concentrated sulphuric acid. If a red or purple coloration, or indeed any coloration other than a yellow or brown to black, makes its appearance, the compound is not to be sought among the carbohydrates. (This test results in the exclusion of several glucosides like salicin and coniferin.)

(3) Add one drop of a one tenth per cent ferric-chloride solution to 1 cc. of a 1 per cent aqueous solution of the substance; or if the latter is very insoluble, to its cold saturated aqueous solution. Unless the solution remains colorless, or, at most, shows a pale-yellow or orange-yellow coloration, the compound is not to be looked for in this genus. (This test excludes certain glucosides like arbutin and esculin.)

SUBDIVISIONS AND CONTENTS OF GENUS II.

The principles guiding the selection and arrangement of species in this genus differ materially from those followed in the case of other genera. The carbohydrates that have been obtained in a pure condition up to the present time are all solids. The genus therefore contains only a single "Division," which is subdivided into two "Sections," and several small "Subsections," whose relations to one another will be readily understood from an inspection of the tables. Section 1 includes all species giving clear solutions in less than ten parts of cold water. It contains all the sugars, monosaccharide and polysaccharide. Many, but not all of them, have a sweet taste. The species of Section 2 are either insoluble in ten parts of cold water, or dissolve to solutions that remain opalescent or turbid after repeated filtration. This is the section of starch, glycogen, and cellulose. The members of both sections are colorless, odorless, and neutral towards indicators.

It will be noticed that the number of species described is comparatively small. The names of a majority of the rare synthetic sugars, such as the glucoses and taloses, l-glucose and l-fructose, the heptoses, octoses, and nonoses, are lacking, as are also many of those of the less accessible natural carbohydrates. The cause of these omissions is the nature of the scheme of analytical procedure adopted. This is simple and systematic, but of such a character that the position of every species described had to be determined by actual experiment. It will not be amiss to remind the reader that the direct application of the tests recommended in this chapter to unknown mixtures is not allowable.

Generic Characteristics.—The carbohydrates seldom melt sharply, because fusion is nearly always preceded by slight decomposition. Their melting-points are accordingly of minor importance as specific properties, and worthless as indications of chemical purity. When determined they should be observed by the capillary-tube method (cf. p. 220) in a bath whose temperature is rising somewhat rapidly. The instability of the sugars towards heat is further manifested by their tendency to pass into the state of uncrystallizeable syrups when their solutions are concentrated by boiling down under the ordinary atmospheric pressure.

The specific rotations of the soluble carbohydrates cover a wide range in their values; are the most characteristic of their physical constants; and will usually be determined in any laboratory that is equipped with the requisite apparatus. The deficiency of many laboratories in this respect is the only reason for not employing the specific rotation as the chief means for fixing the arrangement of the soluble carbohydrate species within their "sections." The description for any sugar in the tables is always for the more common of the two optical isomers bearing the name. The description for the "optical antipode," if it were given, would be the same as that for its isomer, except that the specific rotation would have the opposite algebraic sign.

Many of the soluble carbohydrates reduce Tollen's ammoniacal silver nitrate reagent (cf. p. 22) in the cold, and Fehling's solution (cf. Test 202) on heating; but none of them, even such as have been shown to contain the aldehydic grouping, redden the fuchsine aldehyde reagent of Test I.

Heated with normal potassium hydroxide under the conditions prescribed for the saponification of esters (cf. Test V), some carbohydrates are rapidly attacked, giving dark brown or black solutions and neutralizing much alkali; others, like cane-sugar, remain practically unchanged after long-continued treatment. Some of the reactions of the group that have been found most valuable for diagnostic purposes, such as those leading to the formation of osazones, furfurol, etc., and the use of Fehling's solution, are described in the numbered reactions beginning on page 32.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I].

GENUS II, CARBOHYDRATES.

SECTION 1.

CARBOHYDRATES SOLUBLE IN LESS THAN TEN PARTS OF WATER AT 20°, GIVING SOLUTIONS WHICH ARE NOT OPALESCENT AFTER FILTRATION.

SECTIONAL PROCEDURE.—Apply Test 201 ("Rapidity of Osazone Formation") to 0.1 grm. of the substance.—Then: (1) if a white crystalline precipitate appears within less than one minute, see Subsection A; (2) if no precipitate separates from the hot solution within twenty minutes, see Subsection B; (3) if a yellow or orange-yellow precipitate separates within less than twenty minutes, see Subsection C.

Subsection A. [*Test* 201 *gives a nearly white precipitate within* 1 *minute.*]

† **d-Mannose, $C_6H_{12}O_6$.**—Hard amorph. mass, or pr. fr. 90% alc.; s. 0.4 pt. c. aq.; d. s. c. alc.; i. eth.—$[\alpha]_D = +14 \cdot 4°$.—Taste sweet.—Reduces Fehling's sol. (Test 202).—Test 201 gives a *nearly white* cryst. ppt. of the phenylhydrazone after ½ min. heating, which after recryst. fr. boiling aq. melts at 195°–200° (r. h.)! (The last test is characteristic.)

Subsection B. [*Test* 201 *gives no precipitate after heating for* 20 *min.*]

SUBSECTIONAL PROCEDURE.—Test with Fehling's solution by Test 202. If a heavy red precipitate is obtained, see maltose, lactose, and dextrin; if none appears, or if it is yellowish and very scanty, see saccharose, raffinose, and gum arabic.

† **Maltose, $C_{12}H_{22}O_{11}+H_2O$.**—Fine white ndl., losing aq. at 100–10°. V. s. c. aq.; v. d. s. c. alc.—Tastes as sweet as cane-sugar.—$[\alpha]_D = +137 \cdot 7°$.—In Test 201 no osazone separates fr. the sol. while hot, even after 2 hours' heating.—Oxidation by Test 205 gives saccharic ac., but *no mucic ac.*

† **Lactose (Milk-sugar), $C_{12}H_{22}O_{11}+H_2O$.**—Large, hard, white cryst., losing aq. at 130°; turns yellow abt. 160° and melts abt. 200° d.—S. 6 pt. c., or 2½ pt. h. aq.; i. alc. or eth.—$[\alpha]_D = +52 \cdot 5°$.—In Test 201 no osazone separates fr. the h. sol. even after 2 hours' heating. Taste only faintly sweet.—Oxid. by Test 205 gives *mucic ac.* and saccharic ac.

† **"Dextrin."**—Although commercial dextrin is not a true chemical species, being a mixture of several hydrolytic decomposition products of starch, its practical importance renders some mention of its properties and reactions in this place desirable. It is usually a white or slightly brownish powder of insipid mucilaginous taste; v. s. in h. aq. and for the most part also in c. aq; though in the latter case the sol is apt to be somewhat milky or turbid. Test 201 usually gives no ppt. of osazone in the hot solution after 20 minutes.—Unless unusually free from reducing sugars, Test 202 with Fehling's sol. gives a red ppt.—$[\alpha]_D = +200°$ (approximately).—Unless so much starch is present as to give a blue color, a very dilute sol. of I in KI produces a strong brown coloration Unlike gum arabic it does not give Test 204 with phloroglucine.—For additional tests cf. Allen, vol. 1, p. 419.

† **Saccharose (Cane-sugar), $C_{12}H_{22}O_{11}$.**—Colorless monoclinic cryst. s. in ½ pt. c. aq.; d. s. c. alc.; 100 cc. c. abs. methyl alc. dissolve 0·4 grm.—M. p. abt. 160°–70° d.—$[\alpha]_D = +66° \cdot 5$. Taste very sweet.—In Test 201 the yellow osazone ppt. begins to separate fr. the hot sol. if the heating is continued for abt. 30 min.—Oxid. by Test 205 gives saccharic ac., but *no mucic ac.*

† **Raffinose, $C_{18}H_{32}O_{16}+5H_2O$.**—Ndl., losing all aq. at 110°; when anhydrous melts at 118°–19°.—S. in 7 pt. aq. at 20°; 100 cc. abs. methyl alc. dissolve 9·5 grm. of the anhydrous sugar (dif. fr. saccharose); alm. i. c. ethyl alc.—Taste not noticeably sweet.—$[\alpha], = +104 \cdot 5°$. In Test 201 the yellow osazone does not separate fr. the hot sol. unless the heating is continued for abt. 60 min.—Oxid. by Test 205 gives both saccharic and *mucic acids.*

† **Gum Arabic.**—Although not a true chemical species, this substance gives many of the reactions of this section and may be sometimes sought at this point. It consists in part of calcium arabate, and is a hard gum having a faint odor and insipid mucilaginous taste. It dissolves slowly in about 2 pts. of c. aq. to a thick transparent mucilage, but is i. in alc. It gives Generic Test II, and Specific Tests 203 and 204.—It gives no osazone ppt. in the h. sol. after 20 min. heating in Test 201, and gives little or no ppt. in Test 202 with Fehling's sol.—Oxid. by Test 205 gives mucic ac.—Ammonium oxalate and ammonia ppt. calcium oxalate fr. the aq. sol. For other tests cf. Allen, vol. 1, p. 426.

Subsection C. [*Test* 201 *gives a yellow or orange-yellow precipitate from the hot solution within* 20 *minutes. All species also give a heavy red precipitate with Fehling's solution in Test* 202.]

SUBSECTIONAL PROCEDURE.—Apply Test 203. If no test for furfurol is obtained, see dextrose and galactose. If, on the other hand, furfurol is formed, apply Test 204 with hydrochloric acid and phloroglucine. If the precipitate from Test 204 is of a dark-purple color, see arabinose and xylose; if brown, see levulose, sorbinose, and rhamnose.

† **d-Glucose (Dextrose or Grape-sugar), $C_6H_{12}O_6$.**—Ndl. or crusts fr. alc. (m. p. 146°), or in tbl. w. $1H_2O$ fr c. aq. (m. p. abt. 85°–90°).—Anhydrous dextrose is s. in 1·2 pt. aq. at 17·5°; d. s. c. 90% alc., but v. s. h.; i. eth.—$[\alpha]_D = +52 \cdot 8°$. Tastes half as sweet as cane-sugar. In Test 201 a heavy yellow ppt. of the osazone [m. p. 204°–5° (r. h.)] separates suddenly from the hot sol. *after abt.* 4–5 *min. heating!* Test 205 gives saccharic but *no mucic ac.*

† **d-Galactose, $C_6H_{12}O_6$.**—Small hexagonal tbl. fr. abs. alc., m. p. 168° (r. h.); cryst. fr. aq. w. $1H_2O$, m. p. abt. 118°–20°. E. s. c. aq.; d. s. c. alc.—$[\alpha]_D = +80 \cdot 3°$. Tastes about as sweet as dextrose.—Test 201 gives a heavy yellow to orange-yellow ppt. of the osazone, m. p. abt. 196° (r. h.), separating fr. the hot sol. *after about* 15–19 *min. heating!* Oxid. by Test 205 gives *mucic ac. !*

† **l-Arabinose, $C_5H_{10}O_5$.**—Pr. fr. alc., m. p. abt. 160°. V. s. c. aq.; v. d. s. alc.; i. eth.—$[\alpha]_D = +104°–5°$. The orange-yellow osazone, m. p. 160°, separates fr. the hot sol. in Test. 201 after abt. 10 min. heating; unless the sugar is very pure the osazone often separates in part in the form of brownish-yellow oily drops. Test 204 gives a purplish-black ppt.—Arabinose is best distinguished from xylose by preparing the p-bromphenylhydrazone as described by Fischer [Ber. 27, 2491].

† **Xylose, $C_5H_{10}O_5$.**—Ndl. v. s. c. aq.; alm. i. c. alc. or eth.; m. p. abt. 150°–3°.—$[\alpha]_D = +18.7°$.—The orange-yellow osazone, m. p. abt. 160°, separates fr. the hot sol. in Test 201 after abt. 7 min. heating. Test 204 gives a purplish-black ppt.—† Xylose may be quite easily distinguished from arabinose by conversion into cadmium xylonate by the method of Bertrand [Bull. Soc. [3], 5, 556].

† **d-Fructose (Levulose), $C_6H_{12}O_6$.**—Somewhat hygroscopic cryst. or crusts fr. alc.; m. p. 94° ! Also in ndl. w. $\frac{1}{2}H_2O$ fr. aq. V. s. aq.; *s.* 5 *pt. c. abs. alc.; s. eth.!*—$[\alpha]_D = -90 \cdot 2°$. Tastes as sweet as cane-sugar.—A heavy yellow ppt. of the osazone, m. p. 204° (r. h.), separates from the hot sol. after abt. 2 min. heating in Test 201.—Gives dark, rusty-brown ppt. in Test 204.

† **Sorbinose, $C_6H_{12}O_6$.**—Rhombic cryst. s. in ½ pt. c. aq.; d. s. h. alc.; m. p. 164° !—$[\alpha]_D = -43 \cdot 4°$. Tastes as sweet as cane-sugar.—The yellow osazone, m. p. abt. 164° (r. h.), separates from the hot sol. in Test 201 after abt. 3½ min. heating; it usually separates partly in the form of oily drops, but is easily purified by recryst. from a mixture of acetone and ether.—Test 204 gives a dark, rusty-brown ppt.

† **Rhamnose (Isodulcite), $C_6H_{12}O_5 + H_2O$.**—Hard, glassy cryst. fr. aq. or alc., m. p. below 100°. S. in 2 pt. c. aq.; v. d. s. c. alc.—$[\alpha]_D = +9 \cdot 43°$. Tastes faintly sweet.—The osazone separates from the hot sol. in Test 201 after abt. 9 min., as a heavy yellow ppt. (ndl. fr. bz., m. p. abt. 180° d.).

SECTION 2.

CARBOHYDRATES WHICH EITHER ARE NOT SOLUBLE IN TEN PARTS OF COLD WATER, OR WHICH DISSOLVE, GIVING SOLUTIONS THAT REMAIN STRONGLY OPALESCENT AFTER FILTRATION.

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† **Starch,** $(C_6H_{10}O_5)_x$.—Ordinary air-dried starch is a white, tasteless powder, containing about 18% of water. Under the microscope it is seen to consist of granules showing concentrically stratified structure whose size and shape are often characteristic of the plant by which they were produced. (For details concerning the microscopic identification, cf. Allen, vol. 1, p. 405.)—Starch is undissolved and unacted upon by c. aq., alc., or eth. A few cgrms. of the powder rubbed to a thin cream with cold water and then gradually stirred into 100 cc. of boiling water quickly dissolve to a nearly clear solution. This solution, after being cooled, gives a white ppt. with tannin or with much alcohol.—A few drops of a very dilute solution of I in KI gives an intense deep-blue coloration! The blue solution is temporarily decolorized by warming, or permanently by traces of free alkali. In an alkaline solution the color may be restored by acidifying with dil. HCl. (This characteristic color reaction will be masked by the presence of much erythrodextrine, which gives a deep reddish-brown color with the reagent, unless care is taken to use a very weak iodine solution, and to add it gradually.)

† **Cellulose,** $(C_6H_{10}O_5)_x$.—A white, tasteless, amorphous solid, insoluble in water and all ordinary organic solvents, either cold or hot, but dissolving in Schweitzer's reagent, i.e., in ammonia that has been saturated with cupric hydroxide (obtained by precipitating a cold solution of copper sulphate with an excess of caustic soda and washing the ppt. well with cold water), giving a viscid solution, from which it may be reprecipitated in a flocculent state by neutralization with acid.—After a few seconds' immersion in a cold mixture of 2 vol. conc. H_2SO_4 and 1 vol. aq., cellulose assumes a deep-blue color if wet (either immediately or after hastily rinsing with cold water), with a few drops of 2% iodine solution containing KI. [Unless it has been previously treated with such reagents as $ZnCl_2$ or conc. H_2SO_4, cellulose is not colored blue by the iodine solution.]

† **Inulin,** $C_{36}H_{62}O_{31}$ (dried at 130°).—A tasteless white powder; m. p. 178° d. Under the microscope it is seen to consist of spheroidal cryst. aggregates. Alm. i. c. aq.; v. s. h. aq. giving clear solution which shows tendency to remain supersaturated for a long time; alm. i. alc. $[\alpha]_D = -39\cdot5°$. Easily hydrolyzed by h. dil. HCl, chief product being levulose. Does not reduce Fehling's sol. (Test 202). Test 201 gives a yellow osazone which begins to separate from the hot sol. after abt. 25 min. heating. Gives no coloration with dil. I sol.

† **Glycogen,** $C_6H_{10}O_5$.—White amorphous powder, m. p. abt. 240°. E. s. c. aq. to intensely opalescent sol.! This opalescence is not destroyed by repeated filtration, but is removed by addition of acetic acid. I. alc.—$[\alpha]_D = 198°$.—Test 202 w. Fehling's sol. gives no ppt. Test 201 gives no ppt. of osazone after heating for one hour.

† **Commercial Dextrin.**—Cf. Subsection B. (Filtered sol. in c. aq. often somewhat milky; usually reduces Fehling's sol.)

SECTIONAL AND SPECIFIC CARBOHYDRATE TESTS.

[TESTS 201–300.]

201. Osazone Precipitation.

Place in a dry test-tube having an internal diameter of 13 mm., 0.100 grm. of the carbohydrate, 0.200 grm. of pure phenylhydrazine hydrochloride* (cf. Note below), 0.300 grm. crystallized sodium acetate, and 2.00 cc. of distilled water. The errors in measurement should not much exceed 1 per cent. Close the tube *loosely* with a cork stopper to prevent evaporation, and stand it upright in a tall narrow beaker containing two or three inches of water that is already briskly boiling. Note the exact moment of immersion. Shake the tube occasionally without, however, removing it from the beaker. If a precipitate finally separates, note the number of minutes that have elapsed up to the moment of its appearance. The precipitate usually separates out quite suddenly, so that duplicate experiments will generally give results that agree within about half a minute. Note also whether the precipitate is white, yellow, or orange-yellow, and whether it is crystalline, flocculent, or tends to rise to the surface in oily drops. The properties enumerated are all used either as subsectional or as specific tests in the tables.

If a melting-point of the osazone is desired, and it will often be found an important specific constant, cool the hot solution; collect the precipitate on a very small filter; wash with a little cold water; dissolve in the smallest possible volume of boiling 50 per cent alcohol, and filter hot. If the quantity of precipitate which separates on cooling permits, recrystallize once more in the same manner. Dry the precipitate, first on a bit of porous tile, or between filter-papers, and finally at 100°, and determine the melting-point in a bath whose temperature is rising rapidly.

The fact that the rate of osazone formation is very different for the various sugars was first clearly indicated by Marquenne,† but seems not to have been hitherto very generally known or taken advantage of by analysts. The conditions for the test in its present form are so planned that the monosaccharide sugars (the pentoses and hexoses) all give precipitates in from thirty seconds to twenty minutes. Of the polysaccharide sugars, some, like maltose, give products which do not separate until the hot solution is cooled; others, like saccharose, are gradually hydrolyzed to monosaccharides, which then give the corresponding osazones, but naturally require a longer time for the reaction than when the simple sugar was originally present. The times given in the table for the appearance of precipitates in different cases are based on experiments by several observers, and except for xylose and mannose, several distinct preparations were used for examina-

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* [**Note on Phenylhydrazine Hydrochloride.**—This salt, unless very pure and dry, rapidly decomposes and darkens on keeping. Only a perfectly white and dry salt should be used for the foregoing test. Although the commercial hydrochloride often fails to meet these requirements, a very satisfactory reagent is easily prepared by dissolving a light-colored sample of phenylhydrazine in twelve volumes of strong alcohol, and then precipitating out the hydrochloride by the addition of a sufficient excess of the most concentrated hydrochloric acid. Wash the precipitate thoroughly on a suction-plate, first with alcohol and ether, and then with ether, until it is snow-white throughout. Dry on filter-paper in a warm place for half an hour, and then for at least an hour at 100°. Such a preparation, if white at the start, may be preserved for many months if placed in a tightly stoppered bottle, and not freely exposed to the light.]

† Compt. rend. 112, 799.

tion. Variations of a minute or two from the stated time-values will occasionally occur however, and this should not be overlooked when it is a question of selecting between two species whose values lie close together. The precipitates are all phenylosazones, i.e., di-phenylhydrazones, except that from mannose, which is a simple phenylhydrazone, and is easily distinguished from its associates in being white instead of yellow.

202. Reduction of Fehling's Solution.

Add eight drops of Fehling's Solution * to a solution of approximately 0.03 grm. of the carbohydrate in 3 cc. of water. Boil for two minutes if no precipitate appears before.

Arabinose, xylose, rhamnose, mannose, glucose, galactose, fructose, sorbinose, maltose, and lactose give almost immediately a red to yellow-orange precipitate of cuprous oxide on heating. Inulin, raffinose, saccharose, and gum arabic give *only a scanty yellowish turbidity* after two minutes' boiling. Glycogen, starch, and cellulose give no precipitate after two minutes' boiling. The behavior of commercial dextrin is quite variable.

203. Aniline Acetate Test for Carbohydrates giving much Furfurol with Acid.

Dissolve 0.3–0.4 grm. of the carbohydrate in 5 cc. of hydrochloric acid prepared by mixing one volume of an acid of sp. gr. 1.20 with three volumes of water. Boil for one minute. Then insert a cylindrical roll of freshly prepared aniline-acetate paper,† two inches long, for half its length into the upper end of the test-tube from which the vapors of steam and furfurol are issuing. Continue the boiling one minute longer if necessary.

Certain carbohydrates of Section 1, Subsection C, viz., arabinose, xylose, rhamnose, fructose, and sorbinose, give enough furfurol when thus treated to communicate a bright pink color to the test-paper. The other carbohydrates of this subsection do not occasion noticeable colorations. The coloration sometimes appears in streaks and blotches, but often covers the entire surface of the paper.

204. Color Reactions with Phloroglucine.

Boil 3 cc. of the phloroglucine reagent described below ‡ with about 0.03 grm. of the carbohydrate in a small test-tube. Note the color when boiling is about to begin. Continue to boil until the color darkens very considerably, and the solution begins to appear slightly turbid. This will occur within a minute from the moment when boiling begins. Pour the hot solution without delay onto a wet filter, and rinse the scanty precipitate with a little cold dilute alcohol. Note the color of the precipitate while moist; it is the most characteristic result of the test.

This test is used to distinguish between certain carbohydrates of Section 1, Subsection C. The first coloration on heating with *arabinose* and *xylose* is a pure red to violet-red

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* **Preparation of Fehling's Solution.**—Dissolve 34.64 grms. of pure crystallized copper sulphate in distilled water, and dilute the solution to 500 cc. Dissolve 70 grms. of caustic soda of good quality, and 180 grms. of the best crystallized Rochelle salt (potassium-sodium tartrate) in about 400 cc. of water, and dilute to 500 cc. Keep the solutions in separate bottles, and prepare the Fehling's solution fresh before each series of experiments by mixing the two together in equal volumes.

† **Preparation of Aniline Acetate Paper.**—This is prepared as required for use by wetting strips of thick filter-paper in a mixture of 5 cc. of aniline and 10 cc. of 50 per cent acetic acid, pressing out all excess of the solution between blotting-papers. It should be used while still slightly moist. Xylidine-acetate paper, which has also been recommended by Schiff [A. 239, 380] for the detection of furfurol, is somewhat more sensitive than the paper prepared from aniline acetate. The latter is, however, thoroughly satisfactory for use in the present test.

‡ **Preparation of Phloroglucine Reagent.**—This reagent is made by shaking an excess of powdered phloroglucine with a mixture of equal volumes of concentrated hydrochloric acid and water, until the solution is saturated. The clear solution, unless freshly prepared, is slightly yellow, but remains serviceable for many months and should be kept in stock.

(R-VR), which rapidly intensifies and darkens. The color of the precipitate varies according to the duration of the boiling from a very dark purple (VRT2 or RVT2) to black if the boiling is too long continued. With *rhamnose*, *fructose*, and *sorbinose* the first coloration is yellow-orange (YO), quickly passing through dark orange to dingy brown. The precipitate is of a rusty brown, or dark broken shade of yellow-orange or orange (YO or O), which will easily be changed to a dull black if the boiling is too long continued.

205. Oxidation to Mucic or Saccharic Acid.

Galactose is the only hexose yielding mucic acid on oxidation with dilute nitric acid; and glucose the only one, with the exception of the artificial sugar gulose, that gives saccharic acid. The reaction has the merit of being applicable to carbohydrate mixtures, as well as to the simple sugars and their polysaccharide and glucoside derivatives. Several grams of the carbohydrate must be oxidized to ensure satisfactory results if saccharic acid is to be sought. The method is fully described by Gans and Tollens, A. 249, 215 (1888), and more briefly by Allen, Vol. I, p. 270. A close adherence to all details given in these directions is necessary.

CHAPTER V.

GENUS III. ACIDS

OF

SUBORDER I, ORDER I.

(Colorless Compounds Containing Carbon, Hydrogen, and Oxygen.)

This large and important genus includes all non-aldehydic species of the suborder that contain the carboxyl radical, together with a few acid anhydrides and easily saponified esters that show the same behavior as acids when titrated with decinormal alkali by the method of Generic Test III. Many compounds whose solutions in water or alcohol redden blue litmus, including a few like "carbolic acid," are popularly known as acids, but are too feebly acidic to meet the requirements of this test. Such species are accordingly treated elsewhere, most of them in Genus IV.

GENERIC TEST III.

APPLY PROCEDURE 1 OF THIS TEST FIRST TO EVERY COMPOUND, SOLID OR LIQUID, REGARDLESS OF SOLUBILITY. APPLY PROCEDURE 2 ONLY TO SOLID COMPOUNDS INSOLUBLE IN WATER WHICH IT IS FOUND DO NOT TITRATE LIKE ACIDS IN PROCEDURE 1.

PROCEDURE 1.

(Titration in Water.)*

Weigh out accurately about 0.10 grm. of the dry substance, *finely powdered* if it is a solid, into a beaker of 50 cc. capacity. Add 10–15 cc. of cold distilled water, and one drop of a solution of phenolphthaleïn made by dissolving one part of the indicator in three hundred parts of 50 per cent alcohol. Place the beaker on a sheet of white paper, and titrate cautiously with decinormal soda or baryta until the pink color produced by an excess of one drop of the alkali, after exact neutralization, persists for more than one minute when the solution is constantly stirred.

PROCEDURE 2.

(Titration in Alcohol.)*

If less than 2 cc. of the alkali were required for neutralization in Procedure 1, and if the substance at the same time did not go into solution, and is a solid, repeat the titration, replacing the distilled water by about 25 cc. of strong alcohol of the best

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* **Shorter Alternative Procedure.**—Whenever the substance is not very valuable and is not believed to be an acid, it is allowable to take a small unweighed pinch, or three drops (about 0.1 grm.) of the substance for the titrations. If not more than three or four drops of alkali are neutralized, or if the color transition in the end reaction is not "sharp," the time otherwise required for weighings and calculations will be saved.

quality, using three or four drops of phenolphthaleïn instead of one, and disregarding any precipitate that may form.—[The best commercial alcohol usually reacts acid. This acidity should be exactly neutralized by alkali in each experiment before adding the substance to be titrated.]

Any compound that consumes more than 2 cc. of decinormal alkali in either titration, and that also gives a sharp and normal color transition in the end reaction, should be sought in Genus III. The sharpness of the color transition, and the alkali consumption, are phenomena of coördinate importance. The phrase "sharp color transition in the end reaction" is here used with the restricted, definite meaning given to it in the explanatory observations below. Any compound that yields a solution at the end of the titration that has a pronounced color other than pink is likely to be a species of Genus IV.

Observations on Generic Test III.—Never titrate hot solutions nor substitute some other indicator for phenolphthaleïn.

Never omit to reduce the substance to a uniformly fine powder before beginning a titration, unless it is known in advance that it dissolves quickly in cold water. All but the weakest and most insoluble acids may, with a little patience, be successfully titrated without the use of alcohol if this injunction is observed and the suspended powder is persistently stirred. Even terephthalic acid, which is said to require 67,000 parts of cold water for solution, gives little trouble. But if an acid is at once almost absolutely insoluble and very weak, like stearic and other higher solid fatty acids, an aqueous suspension will not neutralize the alkali, and the use of alcohol becomes indispensable. The sharpness of the color change at the end of a titration is usually more striking in aqueous than in alcoholic solutions.

The end reaction in Generic Test III may be defined as being sharp in the sense intended, when a single drop of decinormal alkali, added at the moment when the solution is exactly neutral but still colorless, suffices to develop a full strong pink color which is not greatly intensified if the quantity of free alkali is increased. Some phenols, β-diketones, and similar compounds, consume more than 2 cc. of the alkali before the appearance of a pink color, but they may be distinguished from the species of Genus III by the lack of sharpness in their "end reactions." That is to say, an excess of a single drop of the alkali, added at the end of the titration of such a substance, produces only an almost imperceptible pinkish coloration, that then gradually increases in intensity when more alkali is added. There is no abrupt transition such as is observed in titrating a true acid whose salts are not hydrolyzed in solution. The quantity of alkali consumed in titrating from colorlessness to a full pink, has been found to diminish as the strength of the acid (as indicated by its "affinity constant") increases. The limits vary from a fraction of a drop to several cubic centimeters. Presence of carbonate in the alkali, or of carbon dioxide in the water, increases the transition interval, and is very detrimental to sharpness whenever the impurity is at all considerable. A decinormal alkali prepared from the purest commercial caustic soda and ordinary distilled water will, however, be found sufficiently pure for practical use. A blank titration of two or three drops of acetic acid will quickly determine the condition of any doubtful alkali solution. Within quite wide limits, the abruptness of the color change in an end reaction is independent of the quantity of substance dissolved. An acid containing an appreciable quantity of a phenol as an impurity will titrate like a phenol, the pink color appearing gradually after the acid has been neutralized. Aromatic oxyacids (e.g. salicylic acid) titrate as sharply as other acids of the same strength that do not contain phenolic hydroxyl. Polybasic acids with several carboxyl groups also titrate sharply, the end reaction first appearing when all the carboxylic hydrogens have been replaced.

Although a small bottle of approximately decinormal alkali, and a glass tube medicine-dropper with a rubber nipple, are all the apparatus that is absolutely necessary for the performance of Test III *as a generic reaction,* it is strongly recommended that the alkali should be carefully standardized, and used from a burette mounted in the manner to be described in Test 301. Accurate neutralization equivalents of an unknown acid may then be quickly determined while making the generic test, without involving any additional manipulations, and will be found nearly or quite as useful as melting-point or boiling-point data in completing the identification.

The time limit stated in the direction to "Titrate to a pink color that does not disappear after stirring for one minute," is imposed for several reasons. The first of these is, that nearly insoluble acids, towards the end of a titration when the quantity in suspension has become small, neutralize the dilute alkali very slowly. Yet, if the stirring were to be continued for a much longer period, the color would eventually fade away through absorption of carbonic acid from the air; or, in the case of many esters, from the gradual neutralization of alkali by saponification. A few esters like methyl formate, dimethyl oxalate, and some esters of hydroxyacids, do neutralize decinormal alkali within the time limit selected, and are, in consequence, described with the acids; but this behavior is very exceptional, as has been found by a large number of ester titrations. Isolated cases may, however, occur in the tables, in which esters or lactones that should have been placed in this genus have been wrongly assigned other positions through this cause.

In titrating acid anhydrides a very characteristic, and at first sight surprising phenomenon, will often be noticed. The solution, instead of becoming pink when the neutral point is passed and alkali is present in excess, remains colorless; but after standing for some time gradually becomes pink. The explanation seems to be that the anhydride attacks the hydroxyl groups of the indicator, as in the Schotten-Baumann Reaction, so that the power to form colored alkali salts is lost. The colorless reaction product is, however, gradually saponified by the excess of alkali present after the titration, and the colored salt of the indicator is again formed. Confirmation of this explanation is found in the fact that direct titrations of acid anhydrides may be successfully made by testing the neutrality of the solution from time to time with fresh pieces of phenolphthaleïn paper. The indicator under these conditions is always present in the free state, and so performs its proper function.

General Physical and Chemical Characteristics of the Acids.—The odors of the liquid acids vary greatly. The sharp penetrating quality, so familiar in the odor of acetic acid, is perhaps the most characteristic element that can be traced in any considerable number of species; but even this property is not common to all species.

The solid acids are in a majority of cases odorless or nearly so, though there are many exceptions to the rule. A sour taste and the power to redden blue litmus are properties common to all acids that are sensibly soluble in water. The power of acids, when dissolved in water or alcohol, to instantly and completely neutralize alkalies, is their most striking chemical characteristic, and has been discussed in the preceding paragraphs.

The melting-points, boiling-points, and neutralization equivalents of the tables always have reference to the dry acids when these can be obtained free from water of crystallization by drying in an oven at 100°–110°. For a few species which can not be easily freed from water of crystallization, the data relate to the air-dried acid. In these exceptional cases the hydrated condition of the acid is always made evident in the tables by the context. The number of acid species that occur combined with water of crystallization which may be expelled below 110° is large.

Genus III has a Division A of solid, and a Division B of liquid, species. Of these divisions A is much the larger. Each division comprises two sections, 1 and 2, of which 1 contains "*soluble acids*," i.e. such as are soluble in less than fifty parts of cold water, and 2 the "*difficultly soluble acids*." Where serious doubts have arisen as to the sectional position of an acid it has been mentioned in two sections. The solubilities of the acids have, however, been more carefully studied than those of any other equally important group of compounds.

To find the section in which an unknown acid is to be sought, it is always necessary to at least roughly determine its solubility. This may be rapidly accomplished as follows:

Weigh out 0.2 grm. of the acid—*in the form of an impalpable powder*, if it is a solid, in a five-inch test-tube. Add cold water in small measured portions from a graduate or pipette, shaking thoroughly and persistently after each addition. If complete solution is effected by 1 cc., the substance will be described* as "*very soluble*," or "v. s."; if by 1–4 cc., as "*easily soluble*," or "e. s."; if by 4–10 cc., as "*soluble*," or "s."; if by more than 10 cc., but less than about 30 cc., as "*difficultly soluble*," or "d. s." Greater degrees of insolubility are expressed by the terms "*very difficultly soluble*," or "v. d. s.," and "*insoluble*," or "i." If the supply of the acid is very limited, it is possible to make the solubility determination in a smaller test-tube, using only half the quantities of substance and solvent that have been recommended.

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* It is impossible to be entirely consistent in the use of this approximate solubility terminology, because many of the solubility data incorporated in the tables are merely literal quotations from authorities who have given no numerical values, and who have probably attached a different and less definite meaning to the terms of this solubility scale.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I].

GENUS III, ACIDS.

DIVISION A, SECTION 1,—SOLID ACIDS "SOLUBLE" IN COLD WATER.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally Soluble (see note, p. 38) in 50 parts of cold water.
15	86	**Methacrylic Ac.**—Cf. Div. B, Sec. 1, b. p. 162°–3°.
15·5	86	† **Isocrotonic Ac.**—Odor like butyric ac.—Cf. Div. B, Sec. 1, b. p. 169°.
17	86	**Trimethylenecarbonic Ac.**, $C_3H_5.CO_2H$. — B. p. 182°–2·5°. G. $1{\cdot}0879^{20}/_4$.—"Somewhat" s. aq.
18	90	† **i-Lactic Ac.**, $Me.CHOH.CO_2H$.—B. p. (12 mm.) 119°.—Ordinarily a hygroscopic syrup containing some anhydride, and hence giving too high a neut. eq.—Misc. w. aq., alc., or eth.—Heated in test-tube decomposes, gives off white vapors and leaves a viscous residue. *Gives α-hydroxyacid Test 302!*—Warm sol. quickly decolorizes neutral permanganate w. effervescence.—† Heat nearly to dryness 1 cc. lactic acid in a large test-tube over a moderate flame, using an inverted closed capillary to prevent bumping. Conduct the vapors through a glass tube abt. 25 cm. long into 2 cc. aq. in a test-tube surrounded by cold water. Test this sol. (no odor of acetaldehyde) by Test 111 for acetaldehyde.—Neutral salts all s. aq.—[d. and l. lactic acids are likewise soluble acids giving the same reactions].
27	112	**Propylacetylenecarbonic Ac.**, $Pr.C\vdots C.CO_2H$.—Violet color w. $FeCl_3$—AgĀ ppt.
29–30	158	**Octanon(7)-oic Ac.**, $Me.CO.C_5H_{10}.CO_2H$.—Tbl. e. s. aq.—AgĀ, tbl. e. s. h. aq.
31	118	**α-Oxyvalerianic Ac.**, $Me.(CH_2)_2.CHOH.CO_2H$.—Hygroscop. ndl.; v. s. aq., alc., or eth. Gives Test 302! Gives anhydride easily.—AgĀ, scales, d. s. c. aq.; $Ca\bar{A}_2$, ndl., s. in 28 pt. aq. at 15°; $Zn\bar{A}_2 +$ 2 aq. s., in 136 pt. aq. at 15°.
32–3	130	**β-Propionylpropionic Ac.**, $Et.CO.(CH_2)_2.CO_2H$.—V. s. aq., alc., or eth. Violet color w. $FeCl_3$.—AgĀ ppt.
33	116	† **Lævulinic Ac.**, $Me.CO.(CH_2)_2.CO_2H$.—B. p. 245°–6°.—Deliquescent; usually met with in liq. state. E. s. aq., alc., or eth. Easily oxid. by CrO_3 mixture.—*Gives iodoform by Test 801 immediately in the cold.* In $CHCl_3$ sol. 4Br gives stable $C_5H_6Br_2O_3$, which cryst. fr. aq. w. m. p. 114°–15°.—Ca and Ba salts e. s. aq.; AgĀ characteristic lfts., s. in 150 pt. aq. at 17°.
35·5	102	**Trimethylacetic Ac.**, $Me_3.C.CO_2H$.—B. p. 163·7° (th. i.).—S. in 45 pt. aq.—Ag, Zn, and Pb salts all ppts. fr. moderately conc. sols.
40–2	144	**ω-Acetylvalerianic Ac.**, $Me.CO.(CH_2)_4CO_2H$.—B. p. 250°–53° at 280 mm.—Cryst. e. s. aq., alc., or eth. AgĀ ppt. lft. fr. h. aq.
43	104	† **α-Oxybutyric Ac.**, $Me.CH_2.CHOH.CO_2H$.—B. p. 255°–60° d. Salts generally deliq. and v. s.—Gives α-hydroxyacid Test 302!
43–4	166	**o-Oxyphenylglycollic Ac.**, $HO.C_6H_4.CO.CO_2H$.—Ndl. fr. bz.; s. aq. (?); e. s. alc. or eth.—Dist. gives CO_2 and salicylic ac. (Test 319).
45	100	**α-Ethylacrylic Ac.**, $CH_2: CEt.CO_2H$.—B. p. 180°.—AgĀ, lft., s. h. aq.—Unsaturated (Test 304).
45·5	100	**Angelic Ac.**—Cf. Div. A, Sec. 2.—B. p. 185° (*th. i.*).
48·5	156	**Diallyloxalic Ac.**—Cf. Div. A, Sec. 2.

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally Soluble (see note, p. 38) in 50 parts of cold water.
54	118	† **Dimethyl Oxalate, $C_2O_4Me_2$.**—B. p. 163·3° (cor.). Monoclin. tbl. Titrates like a monobasic ac.—Add several vols. strong NH_4OH to conc. aq. sol.; a heavy cryst. ppt. of i. oxamide immediately forms.
55–6	192	**δ-Phenyllævulinic Ac., $Ph.CH_2.CO.C_2H_4.CO_2H$.**—Silky ndl.; s. aq.; e. s. alc.—$Ba\bar{A}_2 + 1\frac{1}{2}$ aq. e. s. aq.; $Ag\bar{A}$ curdy ppt., lfts. fr. h. aq.
57–8	130	**Paraconic Ac., $C_4H_5O_2.CO_2H$.**—Deliq. mass. Heated gives citraconic anhydride.
60–2	132	**α-Oxycaproic Ac., $Me.(CH_2)_3.CHOH.CO_2H$.**—Gives Test 302. On long heating at 100° partly sbl. and is slowly changed to a syrupy anhydride i. aq.—Warmed w. CrO_3 mixture gives valerianic aldehyde and acid (odor).
64·5	100	† **Tiglic Ac., $Me.CH:CMe.CO_2H$.**—Pr or tbl. rather d. s. c. aq.; e. s. h. aq.—B. p. 198·5° (th. i.).—Peculiar sharp "spicy" odor.—Gives Test 304 (w. $KMnO_4$ instantly—w. Br_2 only upon heating).—$Ca\bar{A}_2 + 3$ aq., s. c. aq. and, unlike the angelate, more s. h. than c.; mod. s. alc. (unlike angelate).—$Ag\bar{A}$ cryst. scales fr. h. aq.
64·5	144	**2-Methylhexanol(4)-oic(6) Ac., $C_7H_{14}O_3$.**—Lustrous lft., e. s. c. aq. or eth.—$Ag\bar{A}$ scales, e. s. h. aq.
65–6	150	**Benzoylformic Ac., $Ph.CO.CO_2H$.**—Heated gives benzoic ac. (Test 312), CO_2, and benzaldehyde (odor).—V. s. aq.—Ba, Pb, and Ag salts d. s. ppts. The acid ppts. oily fr. salts and solidifies on standing in desiccator. It gives the ketone reactions. Warmed w. conc. H_2SO_4, it gives benzoic Ac. and CO_2.—Cf. Ber. 12, 1505, for additional specific reactions.
66–8	118	**α-Methyl-α-oxybutyric Ac., $Et.CH(MeOH).CO_2H$.**—Cryst. sbl. at 90° in ndl. V. s. aq., alc., or eth. Gives Test 302.—$Ba\bar{A}_2$ v e. s. aq.: $Ag\bar{A}$ s. aq.
69·5–70	50	**β-Dimethylacrylic Ac., $Me_2.C:CH.CO_2H$.**—B. p. 195°.—Sbl. in ndl.—$Pb\bar{A}_2 + H_2O$ lft., e. s. aq.—Unsaturated.
70	114	**2, 3-Dimethyl-buten(2)-oic(1) Ac., $C_6H_{10}O_2$.**—Ndl. fr. aq.; 100 pt. aq. dissolve 5.15 pt. at 19°.—$Ba\bar{A}_2 + 3\frac{1}{2}$ aq., powder, e. s. aq. Turns yellow in air. Unsat.
72	43	† **α-Crotonic Ac., $HCMe:HC.CO_2H$.**—B. p. 185° c.—S. in 12 pt. aq. at 15°.—Ba and Ca salts e. s. aq.; $Ag\bar{A}$ curdy ppt.—Reduction of boiling aq. sol. by Na amalgam gives butyric ac. easily.—Gives Test 304!
73	132	[−], **2-Methyl-pentanol(4)-oic(5) Ac., $C_6H_{12}O_3$.**—Ndl. sbl. at 100° At 225° gives syrupy anhydride.—V. s. aq., alc., or eth.—Zn salt, scales, s. in 300 pt. aq. at 16°, or 204 pt. at 100°.—Gives Test 302.
74	144	**Mesitonic Ac., $Me_2.C(CO_2H).CH_2.CO.Me$.**—Small pr. fr. aq.—S. aq.; v. s. alc. or eth.—Dist. gives an anhydride w. m. p. 24° and b. p. 167°.—Salts v. s. aq.
74–5	138	**αβ-Dioxybutyric Ac., $C_4H_8O_4$ + aq.**—Long deliq. pr.; v. s. aq. and alc.; i. eth. Effloresces over H_2SO_4. Gives Test 302.
74–5	120	**β-Methylisoglyceric Ac., $Me.(CHOH)_2.CO_2H$.**—Pr.; e s. aq. or alc.; d. s. eth. Cryst. w. 1 aq. Effloresces over H_2SO_4.—$Ag\bar{A}$, fr. h. aq., v. stable.—Gives Test 302.
74–6	87	**(β)-s-Dimethyladipic Ac., $CO_2H.CHMe.(CH_2)_2.CHMe.CO_2H$.**—B. p 321°.—E. s. c. aq., alc., or eth. Heated w. dil. HCl at 200° gives α acid w. m. p. 140°.
76	84	**Tetrolic Ac., $MeC\vdots C.CO_2H$.**—B. p. 203°.—Broad tbl., s. aq., eth., or CS_2. Sbl.—Gives Test 304. Dec. at 202° to CO_2 and allylene.—Salts all s. and reduce Au and Hg sols.—Heat w. conc. aq. KOH sol. at 105°. Distil, and test for acetone in the distillate (Test 711).
76	80	**Sec.-Butylmalonic Ac., $Bu.CH.(CO_2H)_2$.—Cryst. fr. bz. E. s. aq., alc., or eth.—Gives Test 303.—$Ag\bar{A}$ ppt.**

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally Soluble (see note, p. 38) in 50 parts of cold water.
77-8	73	**α-Methylglutaric Ac., $CO_2H.CHMe.(CH_2)_2.CO_2H$.**—Pr. v. s. aq., alc., or eth. Boiled 20 min. gives oily anhydride, b. p. 272°–75°.
76–80	81	**[+ or −] Ethoxysuccinic Ac., $CO_2H.CH_2.CHOEt.CO_2H$.**—Pr. v. s. aq. Opt. active.—$Ca\bar{A}$ (100°) v. s. c. aq.
78–9	76	† **Glycollic Ac., $CH_2OH.CO_2H$.**—Lft. fr. eth.; deliq. if not absolutely pure. S. aq. and not easily extracted by eth.—Long heating at 100° gives anhydride, $C_4H_6O_5$, m. p. 128°-30°, i. eth., alc., and c. aq.—Gives Test 302! Solubilities of salts in water:—$Ba\bar{A}_2$, 1 : 7 9; $Ca\bar{A}_2$, 1 : 82 at 10° (easily supersaturates); $Pb\bar{A}_2$, 1 : 32 at 15°; $Cu\bar{A}_2$, 1 : 134; $Ag\bar{A}$ + 1½ aq., e. s. c. aq., e. dec. by h. aq.
79 after Sbl. at 50°	104	**α-Oxyisobutyric (Acetonic) Ac., $Me_2.COH.CO_2H$.**—Hygroscopic pr. v. s. aq., alc., or eth. Gives Test 302.—$Ca\bar{A}_2$ v. s. aq.; $Ag\bar{A}$ scales s. in 14 pt. c. aq.—Fusion w. KOH gives acetone (Test 711).
80	65	† **Citraconic Ac., $Me.C(CO_2H):HC.CO_2H$.**—Dist. gives anhydride, b. p. 213°–4°. Deliq. 4-sided pr. s. in 0.42 aq. at 15°. Aq. sol. boiled w. HCl gives mesaconic acid, which is also formed on evaporating sol. containing mineral acids.—$(NH_4)_2\bar{A}$, boiled w. $FeCl_3$ sol. (avoid excess), gives red ppt.—Ba salt, tbl. v. d. s. c. aq.; $Pb\bar{A}$, ppt. fr. h. sol.; $Ag_2\bar{A}$ ndl. fr. h. aq.—Unsat., but gives Test 901 only w. boiling aq. Br sol.
80	132	**Oxydiethylacetic Ac., $Et_2.COH.CO_2H$.**—Triclin. cryst. Sbl. fr. 50°. V. s. aq., alc., or eth.—$Ba\bar{A}_2$ v. s. aq., alc., or eth. $Zn\bar{A}_2$, scales s. in 301 pts. aq. at 16°, *less s. hot.*—Gives Test 302.
82	87	**Pentylmalonic Ac., $C_5H_{11}.CH.(CO_2H)_2$.**—Clear pr. Dec. at 140° giving CO_2 and œnanthic ac. (Test 303).—V. s. aq., alc., or eth.
82-3	166	**o-Hydrocumaric Ac. (Melilotic Ac.), $HO.C_6H_4.(CH_2)_2.CO_2H$.**—(In Melilotus officinalis). Dist. gives anhydride.—S. in 20 pt. aq. at 20°; e. s. alc., eth., and h. aq.—$FeCl_3$ gives transient bluish color in aq. sol. -Fusion w. KOH gives acetic and salicylic ac. (Test 319).—$Ca\bar{A}_2$ v. d. s. c. aq.; $Ba\bar{A}_2$+3 aq. e. s.; $Pb\bar{A}_2$ cryst. ppt.; $Ag\bar{A}$ curdy ppt. (ndl. fr. h. aq.).
84	166	**m-Methylmandelic Ac., $Me.C_6H_4.CHOH.CO_2H$.**—Lust. pr. fr. bz.; e. s. aq., alc., or eth. Gives Test 302.
83–6	118	**α-Oxyisovalerianic Ac., $Me_2.CH.CH_2OH.CO_2H$.**—Rhomb. tbl. volatile at 100°. V. s. aq., alc., or eth.—Oxid. by CrO_3 mixture.—Dil. H_2SO_4 at 130°-40° gives formic ac. (Test 315) and isobutyric aldehyde.—Ca, Zn, and Ag salts d. s. c. aq.
84	80	**2, 2-Dimethylpentanedioic-(1, 5)Ac., $C_7H_{12}O_4$.**—Woolly, ndl. fr. conc. HCl, e. s. aq.—M. p. of anhydride 38°; b. p. abt. 265°.
85–6	73	**3-Methylpentanedioic(1, 5) Ac., $Me.CH.(CH_2.CO_2H)_2$.**—Glassy cryst. e. s. aq., alc., or eth. Distil. gives anhydride, m. p. 46°; b. p. 283°. —$Ca\bar{A}$ (at 150°) s. aq.; $Ag_2\bar{A}$ ppt. i. aq.
86	81	**i-Ethoxylsuccinic Ac., $CO_2H.CH_2CHOEt.CO_2H$.**—V. s. aq., alc., or eth.—$Ca\bar{A}$ v. s. aq.
87	73	**Isopropylmalonic Ac., $Me_2.CH.CH.(CO_2H)_2$.**—Dist. gives CO_2 and isopropylacetic ac. (Test 303).—E. s. alc. or eth.—Cryst. fr. bz. w. $2C_6H_6$ in long ndl. which effloresce.—$Ag_2\bar{A}$ cryst. powder, i. aq.
87–8·5	79	**trans.-Pentamethylenedicarbonic(1, 3) Ac., $C_5H_8.(CO_2H)_2$.**—Flat. pr. fr. CCl_4, s. in 1 pt. c. aq.—$Ag_2\bar{A}$ v. d. s. aq., stable.
88	134	**Tigliceric Ac., $C_4H_7(OH)_2.CO_2H$.**—Tbl. fr. eth.; v. s. aq.; i. $CHCl_3$.—$Ca\bar{A}_2$, (at 100°), hard white mass, v. s. aq.; s. abs. alc.
89	166	**[−]-Arabonic Ac., $HO.CH_2.(CHOH)_3.CO_2H$.**—Evaporation of aq. sol. gives syrupy anhydride solidifying in dessicator (m. p. 95°–8°)—$Ba\bar{A}_2$ ppt'd cryst. fr. aq. sol. by alc.—Gives Test 302.
89	166	**Methoxylphenylglyoxylic Ac., $MeO.C_6H_4.CO.CO_2H$.**—Ndl. fr. bz. v. s. alc. or eth.
90	108	**n-Heptylsuccinic Ac., $C_{11}H_{20}O_4$.**—Scales, e. s. aq. or $CHCl_3$.—$Ag_2\bar{A}$ i. aq.; $Ca\bar{A}$+ aq., d. s. white powder.

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally Soluble (see note, p. 38) in 50 parts of cold water.
90	178	**Monoethyl Tartrate**, $CO_2Et.(CHOH)_2.CO_2H$.—Deliq. rhombic pr. s. in aq.—$Pb\bar{A}_2$ lft. d. s. c. aq.; $Ba\bar{A}_2+2$ aq. s. c. aq.—Gives Test 302.—Saponification gives tartaric acid.
90		**Terpenylic Ac.**, $C_8H_{12}O_4$.—Cryst. w. 1 aq. (m. p. 57°).—(An oxidation product of oil of turpentine.)—Cryst. s. aq. or eth.—Sbl. at 130°–40°. Heat dec. to CO_2, etc.—CrO_3 easily oxid. to acetic acid (cf. Tests 702 and 311), CO_2, etc., but may be evaporated w. HNO_3 (sp. gr. 1·30) without change.—Monobasic to carbonates; dibasic to hot alkalies.—$Ba\bar{A}$ d. s. h. aq.; $Ba\bar{A}_2$ v. e. s. aq.
91	80	**Propylsuccinic Ac.**, $CO_2H.CH_2.CHPr.CO_2H$.—Cryst. fr. aq. 2·83 pt. s. in 100 pt. c. $CHCl_3$.
90–1	193	**Atrolactic Ac.**, $(Me)(Ph)(OH).C.CO_2H+1\frac{1}{2}H_2O$.—Ndl. or pr. c. s. c. aq.—Ba salt d. s., and Zn salt v. d. s. in c. aq.—Boiled w. conc. HCl gives atropic ac.—Boiling BaO_2H_2 has no action.
92	160	**2, 2, 4-Trimethyl-pentanol(3)-oic(1) Ac.**, $C_8H_{16}O_3$.—Cryst. s. in 50 pt. c. aq.—Ba and Ca salts e. s. aq.
93	166	**Phenyl-β-lactic Ac.**, $Ph.CHOH.CH_2.CO_2H$.—Pr. v. s. c. aq.—At 180°, or by boiling w. BaO_2H_2 or dil. H_2SO_4 gives cinnamic ac. (Test 313).—$Ba\bar{A}_2$, $Zn\bar{A}_2$, $1\frac{1}{2}$ aq. and $Ag\bar{A}$, d. s. c. aq.
93	87	**Isoamylmalonic Ac.**, $C_5H_{11}.CH.(CO_2H)_2$.—Silky ndl. fr. bz.—E. s. aq., alc., or eth. Loses CO_2 on fusion (Test 303).—$Ca\bar{A}$ and $Ag_2\bar{A}$. amorph. ppts.
93–4·5	80	**[+]-β-Methyladipic Ac.**, $C_5H_{10}.(CO_2H)_2$.—B. p. 210°–2° (15 mm.). V. s. alc.; e. s. lgr.—$Ag_2\bar{A}$ ppt.
95	180	**Methyl-β-phenyllactic Ac.**, $Ph.CHOH.CHMe.CO_2H$.—V. s. alc., eth., or warm aq.—At 280° gives CO_2 and allylbenzene.— cryst. ppt.
95	74	**β-Oxyglutaric Ac.**, $CO_2H.CH_2.CHOH.CH_2.CO_2H$.—Ndl. e. s. aq. or alc.—Boiled w. 60% H_2SO_4 gives glutaric acid.
95	79	**d-Citramalic Ac.**, $C_5H_8O_5$.—Very deliq. cryst. mass. Gives Test 302.
96	152	**Phenoxyacetic Ac.**, $PhO.CH_2.CO_2H$.—B. p. 285° w. sl. dec.—Silky ndl. e. s. aq., alc., or eth.—$FeCl_3$ gives yellow ppt.—Cryst. ppt. w. Br aq.—$Ba\bar{A}_2+3$ aq., s. aq.; $Ag\bar{A}$. d. s. ndl.
96	73	**Propylmalonic Ac.**, $Pr.CH.(CO_2H)_2$.—Tbl. fr. bz. which contain no bz. of cryst. (dif. fr. isopropyl comp.).—Gives Test 303.
97·5	68·5	† **Glutaric Ac.**, $CO_2H.(CH_2)_3.CO_2H$.—Monoclinic pr.; 100 cc. aq. sol. contain 42·9 grms. at 0°; v. s. alc. or eth. Boils w. little dec. at 302°–4°.—$Ca\bar{A}$. 4 aq. and $Ba\bar{A}$. 5 aq., v. s. aq.; $Pb\bar{A}$ cryst. ppt.; $Ag_2\bar{A}$ ndl. s. h. aq.—Apply Test 316!
95–100d.	54·5	**cis-1, 2, 3-trans-1-Trimethylenetetracarbonic Ac.**, $C_7H_6O_8$.—E. s. aq., alc., or eth. Gives Test 303.
97–8	166	**Phenyl-α-lactic Ac.**, $Ph.CH_2.CHOH.CO_2H$.—Thick pr. fr. aq.—$Ba\bar{A}_2$ e. s. aq. Gives Test 302. Heated above 140° gives formic acid and α-toluic aldehyde.
98d.	87	**Isoamylmalonic Ac.**, $C_5H_{11}.CH.(CO_2H)_2$.—Silky ndl. (fr. bz.+lgr.); v. s. c. aq. Gives Test 303: $Ca\bar{A}$ amorph. ppt.
98	73	**Ethylsuccinic Ac.**, $CO_2H.CHEt.CH_2.CO_2H$.—Pr. v. s. aq., alc., eth., or $CHCl_3$. Dist. gives liquid anhydride b. p. 243°.—Ba and Zn salts e. s. aq.
99	63	† **Oxalic Ac. (Cryst.)**, $(CO_2H)_2+2H_2O$.—Monoclinic pr. After fusion subl. at 150°–60°. S. in 10.46 pt. aq. at 14·5°; e. s. c. alc.; s. in 79 pt. abs. eth. at 15°; v. d. s. $CHCl_3$.—Apply Test 317!
100	70	† **Citric Ac. (Cryst.)**, $CO_2H.CH_2.C(OH)(CO_2H).CH_2.CO_2H+H_2O$.—Cf. Citric Ac. m. p. 153°. Gives Test 302! Apply Test 314!
100	80	**3, 3-Dimethylpentanedioic(1, 5) Ac.**, $C_7H_{12}O_4$.—Pearly ndl. fr. bz.; e. s. aq., eth., or h. bz.—Dist. or action of acetyl chloride gives anhydride, m. p. 124°–5°.

Melting-point (C.°).	Neut. Equiv.	SOLID ACIDS.—Colorless and generally soluble (see note, p. 38) in 50 parts of cold water.
100	67	† [+ or −] **Malic Ac., $CO_2H.CH_2.CHOH.CO_2H$.**—Deliq. ndl.; cryst. w. difficulty. V. s. aq.; s. alc. or eth. Gives Test 302! Gives with $Pb\bar{A}c_2$ a voluminous white ppt. which melts to resinous mass on boiling w. a little aq.—Salts give no ppt. w $BaCl_2$. White ppt. w. $AgNO_3$. At 175°–200° gives fumaric and maleic acids and maleic anhydride.—Apply color test 314!
100	120	**2-Methyl-2, 3-propanedioic(1) Ac., $C_4H_8O_4$.**—Slowly cryst. syrup; e. s. aq.; d. s. eth.—$Ca\bar{A}_2$ s. aq.
100–1	72	**Ethylmaleic Ac., $CO_2H.EtC{:}CH.CO_2H$.**—Thick pr. e. s. aq. or eth.—Unsat. (Test 304). Heated gives a liquid anhydride. Na amalgam reduces to ethylsuccinic acid.
101–2	80	**s-Methylethylsuccinic Ac.** (fumaroid), **$CO_2H.CHMe.CHEt.CO_2H$.**—Ndl. fr. aq.; e. s. c. aq. Heating gives liquid anhydride, b. p. 245°.
101·5	80	**Butylmalonic Ac. $Me.(CH_2)_3.CH.(CO_2H)_2$.**—Pr. e. s. aq., alc., or eth. Gives Test 303. At 150° gives CO_2 and caproic acid (disagreeable odor).
102–3	98	**Pentinoic Ac., $C_4H_5.CO_2H$.**—Monoclinic tbl. fr. eth.; ndl. fr. bz. V. s. aq.—$Ba\bar{A}_2$, scales fr. dil. alc.; v. s. aq.—Unsat. (Test 304).
103	72	**Allylmalonic Ac., $C_3H_5.CH.(CO_2H)_2$.**—E. s. aq. or eth. Adds Br_2.—$Ca\bar{A}$, d. s. aq.; $Ba\bar{A}$ + aq. pearly lfts. s. in 1 pt. h. aq.; $Ag_2\bar{A}$, i. aq.—Gives Tests 303 and 304.
103–4	132	**α-Hydroxylævulinic Ac., $Me.CO.CH_2.CHOH.CO_2H$.**—E. s. aq.; d. s. eth. Reduces Fehling's sol. At 100° gives an anhydride (ndl. m. p. 263° d.).
[illegible]4	80	**3-Methyl-3-carboxyl-pentanoic (1) Ac., $C_7H_{12}O_4$.**—Clear pr. fr. aq.; e. s. aq., alc., or eth. 100 pt. aq. at 15° dissolve 15·4 pt. acid. Heating at 200° gives an anhyd., b. p. 239°–45°.
105	80	† **n-Pimelic Ac., $(CO_2H).(CH_2)_5.CO_2H$.**—Tbl. fr. aq. s. in 24 pt. aq. at 20°; e. s. eth.—Sbl. without dec.—$BaCl_2$ gives no ppt.; $Ag\bar{A}$ cryst. ppt.; $Ca\bar{A}$ separates as gran. floc. ppt. when saturated sol. is boiled.
106–7	80	**Methylpropylmalonic Ac., $(Me)(Pr).C.(CO_2H)_2$.**—E. s. aq., eth., or $CHCl_3$.—Gives Test 303.
107	80	**Isobutyl Malonic Ac., $Me_2.CH.CH_2.CH.(CO_2H)_2$.**—E. s. aq. or eth.—$Ca\bar{A}$ and $Ag_2\bar{A}$, i. ppts.—Gives Test 303.
107	87	**Isobutylsuccinic Ac., $C_4H_9.C_2H_3.(CO_2H)_2$.**—Cryst. e. s. aq. or eth.—$Ca\bar{A}$ e. s.; $Ba\bar{A}$ d. s.—The anhydride is liquid.
110–1	134	**Angliceric Ac., $C_4H_7.(OH)_2.CO_2H$.**—Ndl. fr. eth. V. s. aq.; i. $CHCl_3$.—Ca salt amorphous, v. s. aq.; i. abs. alc.
111	144	**Hexahydrosalicylic Ac., o-$HO.C_6H_{10}.CO_2H$.**—4-sided tbl. or ndl. e. s. aq. or eth.
111	166	**m-Hydrocumaric Ac., $HO.C_6H_4.(CH_2)_2.CO_2H$.**—"E. s. usual solvents."
111·5	66	**Ethylmalonic Ac., $Et.CH.(CO_2H)_2$.**—Cryst. w. $1H_2O$. Pr v. s. aq. or eth.—Gives Test 303, being completely dec. to CO_2 and butyric ac. (odor) at 160°!—$Na_2\bar{A}$ gives no ppt w $FeCl_3$ (dif. fr. pyrotartaric ac. below).—$Ca\bar{A}$ less s. h. than c; $Ba\bar{A}$ + ½ aq., fine pr. d. s. aq.; $Zn\bar{A}$, 2½ aq. characteristic 6-sided tbl. s. in 456 pt. aq.
112	66	**Pyrotartaric Ac., $Me.CH(CO_2H).CH_2.CO_2H$.**—Triclinic pr. e s. c. aq. or eth. At 200 gives an anhydride.—$Zn\bar{A}$, v e. s. aq.; $Ba\bar{A}\cdot 2$ aq. e. s. aq.; $Ag_2\bar{A}$, ppt., v. d. s. h. aq.
113·5	72	**1-Methylcyclopropanedicarbonic(2, 2) Ac., $Me.C_3H_3.(CO_2H)_2$.**—Silky ndl. fr. bz. S. in 1 pt. c. aq.; e. s. eth.—Distillation gives valerolactone.—Gives Test 303 at 140°—Stable towards $KMnO_4$.—$Ca\bar{A}$ + 5 aq., glassy pr., e. s. aq.; $Ag_2\bar{A}$, floc. ppt. (at 70°).
113·5	200	**Naphthoylformic Ac., $C_{10}H_7.CO.CO_2H$.**—Ndl., e. s. aq. or eth. Oxid. by $KMnO_4$ to α-naphthoic ac.—$Ba\bar{A}_2$, e. s. c. aq.; $Ag\bar{A}$, amorph. ppt.
112–15	192	**Ethylbenzoylacetic Ac., $Ph.CO.CHEt.CO_2H$.**—E. s. alc. or eth. Boiling w. *conc.* alcoholic potash gives mixture of potassium benzoate and butyrate!

Melting-point (C.°).	Neut. Equiv.	SOLID ACIDS.—Colorless and generally soluble (see note, p. 38) in 50 parts of cold water.
114–5d.	91	**Dioxytartaric Ac., $CO_2H.[C(OH)_2]_2.CO_2H$.**—Cryst. mass fr. eth. V. s. aq. Gives Test 303.—The aq. sol., when heated, dec. quantitatively to CO_2 and tartronic ac ! Therefore gives theoretical neut. eq. only at 0°. Salts unstable.
115–16	74	**α-Ethyltartronic Ac., $Et.COH.(CO_2H)_2$.**—Cryst. w. 1 aq. in tbl. w. m. p. 64°–70°.—$Ag_2\bar{A}$, mic. pr. fr. h. aq.
116	136	**Trioxyisobutyric Ac., $(CH_2OH)_2.COH.CO_2H$.**—Pr. fr. alc. v. s. aq.; d. s. alc. or eth.—Gives Test 302.—$Ca\bar{A}_2+4$ aq., s. aq.; $Pb\bar{A}_2$.Aq., d. s. h. aq.
116·5	164	**Hydrocumarilic Ac., $C_8H_7O.CO_2H$.**—Pearly lft. fr. aq.; s aq.; v. e. s. alc. or eth. Dist. w. dec. at abt. 300°.—$Ag\bar{A}$, v. d. s. h. aq.; $Ba\bar{A}_2+2$ aq., e. s. aq.
117	80	**Isopropylsuccinic Ac., $CO_2H.CHPr.CH_2.CO_2H$.**—Cryst. crusts e. s. aq., alc., eth., or $CHCl_3$.—On distill. gives liq. anhydride, b. p 245°-50°. —Fuse w. KOH and acidify w. H_2SO_4. (Odor of butyric ac.). —$BaCl_2$ no ppt. Ag salt, d. s.
117	97	**Benzylmalonic Ac., $Ph.CH_2.CH.(CO_2H)_2$.**—Triclinic, e s. aq. or eth. Test 303 at 180° gives CO_2 and hydrocinnamic ac
117–8	166	**Tropic Ac., $Ph.CH(CH_2OH).CO_2H$.** (prepared fr atropine).—Ndl. or tbl. s. 49 pt aq. at 14 5°; v d. s c bz and CS_2 Gives Test 302.—$Ca\bar{A}_2\cdot 4$ aq., rhombic tbl.—Long boiling w. $Ba(OH)_2$ gives atropic ac.
118	73	**Methylethylmalonic Ac., $(Me)(Et)C.(CO_2H)_2$.**—Pr e. s. aq. or eth.—$Ag_2\bar{A}$, d. s. cryst. powder.—Gives Test 303.
118	152	† **Mandelic Ac., $Ph.CHOH.CO_2H$.**—Rhombic cryst., 16 pt s in 100 pt. aq. at 20°; s. eth.—Gives Test 302! —Dist. or boiled w aq. and MnO_2 gives odor of bitter almonds!—$Ag\bar{A}$ cryst. ppt., tbl. fr. h. aq.; $Ba\bar{A}_2$, s. 12 pt aq. at 24°.
119	74	**Citramalic Ac.** (racemic), **$CO_2H.CH_2.C(OH,Me).CO_2H$.**—Glassy deliq. cryst. v. s. aq —At 200° gives citraconic anhydride.—Gives Test 302 —$CaCl_2$ added to NH_4 salt gives floc. ppt. in conc. sol.—Scaly fr h. dil. sol.
119–20	68	**Mesoxalic Ac., $(HO)_2.C.(CO_2H)_2$.**—Deliq. ndl., v s. aq.; s. eth.—Reduces ammon. $AgNO_3$ sol. when warmed.—Ba, Ca, Pb, and Ag salts v. d. s. c aq.—$Ag_2\bar{A}$ dec. by boiling w. aq., oxalic ac. being among the products.
120d.	85	**Δ'-Tetrahydrophthalic Ac., $C_8H_{10}O_4$** (dried i. v.).—Lfts fr aq.; e. s. aq.—Oxid by alk. $KMnO_4$ to adipic ac —At 100° gives anhydride, m. p. 74°.—$Ba\bar{A}$+aq., gran. ppt —Gives Test 304.
120–1	94	**2, 3, 3-Trimethylpentanediol(2, 4)-dioic(1, 5) Ac.** (racemic), **$C_8H_{12}O_6$.** —(An oxid product of camphoric acid.) Lust lfts., e s aq., alc., or eth.—Heated to 220° dec to water, isobutyric ac. (odor and Test 311!), CO, etc —$Ag_2\bar{A}$ ppt.
123	74	**β-Methylmalic Ac., $CO_2H.CHMe.CHOH.CO_2H$.**—Pr. fr. acetic eth., v. s. aq. or alc —Gives Test 302 —Heat gives citraconic anhydride, etc —$Ba\bar{A}+2\frac{1}{2}$ aq lft d s aq.
123	166	**[−]-Tropic Ac., $Ph.CH(CH_2OH).CO_2H$.**—Cryst. somewhat s. aq.—M. p. of quinine salt 178°.
121–5	80	**Diethylmalonic Ac., $Et_2.C.(CO_2H)_2$.**—Pr, v s. aq. or eth.—Gives Test 303 at 170°–80°, forming CO_2 and diethylacetic acid.—Zn salt cryst. ppt.—$CaCl_2$ precipitates conc. sol of NH_4 salt.
124	80	**Methylisopropylmalonic Ac., $(Me)(Pr).C.(CO_2H)_2$.**—S. aq.—Gives Test 303.—$Ca\bar{A}$, v. d. s aq.; $Ag_2\bar{A}$ ppt.
127[illegible]	166	**[+] Tropic Ac., $Ph.CH(CH_2OH)CO_2H$.**—Pr. fr. eth. S. h. aq. M. p. of quinine salt 186°–7°. Less s. dil. alc than salt of [−] tropic ac.
1[illegible]	80	**s-Dimethylglutaric Ac.** (malenoid), **$CO_2H.C_5H_{10}.CO_2H$.**—Triclinic cryst.—100 pt. aq. at 17° dissolve 4.1 pt.—Acetylchloride gives anhydride in the cold, b. p. 272°.

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
128c.	90	[+ or −]-**Trioxyglutaric Ac., $CO_2H.(CHOH)_3.CO_2H$.**—Cryst. fr. acetone; v. s. aq. or alc. $Ag_2\bar{A}$ ppt., m. p. w. dec. 173°.—Gives Test 302.
129	87	**s-Diethylsuccinic Ac., $CO_2H.EtCH.CHEt.CO_2H$.**—Warty masses; v. e. s. h. aq. or eth.—$Zn\bar{A}$ more s. c. than h.—At 180° gives anhydride.
129	152	**m-Oxyphenylacetic Ac., $HO.C_6H_4.CH_2.CO_2H$.**—V. s. aq. or eth. Gives transient violet color w. $FeCl_3$.
129	73	**s-Dimethylsuccinic Ac. (malenoid), $(MeCH)_2.(CO_2H)_2$.**—Pr. s. in 3·3 pt. aq. at 14°.—W. Conc. HCl at 180° gives much of the malenoid ac., m. p. 209°.
129	166	**Phloretic Ac., p-$HO.C_6H_4.CH(Me)(CO_2H)$.**—S. c. aq. or eth. Gives green color w. $FeCl_3$!—Pb salt bulky ppt.
129–31	81	***β*-Dimethylmalic Ac., $CO_2H.CHOH.CMe_2.CO_2H$.**—Cryst. fr. acetic eth. E. s. aq.; s. eth.—$Ag_2\bar{A}$, ndl. d. s. h. aq. Gives Test 302!
130	58	† **Maleic Ac., $CO_2H.CH:CH.CO_2H$.**—Monoclinic pr. s. in 2 pt. aq. at 10°. Gives Test 901 w. h. bromine water, but does not add Br easily in CCl_4 sol.—Heating *in vacuo* above 100° gives solid anhydride, m. p. 56°–7°.—At 200° in tube gives fumaric acid (d. s. aq., sbl. at 200°).—Aq. sol. gives ppt. w. BaO_2H_2; $Pb\bar{A}c_2$ gives ppt. No ppt. w. $CaCl_2$.—† Place 0·1 grm. acid w. 0·2 cc. aniline in a test-tube w. 10 cm. glass tube as return condenser. Heat 1 hr. at 190°–200°. Cryst. fr. 15 cc. boiling alc. Cool, filter, wash w. 2 cc. cold alc. and recrystallize fr. 10 cc. boiling alc. Dry at 100°–110°. Gives phenylaspartic-anil. white cryst., m. p. 209°–10°.
131	194	**Phenyl-*β*-oxyvalerianic Ac., $Ph.C_2H_4.CHOH.CH_2.CO_2H$.**—E. s. aq.; d. s. c. eth.—Dec. on dist.—$Ba\bar{A}_2$ + aq., lfts. d. s. aq.; $Ag\bar{A}$ curdy ppt.
131	72	**trans-Tetramethylenedicarbonic(1, 2) Ac., $C_4H_6.(CO_2H)_2$.**—Lust. ndl. fr. HCl. Goes easily into anhydride, m. p. 75°.
132	78	**s-Methylethylmalic Ac., $CO_2H.CHEt.(Me)C(OH).CO_2H$.**—Pr. e. s. aq. Dec. on dist. Gives Test 302.
132	52	† **Malonic Ac., $CH_2.(CO_2H)_2$.**—Cryst. s. in less than 1 pt. aq.; s. eth.—Test 303 gives CO_2 and acetic ac.!—Fuming nitric acid causes evolution of CO_2.—† Boil 1–2 cgrm. in a test-tube w. 3 cc. acetic anhydride for 3 minutes; then dilute w. 3 cc. acetic ac. A yellowish-red sol. w. yellowish-green fluorescence will be obtained.—$Ag_2\bar{A}$ stable cryst. ppt.; $Ca\bar{A} + 2H_2O$, alm. i. c. aq.
132	65	**Glutaconic Ac., $CO_2H.CH_2.HC:HC.CO_2H$.**—Pr. e. s. aq. or eth.—$Zn\bar{A}$ less s. h. than c.—$Ag_2\bar{A}$ d. s. h. aq.—Long boiling w. x's acetyl chloride gives anhydride, m. p. 87°.—Reduction w. Na amalgam gives glutaric ac.
133	57	**i-Malic Ac., $C_4H_6O_5$.**—Cryst. Not deliq.—Reactions as for [+ ac.] (Cf. m. p. 100°.)
133	92	**Diallylmalonic Ac., $(C_3H_5)_2.C.(CO_2H)_2$.**—Pr. e. s. aq. or eth. Gives Test 303 and 304.—$Ca\bar{A}$ (at 100°) e. s. aq.; $Ag_2\bar{A}$ d. s. c. aq.
132–4c.	112	**Pyromucic Ac., $C_4H_3O.CO_2H$.**—Sbl. fr. 100° in ndl.—S. in 28 pt. aq. at 15°. V. s. h. aq.; e. s. alc. or eth.—Pine splinter, soaked in conc. HCl and held in vapor evolved on heating dry NH_4 salt in test-tube, becomes deep red!—Sol. in conc. H_2SO_4 warmed w. trace of isatin becomes violet-blue.—Aq. sol. gives reddish-yellow ppt. w. $FeCl_3$.—$Ca\bar{A}_2$ and $Ba\bar{A}_2$ cryst. and s. aq. or alc.—$Pb\bar{A}_2$ + aq. d. s. c. aq.—$Ag\bar{A}$ lft.
135d.	59	**Isosuccinic Ac., $Me.CH.(CO_2H)_2$.**—Pr. v. s. aq.; 100 cc. aq. sol. at 0° contains 44.3 grm.—Test 303 gives CO_2 and propionic ac. (Test 311)!—Ca, Ba, Pb, and Ag salts v. d. s.; Pb salt s. in x's of precipitant.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
135d.	73(?)	† **Acetonedicarbonic Ac., $CO.(CH_2.CO_2H)_2$.**—Ndl. fr. acetic eth. **which** effloresce in the air.—V. s. aq. or alc.; d. s. eth.—Aq. sol. + **$FeCl_3$** gives violet color! Gives Test 303!—Distil a neutral **aqueous** solution of the sodium salt and apply tests for acetone (**Test** 711) to distillate!
130–8	72	**Cis-1, 2-Tetramethylenedicarbonic Ac., $C_4H_6.(CO_2H)_2$.**—Feathery **cryst.** v. s. aq., alc. or eth.—Heated above 300° gives anhydride, m. p. 76°–8°.—Oxid. by $KMnO_4$ to oxalic ac.—Ba$\bar{A}$ separates as 6-sided tbl. on boiling a sol. in ammonia w. $BaCl_2$ sol.
137	72	**Methylglutaconic Ac., $Me.CH.(CO_2H).CH:CH.CO_2H$.**—E. s. aq., alc., or eth.—Unsaturated.
137	152	**o-Oxyphenylacetic Ac., $HO.C_6H_4.CH_2.CO_2H$.**—Ndl. fr. eth.; s. aq.—Dist. gives anhydride, m. p. 49°; b. p. 236°–8°.—Aq. sol. colored violet by $FeCl_3$!
138–9	210	**Veratrinketonic Ac., $(MeO)_2.C_6H_3.C_2O_3H$** (dried).—E. s. aq., alc., or eth.—KOH fusion gives protocatechuic ac.—Pb salt d. s. ppt.
138–9	72	**Cis-Tetramethylenedicarbonic(1, 3) Ac., $C_4H_6.(CO_2H)_2$.**—Pr. v. s. c. aq.—Ba$\bar{A}$ + 2 aq. s. in 150 pt. c. aq., less s. in h. aq.
139	87	**Dimethylethylsuccinic Ac., $CO_2H.CHEt.CMe_2.CO_2H$.**—S. in 27 pt. c. aq.; e. s. alc. or eth.—B. p. 235°–40°.
139		**Anhydrocamphoric Ac., $C_9H_{12}O_5$.**—Sbl. undec.—E. s. aq., alc., or eth Can be recryst. fr. aq.
139–40	73	**α-Dimethylsuccinic Ac., $CO_2H.CMe_2.CH_2.CO_2H$.**—Thick glassy pr. fr. bz.—100 pt. aq. at 14° dissolve 7·52 pt.; e. s. alc. or eth.—At 165°–70° gives anhydride, m. p. 29°.—Ca salt separates from ammon. sol. by $CaCl_2$ only when warmed.
139	101	**Tetrahydroxyterephthalic Ac., $(OH)_4.C_6.(CO_2H)_2$.**—E. s. aq. or alc.; i. eth. No color w. $FeCl_3$.—Ba$\bar{A}$ e. s. aq.
139	182	**Hydrocaffeic Ac., $(OH)_2.C_6H_3.(CH_2)_2.CO_2H$.**—6-sided tbl. fr. aq. E. s. aq. Aq. sol. gives intense green color w. $FeCl_3$! Reduces Fehling's sol. and $AgNO_3$ easily.
140	74	**Ethylenemalonic Ac., $C_2H_4.C.(CO_2H)_2$ + aq.**—Ndl. fr. eth., v. s. aq. or eth.; s. $CHCl_3$.—Gives Test 303 and 304.—$(NH_4)_2\bar{A}$ + $BaCl_2$ gives ppt. almost i. c. aq.
140	79	**Cis-Pentamethylenedicarbonic(1, 2) Ac., $C_5H_8.(CO_2H)_2$.**—Ndl. At 160° gives anhydride (tbl. fr. $\bar{A}$c., m. p. 140°).
abt. 140d.	67	**Isomalic Ac., $Me.COH.(CO_2H)_2$.**—Cryst., e. s. aq., alc., or eth.—Opt. i.—At abt. 160° gives Test 303 yielding CO_2 and lactic acid.—Ba$\bar{A}$ + 2 aq., d. s. h. aq.
140–	80	**s-Dimethylglutaric Ac. (fumaroid), $C_7H_{12}O_4$.**—Pr.—100 pt. aq. at 17° dis. 4.4 pt.—Ca$\bar{A}_2$ floc. ppt.
141d.	63·3	**2, 3-Dicarboxyl-pentanoic(1) Ac., $C_7H_{10}O_6$.**—Cryst. fr. acetone, v. s. aq., alc., or eth.—Heated loses CO_2.—$Ba_3\bar{A}_2$, i. aq. or alc.
140–3	84	**Mesotartaric Ac., $(HO)_2.C_2H_2.(CO_2H)_2$.**—(Cryst. w. 1 aq.)—Tbl. s. in less than 1 pt. c. aq.—KH$\bar{A}$ much more s. than acid tartrate or racemate.—Does not ppt. $CaSO_4$ sol. (dif. fr. racemic ac.). Gives Test 302.—Opt. i.—For microchemical tests cf. R. 17.69.
143–4s.d.	182	**Phenylglyceric Ac., $Ph.(CHOH)_2.CO_2H$.**—V. s. aq. or alc.; d. s. abs. eth.—Gives Test 302, decomposing at 160° to CO_2 and α-toluylic aldehyde.—Ca$\bar{A}_2$·4 aq. d. s. c. aq.
145–6d.	64	**Glutinic Ac., $CO_2H.C\vdots C\ CH_2.CO_2H$.**—E. s. aq., alc., or eth.; i. bz. —Gives Test 303 and 304.—Pb$\bar{A}$ ppt.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
145	226	**Galactosecarbonic Ac.,** $HO.CH_2.(CHOH)_5.CO_2H$.—Ndl., s. aq.—Fusion gives an anhydride.—Gives Test 302.
147	168	**Homogentisic Ac.,** $(HO)_2.C_6H_3.CH_2.CO_2H$.—V. s. aq., alc., or eth.—Fusion gives anhydride of m. p. 191°.—Gives transient-blue color w. dil. $FeCl_3$.—KOH fusion gives hydroquinone, etc.—Cryst. effloresce over H_2SO_4.
148	152	**p-Oxyphenylacetic Ac.,** $HO.C_6H_4.CH_2.CO_2H$.—Flat ndl., s. c. aq.; v. e. s. h. aq.; s. alc. or eth.—Sol. gives pale-violet color w. $FeCl_3$, changing quickly to a dirty grayish green. Dist. w. CaO gives CO_2 and p-cresol. (From urine.)
148	76	**Diglycollic Ac.,** $CO_2H.CH_2.O.CH_2.CO_2H + Aq$.—Rhomb. pr., e. s. aq. or alc.—Dist. w. dec. giving glycollic ac., trioxymethylene, CO and CO_2.—$Ba\bar{A}$, i. aq.; $Ag_2\bar{A}$, gray ppt.; $Cu\bar{A}$ blue ppt.
abt. 150d.	72·7	**l-Camphoronic Ac.,** $C_9H_{14}O_6$.—Cryst. s. in 17 pt. c. aq.; v. s. alc.; e. s. eth.—CO_2 and isobutyric ac. are among products of slow dist.
150–3	58	**cis-1, 2, 3-Trimethylenetricarbonic Ac.,** $C_3H_3.(CO_2H)_3$ (dried at 120°).—E. s. aq. or alc.—Ca salt less s. h. than c.; $Ag_3\bar{A}$ amorphous ppt.
151	81	**α-Oxyadipic Ac.,** $CO_2H.C_3H_6.CHOH.CO_2H$.—Sbl. undec. E. s. aq. alc., or eth.
152	80	**Trimethylsuccinic Ac.,** $CO_2H.CMe_2CHMe.CO_2H$.—E. s. aq. or bz.—$Zn\bar{A}$, mic. pr. e. s. c. aq., but ppt'd by boiling the sol.—Prepare the anilic ac., m. p. 134°, and the anil. m. p. 129°.
152d.	90	**i-Trioxyglutaric Ac.,** $CO_2H.(CHOH)_3.CO_2H$.—Tbl. fr. acetone. V. s. aq. or h. alc. Gives Tests 101 and 302.
152–3	72	**Hexamethylenetricarbonic (1, 4, 4) Ac.,** $C_9H_{12}O_6$.—S. aq.; d. s. eth.—Dec. at 200°. Gives Test 303.
152–3d.	90	**Phenylmalonic Ac.,** $Ph.CH.(CO_2H)_2$.—Pr., e. s. aq., alc., or eth.—$Ca\bar{A}$ cryst. ppt.; $Ag_2\bar{A}$ curdy ppt.—Fusion gives CO_2 and phenylacetic ac. (Test 303).
153	64	† **Citric Ac.,** $CO_2H.CH_2.C(OH)(CO_2H).CH_2.CO_2H$.—Cryst. w. 1 aq. in rhombic pr. (Dry at 130° for m. p.) S. in 0·75 pt. c. aq.; v. s. alc.: 100 pt. c. eth. dissolve 2·26 pt.—Gives Test 302.—Hot conc. H_2SO_4 gives yellow color, but does not char.—$CaCl_2$ gives a white cryst. ppt. with neutral alkali citrates when the sol. is boiled for a few min.,—otherwise only after some hours; an alkali citrate sol. after being made strongly alkaline w. NaOH gives an amorphous ppt. immediately.—$Ca_2\bar{A}_3$ is soluble in HCl, in $\bar{A}c$, in citric ac., in NH_4Cl, and in alkaline citrates.—[Neutral alkali tartrates and oxalates give an immediate ppt. w. $CaCl_2$; calcium oxalate is insoluble in acetic acid. Malic ac. and neutral malates give no ppt. w. $CaCl_2$ unless alc. is also added. A conc. sol. of citric ac., or of an alkali citrate acidified w. acetic ac., gives no ppt. when treated w. a 5% potassium acetate sol. and alc. (dif. fr. tartrate)].—Gives color reac. 314 !
154·5c.	90	**(rac.)-Trioxyglutaric Ac.,** $CO_2H.(CHOH)_3.CO_2H$.—Cryst. fr. acetone v. s. aq. or h. alc.
157	72	**1, 1-Tetramethylenedicarbonic Ac.,** $C_4H_6.(CO_2H)_2$.—Pr. fr. eth. E. s. aq.; s. eth.—Gives Test 303 at 210°.—Ba, Pb, and Ag salts are ppts.
158d.	105	[+ or −] **Talomucic Ac.,** $C_6H_{10}O_8$.—Mic. lft. fr. acetone; e. s. c. aq. or h. alc.—$Ca\bar{A}$ (at 105°), d. s. h. aq.
159d.	54	**Ethenyltricarbonic Ac.,** $(CO_2H)_2.CH.CH_2.CO_2H$.—Pr. e. s. aq., alc., or eth. Test 303 gives CO_2 and succinic ac. (Test 320 !). $Ca_3\bar{A}_2$ and $Zn_3\bar{A}_2$ are more s. in c. than in h. aq.; $Ag_3\bar{A}$ is an amorphous ppt.
d.160	101	**Diacetylsuccinic Ac.,** $CO_2H.CH(MeCO).CH(MeCO).CO_2H$.—Ndl. s. aq. or alc.; d. s. eth.—Heated w. HCl gives carbopyrotritaric ac.
158–9d.	60	**Tartronic Ac.**—See m. p. 185°–7°.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
161d.	65	† **Itaconic Ac., $CH_2{:}C(CO_2H).CH_2.CO_2H$.**—Rhombic octahedra, s. aq. (1 : 2 at 20°); s. alc.; d. s. eth.—Gives Test 304.—Gives red-brown ppt. on boiling w. x's $FeCl_3$.—$Ca\bar{A}\cdot aq.$ s. in 45 pt. aq. at 18°; $Ag_2\bar{A}$ v. d. s. h. aq.—Warmed w. acetylchloride gives anhydride, m. p. 68°.
160–1		**Saccharine.**—Cf. Genus V, Div. A.
161·6c.	132	† **Quinic Ac., $(OH)_4.C_6H_7.CO_2H$.**—Monoclinic pr. s. 2·5 pt. aq. at 9°; less s. alc.; alm. i. eth.—Gives Test 302.—Dry distillation gives phenol, salicylic ac. (Test 319), and benzoic ac. (Test 312).—† Gives pungent odor of quinone on boiling in test-tube w. dil. H_2SO_4 and MnO_2!—Br substitutes.—I and KOH give iodoform (Test 801).—Ca and Pb salts e. s. c. aq.—Occurs in cinchona bark, coffee-beans, etc.
162d.	79	**Teraconic Ac., $Me_2.C{:}C(CO_2H).CH_2.CO_2H$.**—E. s. c. aq., alc., or eth.—Dist. gives aq. and an anhyd. w. b. p. 270°–80°.—$CaCl_2$ gives pulv. ppt. (best on warming).
166	58·7	**Tricarballylic Ac., $CO_2H.CH.(CH_2.CO_2H)_2$.**—E. s. aq. or alc.; d. s. eth.—Sbl. w. dec.—$Ca_3\bar{A}_2.4$ aq., d. s. aq.; $Pb_3\bar{A}_2$ pulv. ppt.—$FeCl_3$ gives floc. ppt.
166–7		**Acetoxyl-α-propionic Ac., $Me.CH(C_2H_3O_2).CO_2H$.**—Ndl. v. s. aq. or alc. After long keeping becomes i. in alc. and does not melt at 300°.—$Ba\bar{A}_2$ v. s. aq.—Boiled w. NaOH gives acetic and lactic ac. salts.
166–7	72	**Methylitaconic Ac., $Me.CH{:}C(CO_2H).CH_2.CO_2H$.**—Pr. s. aq. or eth.—Ba salt cryst. ppt.—Gives Test 304.
166–7	72·7	**Isocamphoronic Ac., $C_9H_{14}O_6$.**—Pr. s. c. aq.; e. s. alc., or eth.—Sbl.—$Ag_3\bar{A}$.—NH_4OH and $BaCl_2$ give no ppt.
167d.	55	**Dicarboxyglutaric Ac., $(CO_2H)_2.CH.CH_2.CH.(CO_2H)_2$.**—V. s. aq., alc.; d. s. eth.—Test 303 gives CO_2 and glutaric ac. (Test 316). Ca, Ba, and Pb salts form ppts.
167·5	164	**Prehnitylic Ac., $Me_3.C_6H_2.CO_2H$.**—Glassy pr. fr. alc. "Somewhat" s. in aq.
168–70	75	† **d-Tartaric Ac., $CO_2H.(CHOH)_2.CO_2H$.**—Monoclinic cryst.—100 pt. aq. dissolve 139 pt. at 20°.—E. s. alc., v. d. s. eth.—Solutions [+]. Apply Tests 302 and 314! $CaCl_2$ gives volum. ppt. from sol. of neutral K or Na salts, but not from solution of the free acid. The ppt. is sol. in mineral and acetic acids, in cold NaOH, and in an excess of alkaline tartrate. From rather dil. sol. it appears slowly and in cryst. form.—$KC_2H_3O_2$ gives a ppt. in tartaric acid sols. (facilitated by diluting with an equal vol. of alcohol). Neutral salts must first be acidified with acetic ac.!—If to an aq. sol. of the acid or a soluble tartrate, 1 drop $FeSO_4$ sol., a few drops H_2O_2 sol. and an x's NaOH be added, a fine deep violet color is immediately produced, which in conc. sols. is so deep as to be nearly black. (Cf. Allen, I, 515.) This color is not given by citric, malic, succinic, or oxalic acids.
169	188	**Naphthol (8)-carbonic Ac., $HO.C_{10}H_6.CO_2H$.**—E. s. aq., alc., or eth.—$Ca\bar{A}_2$ sol. gives w. $FeCl_3$ a violet ppt.
170	72	**trans-Tetramethylenedicarbonic(1, 3) Ac., $C_4H_6.(CO_2H)_2$.**—Sbl. in fine ndl.—S. in 26 pt. aq. at 20°; d. s. eth.—Does not add Br.—Gives an anhyd. w. difficulty, m. p. 50°.
169–71	51·5	† **s-Ethanetetracarbonic Ac., $C_2H_2.(CO_2H)_4$.**—E. s. aq., alc., or eth.—Gives Test 303, yielding CO_2 and succinic ac. (Test 320!). Aq. sol. gives ppt w. $BaCl_2$.
172d.		**Oxalacetic Ac., $CO_2H.CO.CH_2.CO_2H$.**—E. s. aq., alc., or eth.—Gives Test 303. Phenylhydrazine hydrochloride gives 1-phenylpyrazolon (5) carbonic (3) ac.
175	65	**Trimethylenedicarbonic (1, 2) Ac. (fumaroid), $C_3H_4.(CO_2H)_2$.**—Glassy tbl. s. in 5 pt. c. aq.—$Ag_2\bar{A}$ d. s. h. aq.—B. p. (30 mm.) abt. 210°.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
176	79	**Cis-3, 3-Dimethyltrimethylenedicarbonic(1, 2) Ac., $C_7H_{10}O_4$.**—Tbl. rather d. s. c. aq.—Above m. p. gives anhyd., m. p. 56°. Very stable towards $KMnO_4$ and Br.
175d.	226	**d-Mannoheptonic Ac., $C_7H_{14}O_8$.**—S. in 25 pt. c. aq.—Opt. [−].—$Ca\bar{A}_2$ s. h. aq.; $Ba\bar{A}_2$ d. s. c. aq.—Gives Test 302.
175–8		**Glucuronic Anhyd., $C_6H_8O_6$.**—V. s. aq.; i. alc.—Reduces Fehling's sol.—Ac. syrupy and e. s. alc.
177	78	**Diacetylenedicarbonic Ac., $CO_2H.C$ ⋮ $C.C$ ⋮ $C.CO_2H$+aq.**—Tbl. fr. alc.-eth. S. aq.; e. s. alc. or eth.—Turns purplish in light.—Ammon. Cu_2Cl_2 gives a red ppt. at 30°.
178d.	67	**Methyltartronic Ac., $Me.COH.(CO_2H)_2$.**—Rhombic cryst., s. aq.—NH_4 salt ppt'd by boiling $BaCl_2$.—Gives Test 303.
178–9	57	**Acetylenedicarbonic Ac., $CO_2H.C$ ⋮ $C.CO_2H$.**—(Cryst. w. 2 aq.—Cryst. effloresce in air; lose aq. of cryst. over H_2SO_4).—V. s. aq., alc., or eth.—Gives Test 304 easily. Is reduced to succinic ac. (Test 320) by Na amalgam.—Ag. salt v. unstable. $Ba\bar{A}$+aq., d. s. c. aq.
180	80	**s-Methylethylsuccinic Ac. (fumaroid), $CO_2H.CHEt.CHMe.CO_2H$.**—Ndl., 3 pt. s. in 100 pt. aq. at 17°; e. s. eth.; d. s. $CHCl_3$.—A 5% sol. of $Na_2\bar{A}$ gives w. c. $CaCl_2$ no ppt., but w. h. $CaCl_2$ cubical cryst., $Ca\bar{A}$, which disappear again on cooling.
181d.	91	**Oxyphthalic Ac., $C_6H_3.(OH)(CO_2H)_2(4:1:2)$.**—Gives anhyd. on melting.—Rosettes s. in 32 pt. aq. at 10°; s. eth.—Aq. sol. reddish yellow w. $FeCl_3$.—Fuse for a short time w. some resorcine at 200°. Fusion s. in aq. w. greenish fluorescence; KOH turns to dark yellowish red.
183	152	**Oxytoluic Ac., $C_6H_3.(OH)(Me)(CO_2H)(6:1:2)$.**—Ndl. s. c. aq.; v. s. eth.—$FeCl_3$ gives light-brown ppt.—$Ca\bar{A}$, v. s. aq.
184d.	58	**1, 1, 2-Trimethylenetricarbonic Ac., $C_3H_3.(CO_2H)_3$.**—Pr. fr. aq.—Gives Test 303.
185	59	† **Succinic Ac., $CO_2H.CH_2.CH_2.CO_2H$.**—Monoclinic pr., s. in 14·57 pt. aq. at 20°, or in 0·826 pt. at 100°; s. alc.; d. s. eth.; i. $CHCl_3$ or CS_2. Distils at 235° giving anhydride! Burns w. blue smokeless flame.—$CaCl_2$ gives white cryst. ppt. only in conc. sols. of alkaline salts. Ppt. s. in aq., $\bar{A}$c, HCl, or hot NH_4Cl sol.; i. alc.—Although not an α-hydroxy acid, gives a somewhat similar coloration in Test 302.—Apply Test 320!
185	105	**Isosaccharic Ac., $C_6H_{10}O_8$.**—Rhombic cryst., e. s. aq. or alc.; d. s. eth.—Aq. sol. shows birotation.—Dec. on dist.—$Ag_2\bar{A}$, cryst. ppt. which gives silver mirror on warming w. ammonia.
185–7d. (?)	60	**Tartronic Ac., $HO.CH.(CO_2H)_2$.**—(Cryst. w. ½ aq.)—Pr. fr. eth., e. s. aq. or alc.; d. s. eth. when not anhyd.—Sbl. at 110°–120°.—Gives Test 303, yielding glycolid (m. p. 220°).—$Ba\bar{A}$ (at 100°), floc. ppt. changing to lft. v. d. s. h. aq.; $Ag_2\bar{A}$ cryst. ppt. d. s. h. aq.
186–8d.	61·5	**Cyclopentane-tetracarbonic(1, 1, 3, 3) Ac., $C_9H_{10}O_8$.**—Hygroscopic cryst. mass. Gives Test 303.
189d.	58·5	**(β)-3, 4-Dicarboxyl-hexanedioic(1, 6) Ac., $C_8H_{10}O_8$.**—Silky ndl. fr. aq.—100 pt. aq. dis. 27·4 pt. at 19°.—In melting gives an anhyd.—$Ag_4\bar{A}$, amorph. ppt.
189·5	45	† **Oxalic Ac. (Anhydrous), $CO_2H.CO_2H$.**—Octahedra. Takes on water quickly.—S. aq.—For reactions see the hydrated acid on p. 42 of this section!
191d.	58	† **Aconitic Ac., $CO_2H.CH_2.C(CO_2H):CH.CO_2H$.**—Lft. mod. s. c. aq.; v. s. alc.; e. s. eth. (dif. fr. citric ac.).—Sol. boiled w. x's $Ca(OH)_2$ sol. gives no ppt. (dif. fr. citric ac.).—$Ba\bar{A}_2$, s. in 24 pts. aq.; $Ba_3\bar{A}_2$ is ppt.; $Zn_3\bar{A}_2$, i. aq.; $Ag_3\bar{A}$, floc. ppt. fr. $(NH_4)_3\bar{A}$ and $AgNO_3$.—Gives Test 304 (and 901 slowly, hot).—Reduced by Na amalgam to tricarballylic ac.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
192–3d.	66	**Dimethylmalonic Ac., $(CO_2H)_2.C.Me_2$.**—4-sided pr. s. in 10 pt. c. aq.; e. s. eth.—Sbl. in ndl. at abt. 120°.—Gives Test 303, yielding CO_2 and isobutyric ac. (cf. Test 311).
195	87	**Tetramethylsuccinic Ac.**—(Cf. Div. A, Sec. 2.)
198–203d.	58	**Tetramethylenetetracarbonic(1, 1, 2, 2) Ac., $C_4H_4.(CO_2H)_4$.**—V. e. s. aq., alc., or eth. Gives Test 303.
199d.	154	**Protocatechuic Ac., $(OH)_2.C_6H_3.CO_2H$.(3 : 4 : 1).**—(Loses water of cryst. at 100°.)—S. aq.; v. s. alc.; mod. s. eth.—Aqueous sol. + $FeCl_3$ becomes blue-green; on adding Na_2CO_3 changes to dark red!—Pb$\bar{A}$c gives ppt. s. in dil. $\bar{A}$c.—Reduces ammon. $AgNO_3$, but not Fehling's sol.—On distil., or NaOH fusion, gives pyrocatechin and CO_2 (cf. Test 416).
199–200d.	77	**Camphenic Ac., $C_{10}H_{14}O_6$.**—E. s. aq. or eth.—Ba salt, v. e. s. aq.; $Pb_3\bar{A}_2$ (at 100°).
199–200	154	**2, 5-Dioxybenzoic Ac., $(HO)_2.C_6H_3.CO_2H$.**—Ndl. or pr., e. s. aq., alc., or eth.—$FeCl_3$ gives deep-blue coloration! On heating w. $FeCl_3$ sol. gives CO_2 and odor of quinone.—$Ba\bar{A}_2$, v. s. aq.; $Pb\bar{A}_2$, v. d. s. aq.—Reduces ammon. $AgNO_3$ and Fehling's sol. when warmed.—On distil. dec. to CO_2 and hydroquinone.
199–200	76·7	**Camphoic Ac., $C_{10}H_{14}O_6$.**—Cryst. v. s. aq., alc., or eth.—Gives off CO_2 at 300°.—$Pb_3\bar{A}_2$ (at 100°) ppt.; Ba$\bar{A}$ cryst., e. s. aq.
201		**Camphanic Ac., $C_9H_{13}O_2.CO_2H$.**—Sbl. fr. 110°.—S. aq.; e. s. alc. or eth.
abt. 200		† **Tannic Ac., $C_{14}H_{10}O_9$.**—Cf. III, A, 1, m. p. 210°.
202	65	**Mesaconic Ac., Me(CO_2H)C:CH.(CO_2H).**—Ndl. fr. aq. or alc. S. in 37 pt. aq. at 18°; v. s. hot.—Sbl. undec.! Does not give Test 304 easily. Warmed w. acetyl chloride gives citraconic anhyd.—NH_4 salt gives brown floc. ppt. w. $FeCl_3$ (i. h. or in x's of reagent).—Ca and Ba salts mod. s. aq.—Pb$\bar{A}$ and $Ag_2\bar{A}$ ppts.
204	190	**2, 3-Dioxybenzoic Ac., $C_6H_3(OH)_2.CO_2H$.2 aq.**—S. aq.—Gives blue color w. $FeCl_3$, changing to violet w. Na_2CO_3.—Ba and Pb salts v. d. s. aq.—Distil. gives CO_2 and pyrocatechin. (Cf. Test 416.)
205–6	84	† **Racemic Ac., $CO_2H.(CHOH)_2.CO_2H$.**—Triclinic cryst. containing 1 mol. H_2O which effloresce in the air!—Hydrated ac. s. in 4·84 pt. aq. at 20°, or in 48 pt. c. alc.—Gives Tests 302 and 314! Ppts. $CaSO_4$ sol. (unlike tartaric ac.); ppt. s. in dil. HCl and reppt'd at once by NH_4OH (dif. fr. tartaric).—Ba$\bar{A}$, 2½ aq. alm. i. c. aq.—$Ag_2\bar{A}$ less s. than tartrate.
208	152	**5-Oxy-3-toluic Ac., $Me.C_6H_3OH.CO_2H$.**—Tbl. fr. h. aq. "Mod. s. c. aq."—Sbl.—$Pb\bar{A}_2$ cryst. ppt.; $Ca\bar{A}_2$.2 aq., pr. e. s. aq.—Dist. w. CaO gives CO_2 and m-cresol.
209	73	**s-Dimethylsuccinic Ac. (fumaroid), $(CHMe)_2.(CO_2H)_2$.**—Pr. fr. aq.; i. $CHCl_3$.—Acetyl chloride gives anhyd. w. m. p. 43°.
d.210		† **Gallotannic Ac., $C_{14}H_{10}O_9$ (?).**—A light buff-colored powder or scales. Taste very astringent!—S. c. aq.; less s. alc.; i. abs. eth.—1 drop $FeCl_3$ (10% sol.) + 20 cc. aqueous tannin sol. (1 : 5000) gives a color that is deep blue by transmitted light! Gelatine sol. gives immediate white ppt.!—(The last two reactions distinguish from gallic ac.) Alkaline sol. quickly absorbs O and becomes brown! At 210° gives CO_2, pyrogallol, etc.—The salts are amorphous.—Reduces $AgNO_3$ sol. on boiling.
213	79	**trans-3, 3-Dimethyltrimethylenedicarbonic(1, 2) Ac., $C_7H_{10}O_4$.**—Pr. e. s. h. aq.; d. s. eth.; alm. i. $CHCl_3$.—Stable. Heating alone gives no anhyd.
216d.	70	**α-Trimellitic Ac., $C_6H_3.(CO_2H)_3$(1, 2, 4).**—S. h. aq. or eth.—Gives an anhyd. on fusion.—Distil and test distillate for phthalic anhyd. by Test 318–1!—$Ba_3\bar{A}_2$. d. s. aq.—$Ag_3\bar{A}$, ppt. d. s. aq.
218–20d.	65	**1, 1, 3, 3-Hexamethylenetetracarbonic Ac., $C_{10}H_{12}O_8$.**—Pr., s. c. aq.; e. s. h. alc.; d. s. eth.—$Ag_4\bar{A}$ gelat. ppt.—Dec. on melting to CO_2 and dicarbonic acids.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
220	58	**cis-trans-s-1, 2, 3-Trimethylenetricarbonic Ac., $C_3H_3.(CO_2H)_3$.**—S. aq. or alc.—$Ba_3\bar{A}_2$+aq. ppt.; $Ag_3\bar{A}$ ppt.
232	181	**3, 5-Dioxybenzoic Ac., $(HO)_2.C_6H_3.CO_2H.1\frac{1}{2}$ aq.**—Pr. mod. s. c. aq.; e. s. alc. or eth.—Gives no color w. $FeCl_3$ and no ppt. w. Pb$\bar{A}$c.—Fusion w. 8 pts. NaOH gives resorcine (Test 418).—Gives deep-red color on heating at 140° w. 4 pts. conc. H_2SO_4; ppt'd green by aq.
236 (s. h.)	58·5	***α*-3, 4-Dicarboxyl-hexanedioic(1, 6) Ac., $C_8H_{10}O_8$.**—Lft. fr. aq.—100 pt. aq. dissolve 11·8 pt. at 19°; v. s. alc.; d. s. eth.
237d.	63·5	**v-Benzenetetracarbonic Ac., $C_6H_2.(CO_2H)_4$.**—Cryst. w. 2 aq., which it loses above 100°. E. s. aq.—Aq. sol. not easily extracted by eth.—In melting gives an anhyd.—Crystals resemble prehnite.—$Pb_2\bar{A}$, i. aq.; $Me_4\bar{A}$, m. p. 104°–8°; $Me_2\bar{A}$, m. p. 176°–7°.—Aq. sol. of acid gives a cryst. ppt. $Ba\bar{A}_2+H_2O$ when warmed w. $BaCl_2$ sol. (Dif. fr. 1, 2, 3, 5 acid.)
238d.	63·5	***α*-1, 2, 3, 5-Benzenetetracarbonic Ac., $C_6H_2.(CO_2H)_4$.**—E. s. aq.—Conc. HCl ppt's fr. aq. sol. in short ndl. On melting forms an anhydride.—Gives floc. ppt. w. $Pb\bar{A}c_2$; floc. pp. w. $Ca\bar{A}c_2$ on heating; floc. ppt. w. BaO_2H_2, but none w. $BaCl_2$.
264d.	63·5	**s-Benzenetetracarbonic Ac., (Pyromellitic Ac.), $C_6H_2.(CO_2H)_4$.**—In melting gives an anhydride.—Triclinic tbl., 100 pt. aq. dissolve 14·2 pt. at 16°; e. s. alc.—Sbl. giving anhyd. m. p. 286°.—Ca, Pb, and Ag salts are ppts.—$Me_4\bar{A}$, m. p. 138°.
286–8	57	**Mellitic Ac., $C_6.(CO_2H)_6$.**—Fine silky ndl., v. e. s. aq.; e. s. alc.
345–50	70	**(s)-1, 3, 5-Trimesic Ac., $C_6H_3.(CO_2H)_3$.**—Pr. fr aq.—"Moderately" s. c. aq.; v. s. alc.—Sbl. below 300°—$Ba_3\bar{A}_2$·aq., lustrous ndl., alm. i. c. aq.; v. d. s. h. aq.; $Zn_3\bar{A}_2$ pr. alm. i. c. aq.; $Ag_3\bar{A}$, volum. ppt.—$Me_3\bar{A}$, m. p. 143°.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I].

GENUS III, ACIDS.

DIVISION A, SECTION 2,—SOLID ACIDS NOT SOLUBLE IN COLD WATER.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
14	282	† **Oleic Ac., $C_{18}H_{34}O_2$.**—B. p. 232° (20 mm.).—G. $0{\cdot}8908^{11\cdot8}/_4$.—Gives Tests 304 and 901! Absorbs O from the air.—Fused in a test-tube w. x's of moist KOH in a bath the temperature of which is gradually raised from 300°–320°, is converted almost quantitatively into potassium palmitate, acetate, and H.—Dilute one volume of the nitrosyl-sulphuric ac. reagent described on p. 13 with one vol. of aq., and shake the mixture in a test-tube with an equal volume of the oily acid, keeping it well cooled with running tap-water. Set the tube aside in a beaker containing cold water for 15 minutes. A solid mass of elaidic ac. (m. p. after purification 51°–2°) soon separates.
16–7	298	**Ricinoleic Ac., $C_{18}H_{34}O_3$.**—B. p. 250° (15 mm.).—Gives Tests 304 and 901.—Treatment w. nitrosyl-sulphuric acid, as described under oleic ac , gives ricinelaïdic ac., m. p. 50°.—Polymerizes easily.
19·4	166	**Ethylethersalicylic Ac., $EtO.C_6H_4.CO_2H$.**—D. s. c., e. s. h. aq.—$Ba\bar{A}_2$ v. s. aq.
21–3	181	**Umbellulic Ac., $C_{11}H_{22}O_2$.**—Cryst.—B. p. 275°–80° c.—(An ac. fr. fat of Californian Laurel.)
24·4	114	**2-Methylpenten(2)-oic(1) Ac., $C_6H_{10}O_2$.**—B. p. 213° c.—V. d. s. aq.; e. s. eth.—Gives Test 304.—Is volat. w. steam.—$Ag\bar{A}$, ndl. or lft. fr. h. aq.
24·5	184	† **Undecylenic Ac., $Me.C_2H_2.C_7H_{14}.CO_2H$.**— B. p. 165° (15 mm.).—(From distil. of castor-oil i. v.)—G. $0{\cdot}9072\,^{24}/_4$.—$Ba\bar{A}_2$. ndl. or lft. s. in 1073 pt. aq. at 15·5°.—Fuming HNO_3 oxid. to sebacic ac.—Gives Tests 304 and 901!
26	344	**Anacardic Ac., $C_{22}H_{32}O_3$.**—(From Anacardium occidentale.) I. aq.; e. s. alc or eth.—$Ag\bar{A}$ (at 100°) ppt. fr. alc. sol. by $AgNO_3$.
26–7	256	**Diheptylacetic Ac., $CH(C_7H_{15})_2.COOH$.**—Cryst., alm. i. aq.; v. e. s. alc., eth., or bz.—$Ba\bar{A}_2$, fine ndl. fr. alc.; i. aq.
28·5	186	**Undecylic Ac., $C_{11}H_{22}O_2$.**—Scaly cryst. mass.—B. p. 212·5° (100 mm.).—Feeble odor like caproic ac.—$Ba\bar{A}_2$, v. d. s.; $Ag\bar{A}$, i. aq.
29		**Triethyl Methanetricarbonate, $HC.(CO_2Et)_3$.**—B. p. 253°.—Ndl. or pr.—"Is saponified at 0° by KOH to alcohol, CO_2, and malonic ac."! S. in $NaCO_3$ sol.
30		**Acetylperoxide, $(Me.CO)_2.O_2$.**—Flat cryst. w. odor like ozone. "Somewhat" s. aq.—Extremely explosive.—NaOH gives $\bar{A}c$. and sodium peroxide.
30	128	**Hexahydrobenzoic Ac., $C_6H_{11}.CO_2H$.**—B. p. 233°.—D. s. aq.; v. s. alc. or eth.—$Zn\bar{A}_2$ much more s. in c. than in h. aq.—Volat. w. steam.
31	176	**Cinnamenylpropionic Ac., $Ph.CH_2.CH{:}CH.CH_2.CO_2H$.** — Tbl. fr. lgr. —Gives Test 304.—$Ba\bar{A}_2$, d. s. aq.; $Ag\bar{A}$ ppt.
31·3	172	† **Capric Ac., $Me.(CH_2)_8.CO_2H$.**—B. p. 268·4° c.—Feeble odor like perspiration.—Alm. i. c. aq.; v. d. s. h. aq.—Alkali salts alone soluble.—$Ba\bar{A}_2$, lft. fr. h. aq.—G. 0·93 at 37°.

Melting-point (C.°).	Neut. Equiv.	SOLID ACIDS.—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
33	254	**Hypogæic Ac., $C_{16}H_{30}O_2$.**—Ndl. e. s. alc.—B. p. 236° (15 mm.).—Oxidizes in air.—Nitrous acid (cf. oleic ac.) gives gaïdic ac., m. p. 39°. Gives Test 304.
33	114	**Hexen-2-oic-(1) Ac., $C_6H_{10}O_2$.**—Ndl. d. s. aq.—Adds Br_2 in CS_2 sol. (Test 304).—$Ba\bar{A}_2 + 1\frac{1}{2}$ aq., lft.; e. s. alc.; $Ag\bar{A}$, ndl. fr. aq.
33·4	338	† **Erucic Ac., $C_{21}H_{41}.CO_2H$.**—Long ndl. fr. alc. B. p. 264° (15 mm.). Gives Test 304!—Heated to fusion w. dil. HNO_3 and treated w. $NaNO_2$ gives geomet. isomer, brassidic ac., which after cryst. fr. alc. melts at 60°.—$Pb\bar{A}_2$, e. s. h. ctn. or h. bz.
33–4	136	**p-Methylenedihydrobenzoic Ac., $CH_2:C_6H_5.CO_2H$.**—Ndl. fr. lgr. S. h. aq.; e. s. alc. or eth. Gives Test 304.—$Ag\bar{A}$ silky ndl.
34	270	**Oxyhypogæic Ac., $C_{16}H_{30}O_3$.**—White mass.—Boiling alkalies give dioxypalmitic Ac.
36–7	127	**o-Toluic Anhyd., $(Me.C_6H_4.CO)_2.O$.**—B. p. a. 325°.—Cryst. fr. eth. or bz.—Test 307 gives ac. w. m. p. 102°, v. d. s. c. aq.!
37	164	**α-Methylhydrocinnamic Ac., $Ph.CH_2.CHMe.CO_2H$.**—B. p. 272°. Lft. v. d. s. c. aq.—$Ag\bar{A}$, cryst. ppt.
40·5	214	**Tridecylic Ac., $Me.(CH_2)_{11}.CO_2H$.**
41·5	114	**α-Ethylcrotonic Ac.—$C_6H_{10}O_2$.**—Cryst.—Sbl.—D. s. aq.—Fusion w. KOH gives acetic and butyric acids. (Test 311.)
42	164	**Ethylphenylacetic Ac., $Ph.CHEt.CO_2H$.**
42	113	† **Benzoic Anhyd., $(C_7H_5O)_2O$.**—B. p. 360° c.—Rhomb. pr. i. and very slowly attacked by c. aq.; s. alc. or eth. For behavior on titration cf. p. 37. Test 307 gives ac. (cf. Test 312) w. m. p. 121°, nearly i. c. aq.!
43–4	166	**o-Oxyphenylglyoxylic Ac., $HO.C_6H_4.CO.CO_2H$.**—Ndl. Dec. on dist. to CO_2 and salicylic ac. (Test 319).
43·6	200	† **Lauric Ac., $C_{11}H_{23}.CO_2H$.**—Ndl. fr. alc.—Dec. by dist. under normal pressure.—Non-alkali salts all v. d. s. h. aq.—$Ba\bar{A}_2$, pearly lft.
44	240	**Cimicic Ac., $C_{15}H_{28}O_2$.**—Pr. fr. eth.—$Ba\bar{A}_2$. amorph. ppt.—Unsat. (Test 304).
44–5	282	**Isooleic Ac., $C_{15}H_{31}.CH:HC.CO_2H$.**—Rhomb. plates fr. eth.—E. s. alc.; less s. eth.—$Zn\bar{A}_2$ cryst. fr. h. alc. (sep. fr. oleate). $Pb\bar{A}_2$ less s. in eth. than Pb oleate.—Occurs in some commercial "stearic ac."
45·5	100	**Angelic Ac., $Me.CH.MeC.CO_2H$.**—B. p. 185° (th. i.). Long-continued boiling gives isomeric tiglic ac., m. p. 64·5°.—Pr. d. s. c. aq ; e. s. h. aq. -Spicy odor. —$Ca\bar{A}_2 + 2$ aq. alm. i. alc.; s. c. aq.; much less s. at 60°–70°.—$Ba\bar{A}_2 + 4\frac{1}{2}$ aq., e. s. aq.—$Pb\bar{A}_2$ d. s. aq.—Fusion w. KOH gives acetic and propionic acids (Test 311).
46	368	**Paraffinic Ac., $C_{24}H_{48}O_2$.**—Lft. fr. alc.—(Fr. action of fuming HNO_3 on paraffin.)
46–7	200	**Diisoamylacetic Ac., $(C_5H_{11})_2.CH.CO_2H$.**—Ndl. i. aq.; e. s. eth., alc. or bz.
47	150	**m-Ethylbenzoic Ac., $Et.C_6H_4.CO_2H$.**—Ndl. fr. h. aq., alm. i. c. aq.—$Ca\bar{A}_2$ e. s. aq. or alc.—Test 905–1 gives isophthalic ac.
47	252	**Palmitolic Ac., $C_{16}H_{28}O_2$.**—B. p. 240° (15 mm.). Silky ndl.; i. aq.; v. s. alc. or eth.—Fuming HNO_3 oxid. violently.—$Ba\bar{A}_2$, cryst. fr. h. alc.; i. aq.—$Ag\bar{A}$, ppt., blackens in light.—Gives Test 304.
47·5	164	**Benzylpropionic Ac., $Ph.(CH_2)_3.CO_2H$.**—Flat lft. fr. h. aq.; e. s. alc. or eth.—B. p. abt. 290°.—$Ca\bar{A}_2$, v. s. aq.; $Ba\bar{A}_2$, lft., s. aq.
48	280	**Stearolic Ac., $C_{18}H_{32}O_2$.**—Long pr. fr. alc.—D. s. c. alc.; e. s. h.—Distils w. little dec.—Gives Test 304.—Oxid. by fuming HNO_3.—$Ba\bar{A}_2$, ppt. fr. aq.; s. h. alc.
48·5	156	**Diallyloxalic Ac., $HO.C(C_3H_5)_2.CO_2H$.**—Ndl. "rather d." s. aq.; e. s. alc. or eth.—Gives Test 304.—Dec. on distil.—Ca and Ba salts, e. s. c. aq.

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
48·7	150	**Hydrocinnamic Ac., $Ph.CH_2.CH_2.CO_2H$.**—B. p. 279·8° (th. i.).—Ndl. fr. alc. or h. aq.; s. in 168 pt. aq. at 20°.—$Ba\bar{A}_2$, mod. s. ndl.—Boiling with CrO_3 mixture (cf. Test 702) gives benzoic ac. (cf. Test 312).
50	298	**Ricinelaïdic Ac., $C_{18}H_{34}O_3$.**—Ndl.—Oxid. by HNO_3 gives œnanthic ac.
50	310	**Eikosenic Ac., $C_{20}H_{38}O_2$.**—B. p. 267° (15 mm.) (th. i.).—Gives Test 304.—$Ba\bar{A}_2$. Cryst. fr. alc.
51	242	**Pentadecylic Ac., $C_{15}H_{30}O_2$.**—Dec. on distil.—Pearly scales.
51	244	**Oxymyristic Ac., $C_{14}H_{28}O_3$.**—Pearly lft., e. s. alc.—Dec. on distil.—Ca and Ba salts, ppts., d. s. h. aq.
51	164	**o-Isopropylbenzoic Ac., $Pr.C_6H_4.CO_2H$.**—Pr. s. h. aq.—Ba salt v. s. aq.—Test 905 gives phthalic ac. (cf. Test 318–1).
51	296	**Ricinostearolic Ac., $C_{18}H_{32}O_3$.**—Ndl. fr. alc.—I. aq.; e. s. alc. or eth. Gives Test 304. Volatile w. very slight dec.—$Ba\bar{A}_2$ lft. fr. alc.; i. eth.—$Ag\bar{A}$ gran. ppt.; i. eth.
51	258	**Oxypentadecylic Ac., $C_{15}H_{30}O_3$.**—Ndl. fr. dil. alc. (From convolvulin.)
51·5	282	† **Elaïdic Ac., $HC.(C_{14}H_{29})$: $HC.CH_2.CO_2H$.**—Lft. fr. alc.—Solidifies at 44°–45°.—B. p. 234° (15 mm.).—$Ba\bar{A}_2$, $Pb\bar{A}_2$ are ppts.—(Geom. isomer of oleic ac.)
52	178	**1-Methoethylphenethanoic(4) Ac., $Me_2.CH.C_6H_4.CH_2.CO_2H$.**—Ndl. fr. h. aq.—V. s. alc. or eth.—$Ca\bar{A}_2$ heated w. CaO gives cymene.
53	168	**β-Campholenic Ac., $C_{10}H_{16}O_2$.**—B. p. 247°.—Gives Test 304.—I. aq.; v. s. alc. or bz.—$Ca\bar{A}_2$, ndl., e. s. alc.; d. s. aq.
53·8	228	† **Myristic Ac., $C_{14}H_{28}O_2$.**—Lft. d. s. c. alc. or eth.—B. p. 196·5° (15 mm.).—$Ba\bar{A}_2$ cryst. powder; v. d. s. alc. or aq.; $Pb\bar{A}_2$, amorph. powder.
54–6	338	**Isoerucic Ac., $C_{22}H_{42}O_2$.**—Tbl. fr. alc.; rather d. s. alc. or eth.—Adds Br_2 in glacial $\bar{A}c$. sol. (Test 304.)
54·5	270	**Daturic Ac., $C_{17}H_{34}O_2$.**—Small ndl. fr. alc.; i. aq.—$Pb\bar{A}_2$, m. p. 104°–5°.
56–7	49	**Maleic Anhyd., $C_4H_2O_3$.**—Cryst. melt under h. aq., gradually giving maleic ac.—Ac. obtained by Test 307, v. s. aq., m. p. 130°.
56–7	57	**Glutaric Anhyd., $C_5H_6O_3$.**—B. p. 287° c.—Ndl. d. s. h. eth.—Acid obtained by Test 307, s. aq.; m. p. 97·5°.
57	148	**Isocinnamic Ac., HCPh : $HC.CO_2H$.**—Monoclinic pr. fr. lgr.—V. s. alc., eth., or lgr.—Gives Test 304.—On continued boiling gives cinnamic ac. (Test 313) and styrene.—$Ca\bar{A}_2$, s. in 8 pt. aq.
57·5	336	**Behenolic Ac., $C_{22}H_{40}O_2$.**—Ndl. e. s. abs. alc.—Gives Test 304.—Zn. dust and acetic ac. reduces to brassidic ac.—$Ba\bar{A}_2$ ppt. i. aq. and alc.
58	164	**o-Propylbenzoic Ac., $Pr.C_6H_4.CO_2H$.**—Lft. fr. dil. alc.—Test 905 gives phthalic ac.
58–9	178	**δ-Phenylvalerianic Ac., $Ph.(CH_2)_4.CO_2H$.**—Lft. fr. h. aq., e. s. alc.—Ba salt d. s. aq.
59·5	182	**Undecolic Ac., $C_{11}H_{18}O_2$.**—Lft. e. s. alc.—$Ba\bar{A}_2$ v. d. s. c. aq.—B. p. 177° (15 mm.). Gives Test 304.
59·9	270	**Margaric Ac., $C_{17}H_{34}O_2$.**—Cryst.
60 or 65	146	**α-Oxyœnanthylic Ac., $Me.(CH_2)_4.CHOH.CO_2H$.**—D. s. c. aq.—Sbl.
60	338	**Brassidic Ac., $C_{22}H_{42}O_2$.**—Lft. fr. alc.—B. p. 160° (0 mm.) —V. d. s. c. alc.—Less s. in alc. or eth. than erucic ac.—$Pb\bar{A}_2$ v. d. s. h. eth.—KOH fusion gives arachidic ac., m. p. 77°.—Gives Test 304.
61	150	**m-Tolyacetic Ac., $Me.C_6H_4.CH_2.CO_2H$.**—Ndl. e. s. h. aq.—$Ag\bar{A}$, ndl. fr. h. aq.—Amide, m. p. 141°
62·6c	256	† **Palmitic Ac., $Me.(CH_2)_{14}.CO_2H$.**—Ndl. or greasy feeling scales, s. in 10·7 pt. alc. at 20°; e. s. h. alc.—B. p. 339°–56° d.—G $0{\cdot}8527\ ^{62°}/_{4°}$.—**Nearly odorless and tasteless. Nearly or quite neutral to indicators** ***except in alc. sol.***

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
64	330	**Dioxyricinoleic Ac., $C_{18}H_{34}O_5$.**—I. aq.; v. e. s. alc. or eth.—Gives Test 304.
64·5	100	**Tiglic Ac., Me.CH:CMe.CO_2H.**—Gives Test 304; and 901 (*slowly hot*).—Cf. Div. A, Sec. 1.
65	162	(*αβ*)-**Phenylcrotonic Ac., $Ph.CH_2.CH : CH.CO_2H$.**—Ndl fr. h. aq., e. s. alc., eth., and bz.—Gives Test 304.—$Ca\bar{A}_2+3H_2O$ silky ndl.
66·5	298	**Nondecylic Ac., $C_{19}H_{38}O_2$.**—$Ca\bar{A}_2$, cryst. ppt.
67	284	**Palmitoxylic Ac., $C_{16}H_{28}O_4$.**—I. aq.; e. s. abs. alc. or eth.—$Ag\bar{A}$ gran. ppt. fr. alc.
68	56	**Itaconic Anhyd., $C_5H_4O_3$.**—Dist. *in vacuo* gives citraconic anhyd., m. p. 7.°—Rhomb. pr. fr. $CHCl_3$; v. d. s. eth.—Unites rather easily w. aq to form its acid (cf. Test 307).
68	150	**o-Ethylbenzoic Ac., $Et.C_6H_4.CO_2H$.**—Lustrous flat ndl.—Test 905 gives phthalic ac. (cf. Test 318–1).
68	148	**Allocinnamic Ac., HCPh : $HC.CO_2H$.**—Pr. or tbl. fr. lgr.—Aniline salt ppt'd fr. bz. solution by aniline, m. p. 83° (Dif. fr. hydrocinnamic ac.)—Less s. c. lgr. than isocinnamic ac —Gives Test 304.
69	308	**Eikosinic Ac., $C_{20}H_{36}O_2$.**—I. aq.—B p. 270° (15 mm.).
69·5	160	*α*-**Oxycaprylic Ac., $Me.(CH_2)_5.CHOH.CO_2H$.**—Large plates, v. d. s. aq.; e. s alc. or eth.—CrO_3 mixture oxid. to œnanthol and œnanthic ac.—Salts generally d. s.
69·3c.	284	† **Stearic Ac., $Me.(CH_2)_{16}.CO_2H$.**—Odorless, tasteless lft.—Distils w. dec. at abt. 360°.—I. aq.; s. 40 pt. c. alc.; e s. c eth., bz., CS_2, or $CHCl_3$.—Does not dissolve on shaking w c Na_2CO_3 or decinormal KOH.—$CaCl_2$ and $BaCl_2$ give gelat. ppt. w solutions of alkali salts.
70	144	**Monoethyl Fumarate, $CO_2H.C_2H_2.CO_2Et$.**—D s. aq.; e s. alc. or eth. Gives Test 304.—Saponify and identify the fumaric ac.
71–2	180	**3-Methtoethylphenol(2)-methanoic(1) Ac., $C_{10}H_{12}O_3$.**—Ndl. fr. aq.—V. d. s. aq.; e s. alc. or eth.—Volat. w. steam.—Aq. sol. intense violet-blue w. $FeCl_3$!—$Ag\bar{A}$ mic. ndl. d. s. aq.
72	166	**Methoxyphenylacetic Ac., Ph.CH(OMe).CO_2H.**—Tbl. fr lgr D. s. aq. or c. lgr.; e. s. alc. or eth.—$Ca\bar{A}_2$, ppt., rather d. s. c. aq.
72·5		**Carnaubic Ac., $C_{24}H_{48}O_2$.**—(Combined in Carnauba wax.)—E. s alc. or eth.—$Pb\bar{A}_2$ (103°), ppt. m. p. 110°-1°; i. eth.
73	142	*γ*-**Ethoxy-Δ'-tetrahydrobenzoic Ac., $EtO.C_6H_8.CO_2H$.**—E s alc.—Gives Test 304.—$Ag\bar{A}$, ppt.
74	162	*α*-**Benzalpropionic Ac., Ph.CH : CMe.CO_2H.**—B. p. 288° Cryst. e s alc., eth., or bz.—Gives Test 304.—$Ba\bar{A}_2$, d s c aq
75	180	**Phenyl-1'-oxybutyric Ac., $Ph.CHOH.(CH_2)_2.CO_2H$.**—Pr. fr. c $CHCl_3$.—S. h. aq.; v. e s. alc., eth., or $CHCl_3$.—Aq.+HCl at 80° gives anhyd., m. p. 37°.—$Ba\bar{A}_2$, v s aq.; $Ag\bar{A}$, ppt, i aq.
75	296	**Dioctylmalonic Ac., $C_{19}H_{36}O_4$.**—Cryst. fr bz —$Ca\bar{A}$, d. s. aq.—Gives Test 303
75–6	208	*α*-**Hydropiperic Ac., $C_{11}H_{12}O_4$.**—Ndl. fr h. aq.—V. d. s c aq.; e s alc or eth.—$KMnO_4$ oxid. to piperonal (odor like heliotrope!), etc. Gives Test 304 —$Ag\bar{A}$ cryst. ppt
75–6	178	**1-Methyl-3-propylbenzoic(4) Ac., $(Me)(Pr).C_6H_3.CO_2H$.**—Ndl fr. aq.—Volat. w steam.—Ba and Ca salts v s aq. or alc.
75–7	214	**Lanolic Ac., $C_{12}H_{22}O_3$.**—Cryst powder —I. aq. or lgr —$Ba\bar{A}_2$ + aq. ppt.
76·5	136	† **Phenylacetic Ac., $Ph.CH_2.CO_2H$.**—B. p 265·5° c —Thin lft e s. h. aq.; d. s c aq.; v s. alc. or eth.—$Ba\bar{A}_2+3H_2O$, e s aq or alc. $BaCl_2$ gives no ppt Warming w dil. H_2SO_4 and MnO_2 gives benzaldehyde (bitter almond odor, Test 113).
77	312	**Arachidic Ac., $C_{20}H_{40}O_2$.**—Lustrous lft., s in 222 pt 90% alc. at 20°. (Less s. than stearic ac.)—Salts resemble stearates.—Occurs in peanut-oil, etc.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
77–8	382	**Hyænic Ac., $C_{25}H_{50}O_2$.**—Cryst. grains.
78	396	**Cerotic Ac., $C_{26}H_{52}O_2$.**—(In beeswax.)—Tasteless and usually granular.—Alm. i. c. alc. (dif. fr. stearic and palmitic ac.).—Stellate mic. ndl. fr. h. alc.—S. bz. or eth.—Does not dissolve in h. dil. NaOH.
78	312	**Ricinstearoxylic Ac., $C_{18}H_{32}O_4$.**—Ndl. e. s. alc. or eth.—Gives Test 304.—Ba$\bar{A}_2$, volum. ppt.; Ag$\bar{A}$, gran. ppt.
78–80		**Pinoylformic Ac., $C_{10}H_{14}O_5$.**—Lft. fr. h. aq.; v. s. h. aq.; e. s. eth.—Gives soluble $KHSO_3$ compound.
80	176	**γ-Methylhydrinden-β-Carbonic Ac., $C_{11}H_{12}O_2$.**—B. p. 300°–30°.—S. h. aq.; e. s. alc.—Ba$\bar{A}_2$ + 4 aq., ndl., v. s. aq.
80–1	194	**o-Ethylethermelilotic Ac., o-EtO.C_6H_4.C_2H_4.CO_2H.**—Silky ndl. fr. aq.; v. d. s. c., d. s. h. aq.; e. s. alc. or eth.—Ba salt, e. s. aq. turns red at 100°.
80·5	368	**Lignoceric Ac., $C_{24}H_{48}O_2$.**—D. s. c. alc.; e. s. eth., bz., or CS_2.—Pearly lustre.
82	162	**α-Benzalpropionic Ac., Ph.CH : CMe.CO_2H.**—Repeated recryst. gives ac., m. p. 74°. Gives Test 304.
82·5		**Mono-methyl Phthalate, $C_9H_8O_4$.** Examine saponification products.
82–3	272	**α-Oxypalmitic Ac., $C_{14}H_{29}$.CHOH.CO_2H.**—Scales fr. alc.; e. s. alc.
83	106	**Monoethyl Carbopyrotritarate, $C_8H_7O_5$.Et.**—D. s. h. aq.—Lft. e. s. eth.; e. s. alc. Distil. undec.—Ag$\bar{A}$ ppt.
83–5	300	**β-Oxystearic Ac., $C_{18}H_{36}O_3$.**—6-sided tbl. fr. alc. S. in 10·4 pt. alc. at 20°.
84	340	**Behenic Ac., $C_{22}H_{44}O_2$.**—Solidifies at 78°.
84–5	300	**α-Oxystearic Ac., $C_{18}H_{36}O_3$.**—6-sided tbl. fr. eth. S. in 172 pt. alc. at 20°.
84–5	314	**Ketostearic Ac., $C_{18}H_{34}O_4$.**—Silky cryst. fr. dil. alc.—Ag$\bar{A}$, cryst. ppt.
85	176	**Ac.-Tetrahydro-α-Naphthoic Ac., $C_{10}H_{11}$.CO_2H.**—Pr. fr. acetic ether. S. in 1052 pt. c. aq.; v. s. alc.—$KMnO_4 + Na_2CO_3$ sol. decolorizes after 2 min.—Ag$\bar{A}$ ppt.
85–6	218	**Dioxyundecylic Ac., $C_{11}H_{22}O_4$.**—Ndl. fr. aq.; e. s. h. aq. or alc.; d. s. eth.
86	312	**Stearoxylic Ac., $C_{18}H_{32}O_4$.**—Lft. d. s. c. alc.; e. s. h. alc.—Ba$\bar{A}$, semi-solid ppt., i. alc.; Ag$\bar{A}$ cryst. powder.
86	162	**β-Benzalpropionic Ac., Ph.CH : CH.CH_2.CO_2H.**—B. p. 302° (long-continued boiling gives H_2O and α-naphthol, Test 402).—Ndl. fr. h. aq.; d. s. h. aq.: e. s. alc., eth., or CS_2.—Ca$\bar{A}_2$ v. s. aq.
86–7	204	**Monomethyl Camphorate, CO_2H.C_8H_{14}.CO_2M.**—Long ndl. fr. h. aq.; e. s. alc. or eth.— Saponify and test distillate for methyl alcohol by Test 819.
87	56	**Glutaconic Anhyd., $C_5H_4O_3$.**—Ndl. fr. eth., s. in Na_2CO_3 w. effervescence, giving sodium glutaconate (m. p. of acid 138°).
87	240	**Dibenzylacetic Ac., $(Ph.CH_2)_2$.CH.CO_2H.**—Pr. fr. lgr.; i. aq.; s eth.—Ba$\bar{A}_2$ ndl. d. s. h. aq.—Heated w. CaO gives dibenzylmethane.
87	64	**s-Dimethylsuccinic Anhyd. (α), $C_6H_8O_3$.**—B. p. 235°.—S. h. aq. giving s.-fumaroid acid, m. p. 124°, and a little less s.-anti acid, m. p. 195°.
87–8	272	**Lanopalmitic Ac., $C_{16}H_{32}O_3$.**—(In combination in wool grease.)—I. in aqueous KOH, s. in alc.
88–9	178	**(α) o-Methoxycinnamic Ac., MeO.C_6H_4.CH : CH.CO_2H.**—E. s. alc.—Heat gives isomeric (β) ac., m. p. 182°–3°.—Gives Test 304.
88–9	150	**o-Tolylacetic Ac., Me.C_6H_4.CH_2.CO_2H.**—Silky ndl., e. s. h. aq.—Amide m. p. 161°.—Oxid. to phthalic ac. by $KMnO_4$ (cf. Tests 905–1 and 318).
89	282	**Dibenzylacetoacetic Ac., $C_{18}H_{18}O_3$.**
90	452	**Melissic Ac., $C_{30}H_{60}O_2$.**—Silky scales (fr. beeswax).—E. s. $CHCl_3$, CS_2, and h. alc.; alm. i. c. alc. or eth.—Pb$\bar{A}_2$, amorph. ppt.; may be cryst. fr. toluene.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
91	150	**p-Tolylacetic Ac., $Me.C_6H_4.CH_2.CO_2H$.**—B. p. 266°.—Ndl., d. s. c. aq.; e. s. h.—AgĀ ndl., e. s. h. aq.—Amide, lft. fr. h. aq.; m. p. 184°!
91	174	**α-Dihydronaphthoic Ac. (labile), $C_{11}H_{10}O_2$.**—Tbl. fr. lgr.; s. in 552 pt. c. aq.; e. s. alc. or eth.—Gives Test 304.—Boiling w. dil. NaOH gives stable form, m. p. 125°.
91–2	328	**Eikosanol(2)-oic Ac., $C_{20}H_{40}O_3$.**—Silky lft. fr. bz.+lgr.; e. s. alc.—$Ba\bar{A}_2$ (at 100°) floc. ppt.
91–2	178	**Tolylisobutyric Ac., $C_7H_7.CH_2.CHMe.CO_2H$.**—Ndl. fr. lgr.—AgĀ, ppt. v. d. s. aq.
92	180	**Methylethermelilotic Ac., o-$MeO.C_6H_4.C_2H_4.CO_2H$.**—Pr. fr. h. lgr.—D. s. h. aq.
92–3	466	**Coceric Ac., $C_{31}H_{62}O_3$.**—Cryst. powd. fr. h. alc.
93	226	**o-Benzoylbenzoic Ac., $Ph.CO.C_6H_4.CO_2H$.**—Triclin. ndl. (+aq.) fr. h. aq.—Ignited w. Zn dust gives anthracene (Test 912).—Oxime melts at 162°.
94	250	**Alantolic Ac., $HO.C_{14}H_{20}.CO_2H$.**—Ndl. d. s. c. aq.; e. s. alc. or eth.—Loses aq. on fusion giving anhyd., helenine, m. p. 76°.
94	176	**β-Tetrahydronaphthoic Ac., $C_{10}H_{11}.CO_2H$.**—Ndl. fr. dil. alc.; i. c. aq.—Adds Br_2 in the cold, but is not immediately oxid. by Na_2CO_3+$KMnO_4$.
94	180	**4-Methoethylphenol(2)-methanoic(1) Ac., $Me_2.CH.C_6H_3OH.CO_2H$.**—Lft. fr. aq., v. d. s. c. aq.; s. h. aq.; v. s. alc. or eth.—Red-violet color w. $FeCl_3$.—Distil. gives CO_2 and m-propylphenol.—$Ba\bar{A}_2$ d. s. aq.
95–7	164	**p-Toluylcarbonic Ac., $Me.C_6H_4.CO.CO_2H$.**—I. c. aq.; e. s. alc. or eth.—Unstable.—Conc. H_2SO_4+bz gives deep-red sol. changing to blue-violet; red ppt. on dilution.—Oxid. by $KMnO_4$.
95·5	240	**Benzyl-o-tolylacetic Ac., $(C_7H_7)_2.CH.CO_2H$.**—Large cryst. fr. alc.
96	97	**3, 6-Dimethylphthalic(1, 2) Ac., $Me_2.C_6H_2.(CO_2H)_2$.** — Pr. e. s. eth. or alc. "Moderately" s. aq.
96·5	468	**Oxymelissic Ac., $C_{30}H_{60}O_3$.**—Fine ndl. fr. bz.
96–7	356	**α-Oxybehenic Ac., $C_{22}H_{44}O_3$.**—E. s. high-boiling petroleum ether.
97–9	150	**1, 3-Dimethylbenzoic(2) Ac., $Me_2.C_6H_3.CO_2H$.**—Ndl. fr. h. aq.
97	166	**Alorcinic Ac., $C_9H_{10}O_3$.+H_2O** (air-dried).—Ndl. d. s. c. aq.; e. s. alc. or eth. Alkaline sol. becomes cherry-red on standing in air! Reduces Fehling's sol.—Fusion w. 3 pt. KOH gives orcine. Dried over H_2SO_4 melts at 115°.
98	154	**Methyluvinic Ac., $C_7H_9O.CO_2H$.**—Ndl. d. s. aq.; e. s. alc. or eth.—$Ca\bar{A}_2$+4 aq., pearly lft. i. alc.—Boiled w. conc. KOH gives potassium acetate (Test 311).
98–9	206	**Benzyllævulinic Ac., $C_{12}H_{14}O_3$.**—B. p. 230°–35° (40 mm.). Ndl. fr. dil. alc., v. d. s. aq.—Dec. on dist.—H_2SO_4 sol. yellow, but after 1 or 2 days blue-green.—Dibrom. derivative fr. Br in Āc., m. p. 153° d.
98–9	372	**Isodioxybehenic Ac., $C_{22}H_{44}O_4$.**—Tbl. fr. alc., d. s. c. alc. or eth.—AgĀ ppt.
98–9	184	**[−] Pinonic Ac., $C_{10}H_{16}O_3$.**—B. p. (12 mm.), 178°–80°.
98·5	152	**Methylethersalicylic Ac., o-$MeO.C_6H_4.CO_2H$.**—Tbl. or pr. s. in 200 pt. aq. at 30°.—$Ba\bar{A}_2$, v. e. s. aq.—Dec. a. 200° to CO_2 and anisol.
99	164	**s-Dimethylphenylacetic Ac., $Me_2.C_6H_3.CH_2.CO_2H$.**—B. p. 274°.—Mod. s. h. aq.—$Ca\bar{A}_2$+3 aq., e. s. aq.
99	176	**Benzoylacrylic Ac., $C_7H_5O.C_2H_2.CO_2H$.**—Ndl. fr. toluene, d. s. c. aq.; e. s. alc. or eth.—On warming w. alkali gives acetophenone (Test 712).—Heated above m. p. becomes ruby-red.—Gives Test 304.
99	316	**Dioxystearic Ac., $C_{18}H_{36}O_4$.** (from elaïdic Ac.).—Alkaline permanganate gives azelaic, pelargonic and oxalic acids.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. **38**) in 50 parts of cold water.
100·5	208	**Acetylphenyl-β-lactic Ac., $Ph.CH.(MeCO_2).CH_2.CO_2H$.**—Pearly scales.—Dec. at 200° to acetic and cinnamic ac. (Test 313).
102	164	**o-Tolylpropionic Ac., $Me.C_6H_4.C_2H_4.CO_2H$.**—S. h. aq.—H_2SO_4 gives o-methylhydrindon.
102	136	**o-Toluic Ac., $Me.C_6H_4.CO_2H$.**—B. p. 259° (th. i.).—Ndl., mod. s. h. aq.; **v.** s. alc.—Test 905–1 or 3 gives phthalic ac. (Test 318).—$Ba\bar{A}$ e. s. aq.—Amide melts at 138°.
102	164	**1, 3-Dimethylphenethanoic(4) Ac., $Me_2.C_6H_3.CH_2.CO_2H$.**—B. p. 265°.—Ndl. e. s. alc. or eth.—$Ag\bar{A}$ + Aq. e. s. h. aq.
102–2·5	194	**Meconin, $C_{10}H_{10}O_4$ (anhydride of meconic ac.).**—Sbl.—Ndl. s. in 700 pt. c. aq. or 22 pt. h. aq.—Contact w. alkalies gives salts of meconic ac. (free ac. unknown); is not soluble in ammonia.—Found in mother liquors from opium alkaloids.—Heated w. dil. H_2SO_4 and MnO_2 gives opianic ac.
103	192	**(α), o-Ethoxycinnamic Ac., $EtO.C_6H_4.CH:CH.CO_2H$.**—Tbl. v. d. s. c., d. s. h. aq.; e. s. alc. or eth.—$Ba\bar{A}_2$ + 2 aq. e. s. aq.—Heat gives β-ac., m. p. 135°.—Gives Test 304.
103–4	184	**i-Pinonic Ac., $C_{10}H_{16}O_3$.**—Lft. fr. aq. "Rather" d. s. c. aq.; e. s. alc. or eth.—M. p. of oxime 150°.
103–4d.	164	**Benzoylacetic Ac., $Ph.CO.CH_2.CO_2H$.**—D. s. aq.; v. s. alc. or eth.—Alc. sol., colored violet by $FeCl_3$!—Boiled w. KOH sol. gives benzoic ac. (Test 312), and acetophenone. Melts w. dec. to CO_2 and acetophenone (Test 712)! Attacked by Br or alk. permanganate.
104	176	**Phenylangelic Ac., $Ph.CH:CEt.CO_2H$.**—Ndl. v. d. s. c. aq.—CrO_3 mixt. oxid. to benzaldehyde and benzoic ac.! Gives Test 304.
104	176	**Phenylpenten(4)-oic Ac., $Ph.C_2H_4.CH:CH.CO_2H$.**—Tbl. fr. eth., d. s. aq.; e. s. eth.—Gives Test 304.—$Ca\bar{A}+3H_2O$, ndl. d. s. aq.
104–5d.		**Lanoceric Ac., $C_{30}H_{60}O_4$.**—Mic. lft. fr. alc.; d. s. eth. (In combination in wool fat).
105	174	**β-Dihydronaphthoic Ac., $C_{11}H_{10}O_2$.**—Pr. s. in 1734 pt. aq. at 14°.—Oxid. by $KMnO_4$ to phthalic ac. In CS_2 sol. changed by Br to bromanhydride m. p. 140° d.
105	170	**Campholic Ac., $C_{10}H_{18}O_2$.**—B. p. 260°.—Lft. fr. eth.-alc.; alm. i. aq. Volat. w. steam.—Ppt'd fr. sol. of alkali salts by CO_2.—Fuming HNO_3 gives camphoric and camphoronic acids.—$Ca\bar{A}_2+H_2O$, cryst. ppt.
106	94	† **Azelaic Ac., $CO_2H.(CH_2)_7.CO_2H$.**—B. p. a. 360° (sl. d.).—Lft. e. s. h. aq.; s. in 700 pt. aq. at 15°.—S. in 37 pt. c. eth.—$Ca\bar{A}$, v. d. s. gran. ppt. appearing when the ammoniacal sol. of the acid is boiled w. $CaCl_2$! $Zn\bar{A}$, v. d. s. cryst. ppt.—Does not give Test 304.
106	168	**1, 3, 3-Trimethylcyclohexene(1)carbonic(2) Ac., $C_{10}H_{16}O_2$.**—B. p. 138° (11 mm.).—Ndl. fr. h. aq.—Unsat.
106–7	148	† **Atropic Ac., $CH_2:CPh.CO_2H$.**—B. p. 267° d.—Monoclin. tbl. s. in 692 pt. aq. at 19°; s. CS_2.—Oxid. by CrO_3 to benzoic ac. (cf. Tests 702 and 312)!—$Na\bar{A}$ sol. gives no ppt. w. $MnCl_2$. (dif. fr. cinnamic ac.).—$Ca\bar{A}_2+5H_2O$ s. in 43 pt. aq. at 18°.—Gives Test 304!
106–7	152	**m-Methoxybenzoic Ac., $MeO.C_6H_4.CO_2H$.**—Ndl. sbl. undec.—E. s. alc., eth., or h. aq.—Dist. of $Ca\bar{A}_2$ gives phenol (Test 414).
107–8	212	**m-Benzylbenzoic Ac., $Ph.CH_2.C_6H_4.CO_2H$.**—Ndl. fr. aq.; d. s. c. aq.; e. s. alc. or eth.—CrO_3 mixt. oxid. to m-benzoylbenzoic ac.—$Ba\bar{A}_2+4H_2O$, s. aq.; $Ag\bar{A}$, ppt., d. s. h. aq.
108	228	**Phenylethermandelic Ac., $Ph.HC(OPh).CO_2H$.**—Ndl. fr. h. aq., v. d. s. c. aq.—Oxid. by h. dil. HNO_3 to benzaldehyde and picric acid.
108·5	168	† **Dehydracetic Ac. (Methylacetopyronon), $C_8H_8O_4$.**—B. p. 269·9° c.—S. in 100 pt. aq. at 6°; e. s. h. aq., alc. or eth.—1 drop 10% $FeCl_3$ gives yellow or orange (YO–OY) ppt. in aqueous solution!—Sol. in NaOH pale yellow.—Boil w. conc. NaOH and test distillate for acetone (Test 711).—Evaporation of the sol. in v. conc. ammonia gives an amide, m. p. abt. 200°.

Melting-point (C.°).	Neut. Equiv.	SOLID ACIDS.—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
108–9	126	**2, 5-Methylpyromucic Ac., $C_4H_2O(Me).CO_2H$.**—Ndl. d. s. c. aq.; v. s. h. aq.; e. s. eth.—Sbl easily.—$Ba\bar{A}_2$, octahedra, v. s. c. aq.—Warmed w. conc. H_2SO_4 + trace of isatin gives chrome-green color!
109	268	**Dibenzoylacetic Ac., $(Ph.CO)_2.CH.CO_2H$.**—D. s. aq.; e. s. eth.—Alc. sol. gives reddish color w. $FeCl_3$. Boiled w. dil. H_2SO_4 gives benzoic acid and acetophenone (Tests 312 and 712).
109·5	160	**Methylphenylpropiolic Ac., $Me.C_6H_4.C \vdots C.CO_2H$.**—Gives Test 304.—Ag salt explosive ppt.
110	106	**Ethyl Isocarbopyrotritarate, $C_{10}H_{12}O_5$.**—Ndl. fr. h. aq.; v. d. s. c. aq.; e. s. alc. or eth.; e. s. NaOH, Na_2CO_3 or ammonia, but reppt'd by CO_2.—Alc. sol. blue w. $FeCl_3$! Reduces Ag or Cu salts in the cold.
110–11	198	**o-Phenylbenzoic Ac., $Ph.C_6H_4.CO_2H$.**—B. p. 343°.—Ndl. d. s. h. aq.; e. s. h. alc.—$Ca\bar{A}_2 + 2H_2O$, d. s. aq.; ignited w. CaO gives diphenyl, etc.—Fuming HNO_3 at 0° gives nitro deriv., s. alc., m. p. 221°.
110·5	136	**m-Toluic Ac., $Me.C_6H_4.CO_2H$.**—B. p. 263°.—Pr. fr. h. aq. s. in 60 pt. aq. at 100°, e. s. alc. or eth.—Oxid. by CrO_3 mixt. to isophthalic ac. (Tests 905–2 and 318).
112	122	**Brassylic Ac., $CO_2H.(CH_2)_{11}.CO_2H$.**—100 pt. aq. at 24° dissolve 0.74 pt.; e. s. alc. or eth.—$Ca\bar{A} + H_2O$, pulv. ppt.
112	194	**Benzoyllactic Ac., $Me.CH(C_7H_5O_2).CO_2H$.**—Cryst. s. alc. or eth., and in 400 pt. c. aq.—Boiled w. dil. HCl gives benzoic ac. (Test 312) and lactic ac.
112–3	150	**p-Ethylbenzoic Ac., $Et.C_6H_4.CO_2H$.**—Lft. s. h. aq.; e. s. alc. or eth.—$Ba\bar{A}_2 + 2H_2O$, s. in 45 pt. c. aq.—Oxid. to terephthalic ac. (Test 905 and 318).
112–3	166	**Phenoxypropionic Ac., $Me.CH(OPh).CO_2H$.**—V. d. s. c. aq.; e. s. h. aq· e. s. eth.—$Ca\bar{A}_2 + 2H_2O$, v. d. s. alc.; $Ag\bar{A}$, small ndl. blackened by light.
112–5d.	192	**Ethylbenzoylacetic Ac., $Ph.CO.CHEt.CO_2H$.**—Ndl. fr. dil. alc.; e. s. alc· or eth.—Boiling w. *conc. alc.* KOH gives benzoic ac. (Test 312) and butyric ac!—Oxime m. p. 89°–90°.
113	214	**Phenylethersalicylic Ac., $o\text{-}PhO.C_6H_4.CO_2H$.**—B. p. 355° d.—Lft. fr. dil. alc.; v. s. alc. or eth. $NH_4\bar{A}$, m. p. 130°.
114	212	**o-Benzylbenzoic Ac., $Ph.CH_2.C_6H_4.CO_2H$.**—Sbl. in ndl.—D. s. c. aq.; e. s. eth.—Warmed w. conc. H_2SO_4 gives anthranol.—$Ba\bar{A}_2 + 5\frac{1}{2}H_2O$, s. aq.
115	164	**o-Acetophenonecarbonic Ac., $Me.CO.C_6H_4.CO_2H$.**—Cryst. s. conc. H_2SO_4. Sweet taste.—With alc. NH_3 at 100° gives comp., m. p. 204°. Sol. in conc. H_2SO_4 on standing forms isomethylenephtalid, m. p. 215°.
115	288	**Dioxypalmitic Ac., $C_{16}H_{32}O_4$.**—Lft. s. alc. or eth.
115	162	**m-Methylcinnamic Ac., $Me.C_6H_4.CH:CH.CO_2H$.**—Silky ndl. fr. h. aq.; e. s. eth. or bz.—$FeCl_3$ gives egg-yellow ppt. w. NH_4 salt.—Gives Test 304.
115	178	**m-Methoxycinnamic Ac., $MeO.C_6H_4.CH:CH.CO_2H$.**—S. h. aq.; e. s. eth.—Gives Test 304.
115	226	**p-Phenyltolylacetic Ac., $C_7H_7.CHPh.CO_2H$.**—Lft. fr. aq.; v. d. s. c. aq.; s. h. aq.; e. s. alc. or eth.—Oxid. by CrO_3 to p-phenyltolylketone, etc.—$Ca\bar{A}_2 + H_2O$, d. s. h. aq.
116	178	**β-Benzoylpropionic Ac., $Ph.CO.(CH_2)_2.CO_2H$.**—E. s. aq. at 70°· Heated above m. p. turns orange-yellow. $Pb\bar{A}_2 + 2H_2O$, ndl., d. s. c., e. s. h. aq.
116·5	164	**Cuminic Ac., $p\text{-}Me_2.CH.C_6H_4.CO_2H$.**—Triclin. cryst. v. d. s. c. aq.; e. s. eth.—$Ba\bar{A}_2$, lft. s. in 100 pt. aq. at 20°.—Oxid. gives terephthalic ac. (cf. Tests 905–1 and 318).
117		**Pyromeconic Ac., $C_5H_4O_3$.**—Cf. Phenols. $FeCl_3$ gives cherry-red color!
118	180	**Salicylic Ac. Acetate, $o\text{-}C_2H_3O_2.C_6H_4.CO_2H$.**—Fine ndl. fr. h. aq.—$FeCl_3$ gives violet color w. aq. sol.!—Saponification by hot alkalies gives acetic and salicylic acids! (cf. Tests V, 311 and 319).

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
119·6	261	† **Succinic Anhyd., $C_4H_4O_2.O$.**—(For behavior on titration cf. remark on page 37.—Long ndl. fr. alc.; v. d. s. eth.—Test 307 gives ac. s. aq., m. p. 185° (Test 320).
120	152	**o-Oxymethylbenzoic Ac., $HO.CH_2.C_6H_4.CO_2H$.**—Ndl. s. in 0·428 pt. aq. at 20°; s. eth.—In melting or on prolonged standing w. aq. gives phthalid, m. p. 73°.—Salts all soluble.
abt. 120		**Fellic Ac., $C_{23}H_{40}O_4$.**—(In human gall.)—Ndl. fr. dil. alc.; i. aq.; s. alc. or eth.—Taste bitter.—Opt. act.—$Ba\bar{A}_2+4H_2O$, s. in abt. 800 pt. c. or h. aq.—Color reac. w. sugar and H_2SO_4 (cf. H. 11. 274).
d.120	264	**Santonic Ac., $C_{15}H_{20}O_4$.**—Cryst. gradually turn yellow.—D. s. c. aq.; e. s. alc.; d. s. eth.—Fusion on boiling w. aq. gives aq. and santonin. Opt. active.—$Pb.\bar{A}_2$ (at 100°) ppt.
120 or 127	192	**p-Toluyl-β-Propionic Ac., $C_7H_7.CO.C_2H_4.CO_2H$.**—Tbl. fr. lgr., e. s. h. aq., alc., or eth.—Turns red above m. p.—$Ag\bar{A}$ ndl.
121·2c.	122	† **Benzoic Ac., $Ph.CO_2H$.**—B. p. 249·2° c.—Monoclin. lft. or ndl.—Sbl. easily, vapor producing coughing.—S. in 344·8 pt. aq. at 20°, or in 17 pt at 100°; at 15° s. in 2·14 pt. abs. alc., or in 3·19 pt. eth.—Apply Test 312!
122	216	**Diisoamyloxalic Ac., $(C_5H_{11})_2.COH.CO_2H$.**—Silky fibres, s. eth.—Sbl.—$Ba\bar{A}_2$, d. s. c. aq.
122	164	**Cetylmalonic Ac., $Me.(CH_2)_{15}.CH.(CO_2H)_2$.**—Rhomb. tbl. d. s. c. alc.; e. s. eth.-alc.—$Ba\bar{A}$ cryst. ppt.; $Ag_2\bar{A}$ powd. ppt.—Gives Test 303.
123	194	**o-Thymotic Ac., $HO.C_6H_2(Me)(Pr).CO_2H$.**—V. d s. h. aq.; e. s. eth.—Blue color w. $FeCl_3$.!
123	139	**n-Dodecanedicarbonic Ac., $CO_2H.(CH_2)_{12}.CO_2H$.**—Lft. mod. s. c. alc. or eth.
124–5	324	**Lichen-stearic Ac., $C_{18}H_{31}O_2.CO_2H$.**—Pearly plates, i. aq.; e. s. h. bz. or $CHCl_3$.—Not attacked by Br or permanganate.—$NH_4\bar{A}$, pr. fr. h. aq. (m. p. 106°).
125	161	**m-Tolylpropionic Ac., $Me.C_6H_4.C_2H_4.CO_2H$.**—Ndl. fr. h. aq.—Oxid. by Test 905–1 gives isophthalic Ac. (Test 318–2).
125	204	**Benzallævulinic Ac., $Ph.CH:C(CO.Me).CH_2.CO_2H$.**—Cryst. fr $CHCl_3$. S. in conc. H_2SO_4 w. red color!—After boiling w. conc. KOH gives iodoform reac. w. I. (Test 801).
125	179	**α-Dihydronaphthoic Ac., $C_{11}H_{10}O_2$.**—S. in 3215 pt. c. aq.—Br addition-product m. p. 152°.
125–7		**Fluorescine, $C_{19}H_{13}O_3.CO_2H$.**—Ndl. s. $\bar{A}$c. or eth.—Gentle oxid. gives fluoresceïn!
126	150	**1, 3-Dimethylbenzoic(4) Ac., $Me_2.C_6H_3.CO_2H$.**—Sbl.—B. p. 268°.—D. s. h. aq.; e. s. h. alc.—$Ca\bar{A}_2+2H_2O$, and $Ba\bar{A}_2+xH_2O$, e. s. aq.
127	164	**1, 2, 4-Trimethylbenzoic (6) Ac., $Me_3.C_6H_2.CO_2H$.**—Tbl. fr. lgr., v. d. s. c. aq.; s. h. aq.; v. s. alc. or eth.—Volat. w. steam. Distils undecomposed.—Ignited w. CaO gives pseudocumene.
127	178	**m-Isobutylbenzoic Ac., $C_4H_9.C_6H_4.CO_2H$.**—Ndl. fr. lgr.—Amide, ndl. fr. aq., m. p. 130°.
127	180	**m-Acetoxybenzoic Ac., $C_2H_3O_2.C_6H_4.CO_2H$.**—Cryst. s. h. aq.; e. s. alc. or eth.
127–8	166	[+] **Tropic Ac., $Ph.CH(CH_2OH).CO_2H$.**—Hard pr. fr. eth.
128	144	**Lactide, $C_6H_8O_4$.**—B. p. 255°.—Monoclin. tbl. fr. h. abs. alc., alm. i. c. aq.; v. d. s. alc.—Boil w. aq., and apply Test 302 for lactic ac. to the cold solution.—Dry NH_3 gas gives lactamide, s. aq., and alc. M. p. 47°.
128	158	**Oxyroccellic Ac., $C_{17}H_{32}O_5$.**—Lft. of greasy feel, e. s. eth. or $CHCl_3$.—At 160° gives anhyd. m. p. 82°.—$Ag_2\bar{A}$ floc. ppt.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
128	74	† **Phthalic Anhyd., o-$C_6H_4.(CO)_2.O$.**—B. p. 284·5c., subliming in fine long ndl.—Alm. i. c. aq.; s. h. aq. or c alc.—Mix a few mgrms. w. an equal quantity of either phenol or resorcin; barely moisten w. conc. H_2SO_4 and fuse according to Test 402. The fused mass dissolves in dil. alkalies, in the first case with the deep red color of phenolphthalein, or, in the second case, with the strong green fluorescence characteristic of fluoresceïn.
128–9	166	**p-Hydrocumaric Ac., $HO.C_6H_4.(CH_2)_2.CO_2H$.**—Monoclin. cryst., e. s. h. aq., alc., or eth.—Cold sat. aq. sol. becomes blue-gray w. 1 drop $FeCl_3$ sol.—Reacts like tyrosin w. HgN_2O_6.—No ppt. w. $Pb.\bar{A}c_2$ or w. $BaCl_2$ —$Zn\bar{A}_2+2H_2O$, s 130 pt. c. aq.
128–9d.	196	**Camphocarbonic Ac., $C_{11}H_{16}O_3$.**—D. s. aq.; e. s. eth. Fusion gives camphor and CO_2 (Test 715)! $FeCl_3$ gradually added to alc. sol. gives first a dark blue and finally a dark green!—Easily oxid.—Br substitutes easily, giving ac. m. p. 109°.
128–9	170	**Pinonic Ac., $C_9H_{14}O_3$.**—Cryst. fr. $CHCl_3$; d. s. c. aq.; v. d. s. lgr.—B. p. (17 mm.), 187°–93°.
128–30		**Glycollic Anhyd., $C_4H_6O_5$.**—Powder i. c. aq., alc., or eth.; s. h. aq. giving glycollic ac.—Heated above m. p. gives glycollide (m. p. 220°).
128·5	116	**β-Methoxyisocrotonic Ac., Me.C(OMe):CH.CO_2H.**—S alc. or eth. Gives Test 304
130	162	**Hydrindoncarbonic Ac., $C_6H_4.C_3H_5.CO_2H$.**—Ndl. s in 120 pt. aq. at 100°.—$Ba\bar{A}_2$ v. s. aq.—Oxid by alk. $KMnO_4$.—Br substitutes cold.
130–5	139	**Cinnamic Anhyd., $(C_9H_7O)_2O$.**—I. aq; v. d s. c. alc.—Cryst. powd. Test 307 gives acid of Test 313.
130–40d.	220	**Acetophenoneacetacetic Ac., $(C_2H_3O)(C_8H_7O).CH.CO_2H$.**—Heat gives acetophenoneacetone and CO_2.
131	186	**α-Naphthylacetic Ac., $C_{10}H_7.CH_2.CO_2H$.**—E. s. h. aq.; e. s. eth.—Ignition w. CaO gives α-methylnaphthalin.
132	150	**1, 4-Dimethylbenzoic(2) Ac., $Me_2.C_6H_3.CO_2H$.** — B. p. 268° (th. i.) — Ndl. v. d s. h. aq.; v. s. alc.—$Ca\bar{A}_2+2H_2O$, mod. s. aq.—Amide, ndl. d. s. h aq; m. p. 186°.
132	200	**α-Ethylnaphthoic Ac., $Et.C_{10}H_6.CO_2H$.**
132	150	**Roccellic Ac., $C_{17}H_{32}O_4$.**—(In certain algæ.)—Cryst., i. h. aq.; e. s. alc. or eth.; s. Na_2CO_3 —Swells up in conc. KOH, dissolving after dilution w. aq.—$Ag_2\bar{A}$, i. aq; $Ca\bar{A}$, i. aq.
133	148	† **Cinnamic Ac., Ph.CH:CH.CO_2H.**—B. p. 300° without dec., but does not sublime.—Monoclin. pr. fr. alc.—Odor faintly aromatic.—S in 1000 pt. aq at 20°; in 4.3 pt. alc. at 20°; v. s eth.; s. $CHCl_3$; d. s. CS_2 —Warmed w. CrO_3 mixt oxid. easily giving strong odor of benzaldehyde.—Identify by Test 313!
133–3·5	101	**Sebacic Ac., $CO_2H.(CH_2)_8.CO_2H$.**—B. p 243·5° (15 mm.).—Thin lft. s. in 1000 pt. aq. at 17°, or in 50 pt. at 100°; e. s. alc. or eth.—Stable toward CrO_3 mixture —$Ca\bar{A}$, ppt —Ignition w. BaO gives octane. Oxid. w. dil. HNO_3 gives adipic, glutaric, and succinic acids.
133–4	163	**β-Naphthoic Anhyd., $(C_{11}H_7O)_2O$.**—D. s. c. eth.; s. h eth. or h. bz. Obtain acid of m. p. 184° c. by Test 307.
133·5	154	**Cis- (iso) Campholitic Ac., $C_9H_{14}O_2$.**—B. p. 255°–6°.—Pr. fr. dil. alc.—Odor camphor-like —S. 5000 pt. c aq.; e. s. alc.—Unsat.—$Ca\bar{A}_2+3\frac{1}{2}H_2O$, ndl., e. s. aq.; $Zn\bar{A}_2$, s eth.; i aq.
134·5	112	**Sorbic Ac., Me.CH:CH.CH:CH.CO_2H.**—B. p. w. dec. 228°.—Long ndl. fr h. aq.; e. s. alc. or eth.—$Ba\bar{A}_2$, silvery scales scarcely more s. in h. than in c. aq.—Gives Test 304.
135	192	**(β)o-Ethoxycinnamic Ac., $C_{11}H_{12}O_3$.**—Ndl. fr. h. aq.—$Ca\bar{A}_2+2H_2O$, v. d. s. c. aq.—Gives Test 304.
135	162	**Methylatropic Ac., Me.CH:CPh.CO_2H.**—Gives Test 304.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
135	140	**2, 5-Dimethylfurfuranecarbonic (Uvic) Ac., $(Me_2).C_4HO.CO_2H$.**—Ndl. s. 400 pt. h. aq.; e. s. alc. or eth.—Warmed w. 2 drops fuming HNO_3 and then treated w. 6 drops conc. H_2SO_4 gives cherry-red color.—Br substitutes very easily.—With aq. at 160° gives acetylacetone.—$Ba\bar{A}_2+4H_2O$, ndl. d. s. c. aq.; $Zn\bar{A}_2+8H_2O$ (charac. cryst. aggregates) more s. c. than h.
136–7	146	† **Phenylpropiolic Ac., $Ph.C{:}C.CO_2H$.**—V. long hair-like ndl. fr. h. aq.—E. s. alc. or eth.—Melts under h. aq. at 80°.—Boiled w. Zn dust in glacial $\bar{A}$c. gives cinnamic ac. (Test 313).—Reduced by Na amalgam to hydrocinnamic ac.—Salts unstable in h. sol.—Gives Test 304.
136·5	316	**Dioxystearic Ac. (from oleic ac.), $C_{18}H_{36}O_4$.**—Lft. e. s. h. alc.—$Ba\bar{A}_2$, gran. ppt., i. aq. or alc.
137	166	**m-Ethoxybenzoic Ac., $EtO.C_6H_4.CO_2H$.**—Ndl. d. s. h. aq.; s. alc. or eth.—$Ba\bar{A}_2$, e. s. h. aq.
137·5	121	**β-Ethoxyisocrotonic Ac., $MeC(OEt){:}CH.CO_2H$.**—Pr. s. alc. or eth.—Boiled w. dil. H_2SO_4 gives acetone (Test 711).
139	234	**p-Octylbenzoic Ac., $C_8H_{17}.C_6H_4.CO_2H$.**—Lft. fr. h. alc.; v. d. s. h. aq.—$Ag.\bar{A}$ bulky ppt.
140	164	**p-Propylbenzoic Ac., $Pr.C_6H_4.CO_2H$.**—Lft. fr. h. aq. e. s. alc. or eth.—Oxid. by $KMnO_4$ to terephthalic ac. (Tests 925 and 318).
140	87	**Suberic Ac., $CO_2H.(CH_2)_6.CO_2H$.**—B. p. abt. 300° without dec.—Ndl. or tbl. v. d. s. eth.; alm. i. $CHCl_3$; s. in 704 pt. aq. at 15·5°.—$Ca\bar{A}+H_2O$, s. in 161 pts. aq. at 14°.—$Ba\bar{A}$, s. c. aq., less s. h. aq. Ignition w. BaO gives hexane.
140–1	87	**α, s-Dimethyladipic Ac., $CO_2H.CHMe.(CH_2)_2.CHMe.CO_2H$.**—B. p. 321°.—D. s. eth.
141	332	**Trioxystearic Ac., $C_{17}H_{32}(OH)_3.CO_2H$.**—Ndl. fr. h. aq. d. s. eth.
141	138	**Furfuracrylic Ac., $C_4H_3O.CH{:}HC.CO_2H$.**—B. p. 255°–65° d.—Thin ndl. s. 500 pt. c. aq.; e. s. eth. or alc.—S. in conc. HCl w. green color!—Ba salt v. s. aq. or alc.—Gives Test 304.
141–3	316	**Dioxystearic Ac., $C_{18}H_{36}O_4$** (fr. Castor-oil).—I. eth.; d. s. c. alc.—HI reduction gives stearic ac.
141–3	180	**4-Methoethylphenol(3)carbonic(1) Ac., $C_{10}H_{12}O_3$.**—Boils w. decomp.—Ndl. fr. aq., v. d. s. c. aq.; s. h. aq.; v. s. alc. or eth.—Not ppt'd in dil. sol. by $Pb.\bar{A}c_2$; $Ba\bar{A}_2$, e. s. aq.—Long fusion w. KOH gives m-oxybenzoic ac.
142d.	160	**Agaricic Ac., $C_{16}H_{30}O_5$.**—Silvery lft. fr. 30% alc. (Cryst. w. $1H_2O$ which is lost at 100°; loses more aq. in melting.)—Gelatinizes w. boiling aq., dissolves, and cryst. out on cooling.—D. s. alc. or eth.—(Obtained fr. Polyporus officinalis.)—$Ba\bar{A}$, amorph. ppt.; $Ag_2\bar{A}$ (at 90°) gelat. ppt.
142–3	87	† **Hydrochelidonic Ac., $CO.(CH_2.CH_2.CO_2H)_2$.**—Rhomb. tbl. d. s. aq. or eth.; i. bz.; s. alc.—Above m. p. gives anhydride (lft. fr. dil. alc., m. p. 75°). Oxid. by HNO_3 or alk. $KMnO_4$ to oxalic and succinic ac. (Test 320).—$Ba\bar{A}+2H_2O$, e. s. lft.; $Zn\bar{A}+2H_2O$, charac. 6-sided i. lft.
142–4d.	204	**Benzoyltetramethylenecarbonic Ac., $C_{12}H_{12}O_3$.**—Pr. fr. eth. v. d. s. c. aq.; e. s. alc. or eth.—$Ag\bar{A}$ cryst. ppt.
144	150	**1, 2-Dimethylbenzoic(3) Ac., $Me_2.C_6H_3.CO_2H$.**—Glassy pr. fr. alc.—V. d. s. h. aq.—$Ca\bar{A}_2+H_2O$, mod. s. c. aq.; ignited w. CaO gives o-xylene Test 921.
144d.	90	**1-Methylphthalic(2, 3) Ac., $C_6H_3(Me)(CO_2H)_2$.**—Anhyd. melts at 109°–10°.
145	163	**α-Naphthoic Anhyd., $(C_{11}H_7O)_2O$.**—V. s. alc.; s. eth. or bz.—Test 307 gives α-Naphthoic ac., m. p. 160°.
145–6	166	**p-Methylmandelic Ac., $Me.C_6H_4.CHOH.CO_2H$.**—Tbl. fr. h. aq.—Gives Test 302 w. $FeCl_3$.

Melting-point (C.°).	Neut. Equiv.	SOLID ACIDS.—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
146	240	**p-Toluyl-o-benzoic Ac., $Me.C_6H_4.CO.C_6H_4CO_2H$.**—V. d. s. h. aq.; the milky ppt. that separates on cooling gives lft. containing aq. of cryst.—E. s. alc. or eth.—Dec. on dist.—$Ba\bar{A}_2+4H_2O$., d. s. aq.; $Pb.\bar{A}_2$, s. eth. $Na\bar{A}$ melted w. 5-6 pts. KOH gives benzoic ac.+p-toluic ac.
146		**Acetcumaric Ac., $C_2H_3O_2.C_6H_4.C_2H_2.CO_2H$.**—Ndl. e. s. h. aq.—Heated gives coumarin (charac. odor of "sweet grass") and acetic ac.
147–8	122	**Diisoamylmalonic Ac., $(C_5H_{11})_2.C.(CO_2H)_2$.**—E. s. alc. or eth.; v. d. s. aq.—At 175° gives CO_2 and diisoamylacetic ac. (Test 303).
148	212	**Diphenylacetic Ac., $Ph_2.CH.CO_2H$.**—Ndl. e. s. h. aq., alc., or eth. CrO_3 mixt. (cf. Test 905-2) slowly oxidizes to benzophenone (Test 714).—Ba salt ignited w. CaO gives diphenylmethane.
148 sbl.	180	**1, 2, 4-Trimethylphenol(6)-Methanoic(5) Ac., $C_{10}H_{12}O_3$.**—Ndl. fr. dil. alc.; v. d. s. h. aq.—$FeCl_3$ gives transient blue w. dil. alc. sol.—$Ca\bar{A}_2+2H_2O$, glassy pr. s. c. aq.
149·50	164	**1, 2, 4-Trimethylbenzoic(5) Ac., $Me_3.C_6H_2.CO_2H$.**—Long ndl. fr. bz.; d. s. h. aq.; v. s. eth.—The amide melts at 200°-201°.
150	210	**† Opianic Ac., $C_{10}H_{10}O_5$.**—Thin pr. s. in 400 pt. c. or 60 pt. h. aq.; s. alc. or eth.—Mix on a porcelain crucible cover 3 mgr. of the acid, an equal bulk of phenol, and 3 drops conc. sulphuric acid. A strong red-orange color (RO–O) is immediately produced.—$Ba\bar{A}_2+2H_2O$, pr. e. s. aq.—Reduction w. Na amalgam gives meconin.—[Does *not* give Generic Test I.]
150	228	**† Benzilic Ac., $Ph_2.COH.CO_2H$.**—Monoclin. ndl., e. s. h. aq.—Taste slightly bitter.—1 mgr. dissolved in 3 drops conc. H_2SO_4 on a crucible cover at once gives an intense orange-red [OR.] coloration which soon becomes red-violet [RVTI] about the edges.—Gives Test 302.—Oxid. by CrO_3 mixt.—$Ba\bar{A}_2$. e. s. melting under h. aq.
150	148	**Homococaic Ac., $C_9H_8O_2$.**—Ndl. e. s. alc. or eth.—Fuming HNO_3 gives nitro compound, m. p. 226°.
151	152	**4-Oxy-m-toluic Ac., $HO.C_6H_3(Me).CO_2H$.**—Ndl. fr. aq.; d. s. c. aq.; v. s. alc. or eth.—Volat. w. st.—$FeCl_3$ gives intense blue violet color! $Ba\bar{A}_2+2H_2O$, lft. v. s. aq.
151–2	254	**α-Ditolylpropionic Ac., $(C_7H_7)_2.CMe.CO_2H$.**—Cryst. fr. alc. or eth.; e. s. eth. or h. alc.—Volat. without dec.—Heated w. CaO gives p-ditolyethane.—$Ba\bar{A}_2$ pulv. ppt.
152	164	**1, 3, 5-Trimethylbenzoic Ac., $Me_3.C_6H_2.CO_2H$.**—E. s. alc. or eth.; v. d. s. aq.—Dist. undec.—Ignition w. CaO. gives mesitylene (cf. Test 914).—M. p. of amide, 158°.
153c.	73	**† Adipic Ac., $CO_2H.(CH_2)_4.CO_2H$.**—Boils without dec.—Flat ndl. s. in 69 pt. aq. at 15°; v. d. s. eth.; e. s. alc.—May be cryst. without dec. fr. h. conc. HNO_3.—$Ca\bar{A}+H_2O$, d. s. h. or c. aq.; $Ba\bar{A}$, e. s. c. aq., less s. h.; $Zn.\bar{A}$ cryst. ppt. less s. in h. than in c. aq.
153–4	288	**Abietic Ac., $C_{19}H_{28}O_2$.**—(Principal constituent of Rosin.)—Cryst. fr. alc., easily s. alc., eth., or CS_2.—Salts amorph.—Addition of a little acetic anhyd. and a drop of H_2SO_4 to a $CHCl_3$ sol. gives a purple color, quickly changing to intense blue.
154d.	168	**p-Methoxysalicylic Ac., $HO.C_6H_3(OMe).CO_2H$.**—S. in 40 pt. h. aq.; e. s. alc. or eth.—$FeCl_3$ gives sol. intense red-violet color.
154–5	212	**p-Benzylbenzoic Ac., $Ph.CH_2.C_6H_4.CO_2H$.**—Ndl. fr. h. aq.; e. s. eth.—$Ca\bar{A}_2$, ppt. CrO_3 gives p-Benzoylbenzoic ac.
154–5	302	**p-Tolyldiphenylmethanecarbonic Ac., $Me.C_6H_4.CHPh.C_6H_4.CO_2H$.**—Ndl. fr. alc.
154–5	141	**Photosantonic Ac., $C_{15}H_{22}O_5$** (dried at 100°).—Pr. fr. alc.; v. d. s. c. aq.; e. s. alc. or eth.—$Ag_2\bar{A}+3H_2O$, curdy ppt.
154–5d.	164	**Phenylpyruvic Ac., $Ph.CH_2.CO.CO_2H$.**—Lft. fr. $CHCl_3$; v. d. s. h. aq.; e. s. alc. or eth.—Alc. sol. gives intense blue-green color w. $FeCl_3$.—Gives off CO_2 in melting.—Na amalgam gives phenyllactic ac.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, **p. 38**) in 50 parts of cold water.
155	125	**Stilbenedicarbonic Anhyd., $C_{16}H_{10}O_3$.**—B. p. 236° (15 mm.).—Find ndl.—Sbl. undec.—I. c., v. d. s. h. aq.; i. Na_2CO_3.—Is oxid. in cold by $KMnO_4$ to benzoic ac. (Test 312).—[The free ac. is unknown.]
155		**Isodehydracetic Ac., $C_8H_8O_4$.**—Ndl. fr. c. alc.; d. s. c., v. s. h. aq.—At 200°–245° loses CO_2.—Warmed w. $Ba(OH)_2$ splits to CO_2, mesityl oxide and oxymesitenecarbonic ac.
d. abt. 155	74	**Dioxymaleic Ac., $CO_2H.C(OH):C(OH).CO_2H$.**—Pearly lft., d. s. c. aq. or eth.; e. s. alc.—Heated w. aq. dec. to CO_2 and glycolaldehyde.—$FeCl_3$ gives blackish color, becoming violet upon addition of KOH.—$Ba\bar{A}+2H_2O$ (dried i. v.), cryst. ppt.
155–6	180	**p-Oxyisopropylbenzoic Ac., $Me_2.C(OH).C_6H_4.CO_2H$.**—Pr. fr. h. aq., e. s. alc. or eth.—Oxid. by CrO_3 mixt. (Test 905–2) gives terephthalic ac. (Test 318).—$Ba\bar{A}_2+H_2O$, v. s. aq.; $Ag\bar{A}$, tbl. d. s. h. aq.
156–7	256	**Dibenzylglycollic Ac., $(PhCH_2)_2.C(OH).CO_2H$.**—4-sided pr. fr. alc.; e. s. eth. Boiled w. KOH (G. 1·2–1·3) gives oxalic ac. and toluene.
156–7	250	**Isatronic Ac., $C_{17}H_{14}O_2$.**—Lft. fr. dil. alc.—$Ca\bar{A}_2$, volum. ppt., d. s. h. aq.
156–7 (r. h.) ((s.h.) 124–8d.)	188	**2-Oxynaphthoic(1) Ac., $HO.C_{10}H_6.CO_2H$.**—V. s. alc.—Alc. sol. gives blue color w. $FeCl_3$.—Fusion or long boiling w. aq. gives CO_2 and β-naphthol (Test 413). $Ba\bar{A}_2$ ppt. (dif. fr. salicylic ac.).
157–8	64	**α-Trimellitic Anhyd., $C_9H_4O_5$.**—Cryst. d. s. c., e. s. h. aq.—M. p. of trimellitic ac. (Test 307), 216° d.
158	192	**p-Isoamylbenzoic Ac., $Me_2.CH.(CH_2)_2.C_6H_4.CO_2H$.**—Ndl. fr. h. aq.—E. s. alc. or eth.—Oxid. to terephthalic ac. (Test 905–1).
158c.	138	† **Salicylic Ac., $o\text{-}HO.C_6H_4.CO_2H$.**—Ndl. fr. h. aq., s. in 370 pt. aq. at 20°, v. s. alc. or eth.; e. s. $CHCl_3$.—Sol. in aq. (1:10,000) gives purple coloration (RV–VR) w. 1 drop 10% $FeCl_3$ sol. (cf. Test 401)!—Apply Test 319!
159	224	**Stilbene-o-carbonic Ac., $Ph.CH:CH.C_6H_4.CO_2H$.**—E. s. alc. or $CHCl_3$.—Gives Test 304.
159	242	**Diphenyllactic Ac., $Ph_2.CH.CHOH.CO_2H$.**—Ndl. fr. h. aq., e. s. alc. or eth.
159–60	79	**trans-Pentamethylene-1, 2-dicarbonic Ac., $C_5H_8.(CO_2H)_2$.**—E. s. h. aq.—$CaCl_2$ boiled w. $(NH_4)_2\bar{A}$ sol. gives ppt.
159·5	214	**p-Phenoxybenzoic Ac., $PhO.C_6H_4.CO_2H$.**—Coffin-shaped pr. fr. $CHCl_3$.—E. s. alc. or eth.—Heated w. baryta gives phenylether.
160	172	**α-Naphthoic Ac., $C_{10}H_7.CO_2H$.**—Ndl. e. s. h. alc.; v. d. s. h. aq.—$Ca\bar{A}_2+2H_2O$, ndl. s. in 93 pt. aq. at 15°.—Ignition w. CaO gives naphthalene (Test 915).
160–1	198	**m-Phenylbenzoic Ac., $Ph.C_6H_4.CO_2H$.**—Lft. e. s. alc. or eth.—$Ba\bar{A}_2+3\frac{1}{2}H_2O$, ndl. e. s. aq. (dif. fr. para ac.).—Oxid. by Test 905–1 gives isophthalic ac. (Test 318–2).
160–1	162	**p-Propenylbenzoic Ac., $CH_2:CMe.C_6H_4.CO_2H$.**—Lft. d. s. h. aq.; v. s. alc. or eth.—$Ba\bar{A}_2+H_2O$, lft. v. s. aq.—Gives Test 304.
161	113	**Hemipinic Ac., $(MeO)_2.C_6H_2.C_2OH$.**—M. p. varies much according to method of heating. Cryst. fr. h. aq. w. xH_2O.—$FeCl_3$ gives orange color w. aq. sol.—W. KOH at 220° gives protocatechuic ac.—$NH_4\bar{A}+H_2O$ at 110° gives hemipinimide, ndl. fr. alc., m. p. 228°–30°, alc. sol. fluorescing blue.
161	206	**β-Dihydronaphthoic Ac. (stable form), $C_{11}H_{10}O_2$.**—Lft. i. c. aq.; e. s. alc. or eth.—Easily oxid. to phthalic ac. (Test 318) by $KMnO_4$.
161	288	**p-Triphenylmethanecarbonic Ac., $Ph_2.CH.C_6H_4.CO_2H$.**
161–2	226	**m-Benzoylbenzoic Ac., $Ph.CO.C_6H_4.CO_2H$.**—Sbl. in lft.—E. s. alc. or eth.—Fusion w. KOH gives benzoic ac. (Test 312).
162	288	**o-Triphenylmethanecarbonic Ac., $(C_6H_5)_2.CH.C_6H_4.CO_2H$.**—I aq.; e. s. alc. or eth.—Ignition w. BaO_2H_2 gives triphenylmethane.—Dissolve 1 pt. ac. in 3 pt. conc. H_2SO_4, ppt. sol. w. aq.; wash ppt. w. cold NaOH and recryst. fr. abs. alc. Phenylanthranol is formed, yellow. ndl., m. p. 141°–4° d.

Melting-point (C.°).	Neut. Equiv.	SOLID ACIDS.—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
162	226	**Diphenyleneglycollic Ac., $C_{14}H_{10}O_3$.**—(Dried at 80°.)—Cryst. w. $\frac{1}{2}H_2O$.—V. d. s. c., e. s. h. aq.; s. alc. or eth.—Warmed w. conc. H_2SO_4 gives indigo-blue sol.!—$Ca\bar{A}_2+2H_2O$, d. s. c. aq.
163	150	**1, 2-Dimethylbenzoic (4) Ac., $Me_2.C_6H_3.CO_2H$.**—Pr. fr. alc.; v. d. s. h. aq.—$Ca\bar{A}_2+2H_2O$ and $Ba\bar{A}_2$ e. s. aq.
163–4	152	**2-Oxy-m-toluic Ac., $HO.C_6H_3(Me).CO_2H$.**—Ndl. e. s. h. aq.—Intense violet color w. $FeCl_3$.—$Ca\bar{A}_2$ e. s. aq.
164	178	**p-Isobutylbenzoic Ac., $Me_2.CH.CH_2.C_6H_4.CO_2H$.**—Sbl. in ndl.; e. s. alc. or bz.—$Ca\bar{A}_2$ tbl. d. s. c. aq.—M. p. of amide 171°, ndl. fr. aq.
164	250	**Atronic Ac., $C_{17}H_{14}O_2$.**—Alm. i. h. aq.; e. s. alc.—$Ca\bar{A}_2+6H_2O$, ppt d. s. h. aq.—Unsat.
164	142	**Diphenylglutaric Ac., $CO_2H.CH(Ph).CH_2.(Ph)HC.CO_2H$.**—Ndl. fr. h. aq.; v. d. s. h. aq.
164–5	79	**Ethylitaconic Ac., $C_7H_{10}O_4$.**—D. s. aq.—Unsat. (cf. Test 304).
165	178	**1, 2, 3, 4-Tetramethylbenzoic(5) Ac., $Me_4.C_6H.CO_2H$.**—Ndl. fr. alc.—$Ba\bar{A}_2$ e. s. alc. or aq.
165–6	194	**o-Hydrocinnamocarbonic Ac., $CO_2H.C_6H_4.(CH_2)_2CO_2H$.**—Ndl. e. s. h. aq.—$Ba\bar{A}$, v. s. aq.
166	150	**Dimethylbenzoic(5) Ac., $Me_2.C_6H_3.CO_2H$.** — Pr. v d. s. h. aq.; e. s. alc.—$Ca\bar{A}_2$ ignited w. CaO gives p-xylene.—M. p. of amide 133°.
167	80	**Phenylsuccinic Ac., $CO_2H.CHPh.CH_2.CO_2H$.**—E. s. h. aq.—$(NH_4)_2\bar{A}$ boiled w. $CaCl_2$ sol. gives pulv ppt.
167·5	164	**Prehnitilic Ac., $Me_3.C_6H_2.CO_2H$.**—Glassy pr. fr. alc. "Somewhat s. in aq."
168	152	**Methylphenol(3)-methanoic(2) Ac., $HO.C_6H_3(Me).CO_2H$.**—Ndl. fr. aq. S. in 700 pt. c. aq.; e. s. h. aq.; e. s. alc. or eth.—Aq. sol. gives intense blue-violet w. $FeCl_3$.—Ca salt v. e. s. aq.
168–9	194	**Ferulic Ac., $MeO.C_6H_3OH.C_2H_2.CO_2H.(3, 4, 1)$.**—Ndl. s. h. aq.—After long boiling reduces Fehling's sol.—Floc. yellow. ppt. w. $Pb\bar{A}c_2$.
168–9	94	**Cinchoic Ac., $C_7H_8O_6$.**—Tbl. e. s. h. aq.; d s. eth.—$Ba\bar{A}+3H_2O$, silky ndl., d. s. aq.
169	162	**o-Methylcinnamic Ac., $Me.C_6H_4.CH:CH.CO_2H$.**—Ndl. fr. bz.—Unsat.
169–70	80	**s-Methylethylsuccinic Ac. (fumaroid), $CO_2H.CHMe.CHEt.CO_2H$.**—S. in 51 pt. aq. at 16°.—$Ba\bar{A}+5H_2O$, e. s. aq.
171	178	**p-Methoxycinnamic Ac., $MeO.C_6H_4.CH:CH.CO_2H$.**—Ndl. s. alc.—Unsat.
171–2		[+ and −] **Isocamphoric Ac., $C_{10}H_{16}O_4$.**—S. in abt. 300 pt. c. aq.
171·5–2·5	184	**Camphenylic Ac., $C_{10}H_{16}O_3$.**—Opt. inact.—$Ag\bar{A}$ cryst. ppt.
172	224	**α-Phenylcinnamic Ac., $Ph.CH:CPh.CO_2H$.**—Ndl. e. s. alc. or eth.—Unsat. "(Does not add Br)."—Sbl.
172	152	**Oxytoluic Ac., $Me.C_6H_3OH.CO_2H(1, 4, 2)$.**—Pr. e. s. h. aq.; v. s. alc. or eth.—Brown ppt. w. $FeCl_3$.
172–3		**Oxytoluic Ac., $Me.C_6H_3OH.CO_2H(1, 6, 3)$.**—(Loses $\frac{1}{2}H_2O$ of cryst. at 100°.)—Ndl. e. s. h. aq., alc., or eth. $Cu\bar{A}_2+\frac{1}{2}H_2O$, floc. ppt.; characteristic dark-green crystals fr. h. aq.—M. p. of methylester 67°.
172·5–3	79	**Ethylmesaconic Ac., $C_7H_{10}O_4$.**—Lft. d. s. c. aq.; e. s. h. aq., alc., or eth.—Ca salt separates in ndl. on heating c. sat. sol.
173	226	**Methyldiphenylacetic Ac., $MeCPh_2.CO_2H$.**—B. p. a. 300°.—E. s. eth. or h. alc.—$Ba\bar{A}_2+2H_2O$, cryst. ppt.—Oxid. by CrO_3 mixt. to benzophenone and benzoic ac. (Tests 714 and 312).
173	348	**Tetraoxystearic Ac., $C_{18}H_{32}O_2.(OH)_4$.**—(Fr. oxid. of linoleic ac.) Silky ndl. or pr. fr. bz.—I. c. aq. or eth.; s. in 2000 pt. h. aq.; d. s. alc.—Alkaline $KMnO_4$ gives azelaic ac.—$Ba\bar{A}_2$, floc. ppt.
173–4	240	**Ethyldiphenylacetic Ac., $Et.CPh_2.CO_2H$.**—Lft. fr. dil. alc.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
173·5	276	**Naphthoyl-o-benzoic Ac., $C_{10}H_7.CO.C_6H_4.CO_2H$.**—Pr. fr. dil. alc.—V. d. s. h. aq.—H_2SO_4 gives naphthanthraquinone.—Ba salt, e. s. aq. or alc.
174		**Terebic Ac., $C_7H_{10}O_4$.**—Large monoclin. cryst. fr. alc.; d. s. c. aq.—Not attacked by fuming HNO_3.—W conc. BaO_2H_2 sol. at 150° gives acetone (Test 711) and succinic ac. (Test 320).—Pb and Ag salts e. s. aq.
175	210	**Fluorenecarbonic (4) Ac., $C_{14}H_{10}O_2$.**—Cryst. e. s. alc. or eth.—M. p. of methyl ether 64°.
175	108	**1, 2-Naphthalenedicarbonic Ac., $C_{10}H_6.(CO_2H)_2$.**—Cryst. s. h. aq.—Fusion gives anhyd., m. p. 165°.—$Ba\bar{A}_2$ d. s. ndl.
175	90	**Homophthalic Ac., $CO_2H.C_6H_4.CH_2.CO_2H$.**—Fusion w. soda lime gives toluene (cf. Test 918).—$Ba\bar{A}$, e. s. aq.
175–6		**Camphoronic Anhyd., $C_{18}H_{22}O_9$.**—Alm. i. c. alc., eth., or lgr.—S. in alkalies (forming camphoronic ac., e. s. aq.; m. p. 136°).
176d.	170	**Orsellinic Ac., $Me.C_6H_2(OH)_2.(CO_2H)(1, 3, 5, 4)$.**—Cryst. w. $1H_2O$. E. s. alc. or eth.—Gives purple-violet color w. $FeCl_3$.—Boil w. aq. and test sol. for orcine (cf. p. 95).—$Ba\bar{A}_2+xH_2O$ v. s. aq.
176–7	136	**p.-Toluic Ac., $Me.C_6H_4.CO_2H$.**—B. p. 275° c.—V. s. h. aq.; e. s. alc. or eth.—Oxid. to terephthalic ac. by Test 905–2.—The amide melts at 156°. Odor of methylester intense and agreeable; m. p. 32°.
177c.	152	**Oxytoluic Ac., $C_6H_3(Me)(HO).CO_2H(1, 3, 4)$.**—Sbl.—Ndl. fr. h. aq.—Gives intense violet color w. $FeCl_3$! $Ca\bar{A}_2+3H_2O$, e. s. aq.
177	308	**β-Triphenylpropionic Ac., $Ph_3.C.CH_2.CO_2H$.**—Pr. e. s. alc. or eth.—$Ba\bar{A}_2$, ppt., d. s. h. aq.
178–9	248	[+] **Santonous Ac., $C_{15}H_{20}O_3$.**—Ndl. d. s. c. aq.; e. s. eth. or Na_2CO_3 sol.—$Me\bar{A}$, m. p. 81°–84°.
179	166	**Oxymesitylenic Ac., $Me_2.C_6H_2(OH).CO_2H(1, 3, 4, 5)$.**—Ndl. d. s. h. aq.; e. s. eth.—Gives intense blue w. $FeCl_3$! $Ca\bar{A}_2+xH_2O$, e. s. h. aq.
179	178	**1, 2, 4, 5-Tetramethylbenzoic Ac., $Me_4.C_6H.CO_2H$.**—Lft. v. s. alc.—Sbl.—M. p. of methylester 59°.
(r.h.) 179–82d.	113	**m-Hemipinic Ac., $C_6H_2.(CO_2H)_2(MeO)_2(1, 2, 4, 5)$.**—Sometimes cryst. w. 1 or 2 mols. H_2O.—Pr. d. s. aq.—$FeCl_3$ gives orange-red ppt. in the aq. sol.! Fusion w. KOH gives protocatechuic ac.
180–1	202	**α, α-Methylphenylfuranecarbonic Ac., $C_{12}H_{10}O_3$.**—Sbl. in ndl.—E. s. alc. or eth.; d. s. h. lgr.—Very easily oxid. to benzoic ac. (Test 312) by alkaline permanganate. $K\bar{A}+xH_2O$ ndl. almost i. in x's of alkali.
180·7c.	100	† [+] **Camphoric Ac., $C_{10}H_{16}O_4$.**—Cryst. s. in 160 pt. aq. at 12° or in 11–12 pt. at 100°; v. s. alc., i. CS_2.—Heated in test-tube w. conc. H_2SO_4 evolves CO, which burns w. pale-blue flame.—$Ba\bar{A}+4\frac{1}{2}H_2O$, s. in 1 pt. aq.; $Pb\bar{A}$, i. ppt.—$Na_2\bar{A}$ sol. boiled w. sol. of $MnSO_4$ gives ppt. which redissolves as sol. cools.—The properties of the [−] ac., except the optical ones, are like those of the [+] acid.
181	182	**Veratric Ac., $(MeO)_2.C_6H_3.CO_2H(3, 4, 1)$.**—Cryst. w. $1H_2O$.—Sbl.—D. s. h. aq.; v. s. alc. or eth. Yellow color w. $FeCl_3$.—$Ba\bar{A}_2+6H_2O$, ndl., d. s. c. aq.
181	180	**1, 2, 4-Trimethylphenol(5)-carbonic(6) Ac., $C_6H.(Me)_3(OH)(CO_2H)$.**—Ndl. mod. s. eth.; d. s. other solvents.—Sbl.—Alc. sol. blue w. $FeCl_3$!—Dist. gives CO_2 and pseudocumene (cf. Test 917).
183	152	**Methylphenol(6)-carbonic(2)-Ac., $Me.C_6H_3(OH).CO_2H$.**—Brown ppt. w. $FeCl_3$.—Cf. Sect. 1.
183	144	**s-Diphenylsuccinic Ac., $CO_2H.(CH.Ph)_2.CO_2H+H_2O$.**—Solidifies after melting and fuses again at 220°. V. s. alc.—$Ba\bar{A}_2+2H_2O$, v. d. s. c. aq.
184c.	172	**β-or Iso-Naphthoic Ac., $C_{10}H_7.CO_2H$.**—B. p. a. 300°.—Silky ndl. v. d. s. h. aq. or c. lgr.; e. s. alc. or eth.—$Ba\bar{A}_2+4H_2O$, ndl. s. in 1400 pt. aq at 15°. $Ca\bar{A}_2+3H_2O$, ndl. fr. h. aq.; s. in 1800 pt. aq. at 15°.—Methylester, m. p. 77°.—Test 905–1 gives trimellitic ac.

Melting-point (C.°).	**Neut. Equiv.**	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
184	105	**Phoronic Ac., $C_{11}H_{18}O_5$.**—Froths in fusing; gives anhyd. at 190° (m. p. 138°).—Lustrous pr. fr. dil. alc.; d. s. h. aq.—$Ca\bar{A}$, s. h. aq.
184d.	83	† **Phthalic Ac., o-$C_6H_4(CO_2H)_2$.**—In melting gives the anhyd. **which** sbl. v. e. and melts at 128°.—Rhomb. cryst. s. in 185 pt. aq. at 14°, or in 5·5 pt at 99°. S. in 146 pt. eth. at 15°; e. s. alc.; i. $CHCl_3$.—Apply Test 318!—[The m. p. given (Lossen, A., 144,76), according to Ador (A. 164, 230), holds only for acid that has been prepared by the usual method of precipitation from a soluble salt. A specially purified acid, made from water and the anhyd., is said to melt, when in the powdered condition, at 203°.]
184·2c.	152	**Anisic Ac., p-MeO.$C_6H_4.CO_2H$.**—B. p. 275°–80°.—Monoclin. cryst. alm. i. c. aq.; s. h. aq.; e. s. alc.—$Ba\bar{A}_2$ rhombic tbl. d. s. aq.—In sealed tube w. conc. HCl at 130°, or fusion w. KOH, gives p-oxybenzoic ac.—Ignition w. BaO gives anisol.
185	180	**p-Acetoxybenzoic Ac., $C_2H_3O_2.C_6M_4.CO_2H$.**—Silvery lft fr. $CHCl_3$.
185d.	70	**1, 2, 3-Hemimellitic Ac., $C_6H_3.(CO_2H)_3$.**—Rather d. s. c. aq.—$Ba_3\bar{A}_2+5H_2O$, e. s. aq. (dif. fr. phthalic ac.).—Above 185° gives sublimate of phthalic anhyd. and benzoic ac.; which hence gives fluoresceïn in Test 402–1 like phthalic ac.
185–6	188	**1-Naphtholcarbonic(2) Ac., HO.$C_{10}H_6.CO_2H$.**—Stellate ndl., e. s. eth. or bz.; v. d. s. h. aq.—Sol. of $K\bar{A}$ gives blue color w. $FeCl_3$.—$Ba\bar{A}_2$ d. s. aq. Long boiling w. aq. gives CO_2 and α-naphthol (Test 412).
185–90	196	**Choleic Ac., $C_{24}H_{40}O_4$.**—(In ox-gall.)—Ndl. fr. h. alc.—Cryst. fr c. alc. w. $1\frac{1}{2}H_2O$, then having m. p. 135°–40°.—S. in 22,000 pt. c. aq.; v. d. s. eth.—At 170°–80° gives an anhyd. Boiled w. HCl becomes resinous.
186·5	248	**Chrysenic Ac., $C_{10}H_6.(Ph)(CO_2H)(2, 1)$.**—Lft. fr. bz.; e. s. alc. or eth.—$Ba\bar{A}_2$, e. s. aq.
187–8	274	**Podocarpic Ac., $C_{17}H_{22}O_3$.**—V. d. s. bz.; e. s. eth.—Weak ac.—Ca salt ignited gives p-cresol.—(In a resin fr. Podocarpus Cupressina.)
188–9	176	**β-Methylcumarilic Ac., $C_{10}H_8O_3$.**—Ndl. fr. dil. alc.—Sbl.—Rapid heating gives CO_2 and β-methylcumaron.—$Ba\bar{A}_2+3H_2O$, cryst. fr. h. aq.
189	114	**Tetrinic Ac., $C_5H_6O_3$.**—B. p. 292° d.—Cryst. s. in 66 pt. aq. at 13·5°; e. s. eth. or h. aq.—$Ba\bar{A}_2+1\frac{1}{2}H_2O$, e. s. c. aq.—Reacts w. phenylhydrazine.—Heated w. KOH at 150° gives much formic (Test 315) and propionic ac. (Test 311).—The residue left upon evaporating w. dil. $NaNO_2$ sol. becomes blue when moistened w. a little conc. HNO_3.
191	164	**m-Cumaric Ac., HO.C_6H_4.CH:CH.CO_2H.**—Pr. e. s. h. aq. or eth.
191		**i-Isocamphoric Ac., $C_{11}H_{16}O_4$.**—100 pt. aq. at 20° dissolve 0·203 pt.
192	162	**o-Cumarilic Ac., $C_9H_6O_3$.**—B. p. 310°–15°.—S. h. aq.; v. s. alc.—KOH fusion gives salicylic acid (Test 319).—Ba salt d. s. aq.
192	87	**s-Diethylsuccinic Ac. (fumaroid), $CO_2H.(CHEt)_2.CO_2H$.**—Sbl.—V. d. s. c. aq.; e. s. eth.—$Zn\bar{A}+2H_2O$, more s. c. than h.
192	86	**cis-Hexahydrophthalic Ac. (malenoid), $C_6H_{10}.(CO_2H)_2$.**—4-sided pr. fr. aq. d. s. aq.—Ba salt less s. in h. than c. aq.
194	72	**Ethylfumaric Ac., CO_2H.CEt:HC.CO_2H.**—D. s. aq.; e. s. eth.
194	226	**p-Benzoylbenzoic Ac., Ph.CO.$C_6H_4.CO_2H$.**—Sbl. in lft.—D. s. h. aq; e. s. eth.—$Ba\bar{A}_2+2H_2O$, d. s. c. aq.
195	166	**p-Ethoxybenzoic Ac., EtO.$C_6H_4.CO_2H$.**—Ndl. alm. i. h. aq.—$Ca\bar{A}_2$, ndl fr. h. aq.
195	72	**3-Hexenedioic Ac., $CO_2H.CH_2$.CH:CH.$CH_2.CO_2H$.**—Pr. d. s. c. aq. or eth.—Na amalgam reduces to adipic ac.
195	73	**s-Dimethylsuccinic Ac. (fumaroid), CH(Me)(CO_2H).CH(Me)CO_2H.**—Ndl. d. s. c. aq.; e. s. eth.—Dist. gives anhyd., m. p. 87°.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
195	409	**Cholic Ac., $(CH_2OH)_2.C_{20}H_{31}.CH(OH).CO_2H$.**—Cryst. w. 1 aq.—I. c. aq.; v. d. s. h. aq.; d. s. eth.—Warming w. a little sugar sol. and conc. H_2SO_4 gives a violet-red color! $Ba\bar{A}_2+7H_2O$, s. c. aq.—Aq. sol. dec. by CO_2.—Oxid. by $KMnO_4$.—To 0·02 grm. ac. in 0·5 grm. alc., add 1 cc. $\frac{1}{10}$ normal sol. of I in KI, and gradually dilute w. aq.; ndl. w. yellow metallic lustre, blue by transmitted light, separate. (Dif. fr. other gall acids.)
d. 195	96	**Benzalmalonic Ac., $Ph.CH{:}C.(CO_2H)_2$.**—V. s. h. aq.; "d. s." c. aq.; s. eth.—$Na_2\bar{A}+BaCl_2$ gives ppt., sm. ndl. on boiling (no ppt. cold). Test 303, at 195°–200° gives CO_2 and cinnamic ac. (Test 313).
195d.	87	**Tetramethylsuccinic Ac., $CO_2H.(CMe_2)_2.CO_2H$.**—100 pt. aq. at 13·5° dissolve 0·48 pt.; s. eth.—Fusion gives anhyd. w. camphor-like odor, m. p. 147°.
d. 195–200	170	**Pyrogallocarbonic Ac., $C_6H_2(OH)_3.CO_2H$(2, 3, 4, 1).**—Silky ndl. fr. h. aq.; s. 767 pt. c. aq.; v. s. eth.—Colored violet by v. dil. $FeCl_3$.—Reduces ammon. $AgNO_3$ sol. in the cold.—(Cryst. w. $\frac{1}{2}H_2O$.)
196–7d.	108	**Cineolic Ac., $C_{10}H_{16}O_5$.**—Cryst. s. in 70 pt. c. aq.; e. s. eth.—Dec. by heat to CO_2 and an ac. $C_9H_{16}O_3$.—(An oxid. product of cineol.)
197	162	**p-Methylcinnamic Ac., $Me.C_6H_4.CH{:}CH.CO_2H$.**—Mod. s. h. aq.—Ndl. fr. bz.
199	154	**Protocatechuic Ac.**—Cf. Ac. of Sect. 1.
199		**Lithobilic Ac., $C_{30}H_{58}O_6$.**—Mic. cryst. e. s. alc.; i. aq.; s. eth. Warm conc. HCl colors intense red-violet. Gives Pettenkofer's reaction. —$Ba\bar{A}_2+6H_2O$, i. aq.
199	166	**1, 2-Dimethylphenol(5)carbonic(4) Ac., $Me_2.C_6H_2(OH).CO_2H$.**—Ndl. d. s. h. aq.; e. s. alc. or eth.—Gives intense blue-violet color w. $FeCl_3$! $Ba\bar{A}_2$, d. s. c. aq.
200	304	**Triphenylcarbinol-p-carbonic Ac., $Ph_2.COH.C_6H_4.CO_2H$.**—I. aq.; e. s. eth.—Ba salt v. d. c. s. aq.
200	174	**γ-Methylindene-β-carbonic Ac., $C_{11}H_{10}O_2$.**—Ndl. fr. alc.—Warmed w. MnO_2 and conc. KOH gives a blue solution.
200	138	† **m-Oxybenzoic Ac., $HO.C_6H_4.CO_2H$.**—Dist. undec. Tastes faintly sweet (dif. from para acid).—S. 108 pt. aq. at 18°.—No color w. $FeCl_3$.—$Ca\bar{A}_2+3H_2O$, s. aq.—0·02 grm. boiled w. 5 cc conc. H_2SO_4 gives orange-red (OR) sol. (Dif fr. o- and p-ac, the o-acid giving only pale-yellow, and the p-acid giving orange-yellow (OYT1) when treated in this way.)
200	164	**p-Acetylbenzoic Ac., $Me.CO.C_6H_4.CO_2H$.**—Sbl.—Ndl. rather d s. h. aq.; e. s. eth.—$Ba\bar{A}_2+\frac{1}{4}H_2O$, s. h. aq.
201	298	**Picenic Ac., $C_{10}H_7.C_{10}H_6.CO_2H$.**—Flocks fr. alc.; s. alc. or $CHCl_3$.—Heated w. $Ca(OH)_2$ (i. v.) gives β-binaphthyl.
201		[−] **Camphanic Ac., $C_{10}H_{14}O_4$.**—Rhombohedra fr. eth.—Volat. w. st.—Sbl. easily fr. 110°.—W. aq. at 180° gives CO_2 and a hydrocarbon C_8H_{14}, b. p. 119°.
203	302	**4-Methyltriphenylmethane-2-carbonic Ac., $C_{21}H_{18}O_2$.**—Dist. undec.—Ignition w. $Ba(OH)_2$ gives p-methyltriphenylmethane.
204	212	**m-Tolylbenzoic Ac., $Me.C_6H_4.C_6H_4.CO_2H$.**
204–5		**Lithofellic Ac., $C_{20}H_{36}O_4$.**—(Cryst. w. $1H_2O$ fr. 33% alc.)—S. h. alc. or h. eth. Gives intense red color w. conc. HCl.—(Found in benzoars.)
204–5	92	**Methylfurfurancarbonacetic Ac., $C_4HO.(Me)(CO_2H)(CH_2.CO_2H)$.**—Sbl. undec.—Short ndl., v. d. s. c. aq.; e. s. alc.; s. eth.—NH_4 salt heated gives pyrrol-red.—$Ca\bar{A}$, cryst. ppt. i. h. aq.

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
204–6d.	154	**2, 4-Dioxybenzoic Ac., $(OH)_2.C_6H_3.CO_2H$.**—Cryst. w. $3H_2O$.—S. 381 pt. aq. at 17°.—Aq. sol. colored violet by little $Ca(OCl)_2$ sol.—$Ba\bar{A}_2$ e. s. aq.—$Pb\bar{A}c_2$ gives no ppt.
205d.	91	**Furalmalonic Ac., $C_4H_3O.CH:C.(CO_2H)_2$.**—Pr. alm. i. c. aq.; s. alc. or eth.—$Ag\bar{A}$; curdy ppt.—Loses CO_2 on fusion, giving furfurol acrylic ac.
205–10d.		**Coumalic Ac., $C_5H_3O_2.CO_2H$.**—Sm. pr. d. s. c. aq.; s alc. or eth.—Reduces ammon. $AgNO_3$ or Fehling's sol. on warming.—Boiled w. dil. H_2SO_4 gives crotonic ald.—Boiling aq. sols. of salts gives carbonates.
206	198	**β-Isoatropic Ac., $C_{18}H_{16}O_4$.**—Tbl. fr. h. aq.—Cryst. ppt. w. $BaCl_2$.—Continued heating at 225° gives α-ac., m. p. 237°
206	164	**p-Cumaric Ac., $HO.C_6H_4.CH:CH.CO_2H$.**—V d. s. c., e. s. h. aq.; v. s. eth. or alc.—Alc. sol. becomes golden brown w. $FeCl_3$.—Fusion w. KOH gives p-oxybenzoic ac
206	97	**2, 6-Dimethylterephthalic Ac., $Me_2.C_6H_2.(CO_2H)_2$.**—Ndl. fr. alc ; e. s. eth.—Sbl undec.—$Ba\bar{A}+3H_2O$, pearly lft
206d. (s. h.)		† **Mucic Ac., $CO_2H.(CHOH)_4.CO_2H$.**—Sandy cryst. powder s. in 300 pts. aq. at 14°; i. alc —† Mix 0·01 grm. acid w. 5 drops conc. ammonia in 5-in. test-tube. Evaporate to dryness. Hold soft pine splinter that has been soaked in conc. HCl for several min. in upper part of tube, and ignite residue strongly. Pyrrol vapors evolved develop bright-red color in splinter! ("Pyrrol reaction,"—a simple test, but also given by some other substances)—(M p higher w. rapid heating.)
206d.	222	**α-Anthracenecarbonic Ac., $C_{15}H_{10}O_2$.**—Silky pale-yellow ndl , d. s. h. aq.—Br subst. easily. Oxid. by CrO_3 in $\bar{A}c$ sol. gives anthraquinone.—Dist w. soda lime gives anthracene (Test 912).
206–7c.	152	**2-Oxy-p-toluic Ac., $HO.C_6H_3Me.CO_2H$.**—E s h. aq ; s. eth.; i $CHCl_3$.—Sbl.—Gives no color w $FeCl_3$.—Ignited w CaO gives o-cresol.
207	168	† **Vanillic Ac., $C_6H_3.(MeO)(OH)CO_2H.(3, 4, 1)$.**—Ndl fr. h. aq.; s. 850 pt aq. at 14°; e s eth —Odorless if pure.—Gives no color w. $FeCl_3$.—Salts w. exception of those of Pb and Ag generally soluble.—$Ag\bar{A}$ blackens in h. aq.—Dist of Ca salt w. slacked lime gives pure guiacol (cf. p 91)
208	164	**o-Coumaric Ac., $HO.C_6H_4.CH:CH.CO_2H$.**—D s. c. aq ; d. s. eth ; e. s. alc. —Sbl.—Dec on dist into CO_2 and phenol. (Test 414.)—Fusion w. KOH gives salicylic and acetic acids—Dil. ammonia gives a yellow sol . pale green by reflected light.—$FeCl_3$ gives a yellow-red ppt —$Ba\bar{A}_2+H_2O$, e s aq.
208	100	**i. Camphoric Ac., $C_{10}H_{16}O_4$**—Difficult to cryst—100 pt c. aq. dissolve 0·239 pt.; v s eth —Ba salt ndl. s. in 10 pt aq.
210	138	† **p-Oxybenzoic Ac., $HO.C_6H_4.CO_2H$.**—Pr w $1H_2O$ fr h aq S in 126 pt aq at 15°—Gives amorph. yellow ppt w $FeCl_3$—Dist. dec to phenol (Test 414) and CO_2—Taste not sweet like that of meta ac.
abt. 210	198	**α-Naphthylacrylic Ac., $C_{10}H_7.CH:CH.CO_2H$.**—I h. aq.
210–1	188	**α-Oxy-β-Naphthoic Ac., $HO.C_{10}H_6.CO_2H$.**—Ndl s h. aq.—Gives dirty-red ppt w $FeCl_3$, becoming black on boiling.
210·5	192	**Pentamethylbenzoic Ac., $Me_5.C_6.CO_2H$.**—Cryst. fr h. aq—Sbl.—Methylester m. p 67 5°.
215	86	**Γ trans-Hexahydrophthalic Ac. (fumaroid), $C_6H_{10}.(CO_2H)_2$.**—Lfts. s. in 434 pt. c. aq.—C. alk. permanganate does not attack—Ca salt d. s. aq.
215	85	**Δ^2-Tetrahydrophthalic Ac., $C_8H_{10}O_4$.**—S in 114 pt. aq. (10°). Decolorizes alkaline permanganate sol. at once in the cold, forming oxalic ac and succinic ac.
215	**164**	**1, 2, 3-Trimethylbenzoic(5) Ac., $Me_3.C_6H_2.CO_2H$.—Cryst v. d. s. h aq.; s. eth.—Ca salt d. s. c. aq.—Ignited w. CaO gives 1, 2, 3-$Me_3.C_6H_3$.**

Melting-point (C.°).	Neut. Equiv.	**SOLID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
215	84	**$\Delta^{2,6}$-Dihydrophthalic Ac., $C_6H_6.(CO_2H)_2$.**—Pr. v. d. s. c. aq.; e. s. h.—$Ba\bar{A}$, s. c. aq., less s. h. aq.
215–6d.	247	***Santononic Ac., $C_{30}H_{38}O_6$.**—Pearly lft. fr. alc.; i. aq.; e s. alc.; d. s. eth.—$Ag_2\bar{A}$, ppt.
216	188	**Oxynaphthoic Ac., $C_{10}H_6.(OH).CO_2H(2, 3)$.**—E. s. alc., eth.—Rhomb. lft. fr. h. aq.; e. s. eth.—Sol. becomes blue w. $FeCl_3$!
216–7	206	**Piperic Ac.**—Pale-yellowish ndl.—Cf. Suborder 2.
217	302	**3-Methyltriphenylmethane(6)carbonic Ac., $Ph_2.CH.C_6H_3(Me).CO_2H$.** —Tbl. fr. eth. or alc., i. aq.; e. s. alc. or eth.—Dist. undec.—Ignited w. $Ba(OH)_2$ gives m-methyltriphenylmethane.—$Ba\bar{A}_2+H_2O$, i. ppt.
218–9	198	**p-Phenylbenzoic Ac., $Ph.C_6H_4.CO_2H$.**—Sbl. in ndl.—V. d. s. h. aq.; e. s. alc. or eth.—$Ba\bar{A}_2$, lft. v. d. s. h. aq.
219d.	100	**Diphenylmethanetricarbonic Ac., $(CO_2H.C_6H_4)_2.CH.CO_2H$.**—S. h. aq.—M. p. of trimethylester 145°.
220–1	91	**Camphoric Anhyd., $C_{10}H_{14}O_3$.**—B. p. a. 270° (undec.). Long rhomb. pr. fr. alc.—V. d. s. aq.—Boiling aq. slowly gives camphoric ac., v. d. s. aq. m. p. 187°.—Opt. inact.
221	210	**Diphenyleneacetic Ac., $(C_6H_4)_2CH.CO_2.H$.**—Alm. i. aq.; e. s. alc. or eth.—Ignition w. CaO gives fluorene.
223	166	**1, 3-Dimethylphenol(2)benzoic(5) Ac., $Me_2.C_6H_2OH.CO_2H$.** — Sbl. — Hair-like ndl. fr. h. aq.; e. s. eth.—$Ba\bar{A}_2$ mod. s. c. aq.
227·5–28	166	**Piperonylic Ac., $CH_2.O_2.C_6H_3.CO_2H$.**—Sbl. in pr.; ndl. fr. alc.; d. s. h. aq., e. alc. or eth.—$Ca\bar{A}_2+3H_2O$, s. in 161 pt. aq. at 15°.—$Ag\bar{A}$ cryst. ppt. s. h. aq.
228	194	**Isoferulic Ac., $C_6H_3.(C_2H_2.CO_2H).(OH)(MeO).(1, 3, 4)$.**—Ndl. d. s. c. aq.; e. s. alc. or eth.—$Ca\bar{A}_2+2H_2O$, d. s. ndl.
228	148	**γ-Truxillic Ac., $C_{18}H_{16}O_4$.**—V. d. s. aq.; e. s. eth.—Dist. gives cinnamic ac. (cf. Test 313). Alkaline permanganate gives benzoic ac. (Test 312).—$Ag_2\bar{A}$ ppt.
229	121	**Biphenyl-1,10-dicarbonic Ac., (Diphenic Ac.). $CO_2H.C_6H_4.C_6H_4.CO_2H$.** —Sbl. in ndl. S. h. aq.; e. s. eth.—$Ba\bar{A}+4H_2O$, e. s. aq.—Heated w. Zn dust gives diphenyl.
abt. 230	160	**Indenecarbonic Ac., $C_{10}H_8O_2$.**—Sbl.—V. s. eth.
230–1	90	**2, 5-Dimethylfurandicarbonic(3, 4) (Carbopyrotritaric) Ac., $Me_2.C_4O.(CO_2H)_2$.**—Sm. ndl. fr. h. aq., alm. i. c. aq.; e. s. alc.; s. eth.; v. d. s. CS_2.—Fusion w. KOH gives succinic ac. (Test 320) and acetic ac.—$Ca\bar{A}+Ba\bar{A}$, cryst. ppts. fr. h. aq.; $Ag_2\bar{A}$, ppt.
222–40d.		† **Gallic Ac., $(HO)_3.C_6H_2.CO_2H(3, 4, 5, 1)$.**—Cryst. w. $1H_2O$ (lost at 120°) in silky ndl. S. 130 pt. aq. at 12·5°.—Aq. sol. absorbs O from air and turns brown during titration; gives no ppt. w. sol. of gelatine (dif. fr. tannic ac.).
234–7	188	**α, α-Oxynaphthoic Ac., $HO.C_{10}H_6.CO_2H$.**—Sbl.—S. h. aq.; e. s. alc.—Fusion w. CaO gives α-naphthol (Test 412).—Aq. sol. gives dirty-violet ppt. w. $FeCl_3$.
237	148	**α-Isoatropic Ac., $C_{18}H_{16}O_4$.**—V. d. s h. aq.; alm. i. eth.—$Ca\bar{A}_2+2H_2O$, alm. i. ppt.—Warm conc. H_2SO_4 gives CO. CrO_3 gives anthraquinone (Test 1011).
237–8	90	**Homoterephthalic Ac., p-$CO_2H.C_6H_4.CH_2.CO_2H$.**—S. h. aq.; alm. i. eth. —$Ag_2\bar{A}$, cryst. ppt.
238	154	**2, 5-Diphenylfurandicarbonic(3, 4) Ac., $C_4O(Ph)_2.(CO_2H)_2$.**—D. s. aq.; e. s. alc. or eth.—Sol. in conc. H_2SO_4 becomes blue on warming!—Ignition w. soda-lime gives acetophenone (Test 712).
243	212	**p-Phenyltolylcarbonic Ac., $Me.C_6H_4.C_6H_4.CO_2H$.**—D. s. h. aq.
243	91	**2-Oxyisophthalic(1, 3) Ac., $HO.C_6H_3.(CO_2H)_2$.** — Cryst. w. $1H_2O$. — S. h. aq.; v. d. s. c. aq.; e. s. eth.—Aq. sol. cherry red w. $FeCl_3$! Solutions fluoresce blue-violet; color destroyed by alkali.—Dist. gives CO_2 and salicylic ac. (Test 319).

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Neut. Equiv.	SOLID ACIDS.—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
245	210	**Fluorenic Ac., $C_{14}H_{10}O_2$.**—Sbl. undec.—Alm. i. h. aq.; e. s. h. alc.—$Ba\bar{A}_2+3H_2O$, lft. d. s. c. aq.—Ignition w. CaO gives fluorene.
247	150	**Isocholanic Ac., $C_{25}H_{38}O_7$.**—Pearly scales alm. i. aq. or eth.; e. s. alc.—$Ba_3\bar{A}_2$ d. s. h. aq., not pptd. by CO_2.
250	168	**Isovanillic Ac., $C_6H_3.(MeO)(OH)CO_2H$(4, 3, 1).**—Sbl. undec.; alm. i. c. aq.; d. s. h. aq.—Gives yellow color w. $FeCl_3$.
250d.	140	**Comanic Ac., $C_5H_3O_2.CO_2H$.**—D. s. aq.—No color w. $FeCl_3$.—$Ba\bar{A}_2$, e. s. aq.—Boiled w. baryta water gives acetone (Test 711), oxalic (Test 317) and formic (Test 315) acids.
251	222	**β-Phenanthrenecarbonic Ac., $C_{14}H_9.CO_2H$.**—Sbl.—Alm. i. aq.; s. eth.—$Ba\bar{A}_2+6H_2O$, v. d. s. c. aq.—Ignition w. soda-lime gives phenanthrene (cf. Test 916).—Oxid. w. CrO_3 gives phenanthrenequinone (cf. Test 1013).
(r. h.) 252d.	135	**β-Bibenzyldicarbonic Ac., $C_{14}H_{12}.(CO_2H)_2$.**—Ndl. fr. alc.; i. aq.; s. in 89 pt. abs. alc.—CrO_3 oxid. to benzoic ac. (Tests 905-2 and 3).—Ba salt e. s. aq.
250–60		**Lactic Anhyd., $C_5H_9O_3,CO_2H$.**—Yellowish amorph. mass alm. i. aq.; e. s. alc. or eth.—Alkalies immediately give lactic-acid salts.—Heated, dec. to CO, CO_2, lactide and citraconic ac.
256d.	292	**β-o-Oxynaphthoylbenzoic Ac., $HO.C_{10}H_6.CO.C_6H_4.CO_2H$.**—V. d. s. h. aq.; e. s. alc. or eth.—Fusion w. KOH gives β-naphthol and phthalic ac. (Tests 413 and 318).
255–60	162	**p-Isopropenylbenzoic Ac., $CH_2:CMe.C_6H_4.CO_2H$.**—Ndl. d. s. c. alc.—$Ba\bar{A}_2+H_2O$, amorph. ppt.—Br_2 adds very slowly.
d. 260	180	**Umbellic Ac., $C_6H_3.(OH)_2(CH:CH.CO_2H)$(2, 4, 1).**—S. h. aq.; i. eth.—Browns at 240°.—Reduces ammon. $AgNO_3$ on warming.—$Ba\bar{A}_2$ s. aq.—$Ag\bar{A}$ becomes resinous on boiling.—$FeCl_3$ gives dirty-brown coloration.
d. a. 260		**Comenic Ac., $HO.C_5H_2O_2.CO_2H$.**—S. 16 pt. h. aq.; i. abs. alc.—Pale-yellowish crusts.—Dec. by heat gives CO_2 and pyromeconic ac.—Br substitutes readily.—Red color w. $FeCl_3$.—$Ag_2\bar{A}$ yellow ppt. fr. NH_4 salt.
261d.	211	**Tetraphenylsuccinic Ac., $CO_2H.(CPh_2)_2.CO_2H$.**—E. s. eth.
262d.	92	**2, 6-Pyrondicarbonic [Chelidonic] Ac., $C_7H_4O_6$.**—Silky ndl. w. $1H_2O$ fr. h. aq.; d. s. c. alc.—Many salts yellowish.—Boiling w. milk of lime gives acetone (Test 711) and oxalic ac. (Test 317).
264d.	294	**Triphenylacetic Ac., $Ph_3.C.CO_2H$.**—Softens at 230°.—Ignition w. CaO gives triphenylmethane.
266	222	**α-Phenanthrenecarbonic Ac., $C_{14}H_9.CO_2H$.**—Lft. fr. h. $\bar{A}$c.—Reactions like β-ac. (m. p. 251°).
267	237	**Pyrenecarbonic Ac., $C_{16}H_9.CO_2H$.**—Sbl.—Yellowish warty mass, s. h. alc. or eth.—Heated w. CaO gives CO_2 and pyrene.
270	230	**Biphenyldiol(3, 8)-carbonic(1) Ac., $HO.C_6H_4.C_6H_3(OH).CO_2H$.**—Gives green color w. $Ca(OCl)_2$ sol.—Gives chocolate ppt. w. $FeCl_3$.
abt. 270 (m. p. of anhyd.)	108	**Naphthalic Ac., $C_{10}H_6.(CO_2H)_2$(1, 8).**—The anhyd. is formed at 150° without melting.—Silky ndl. fr. alc.; alm. i. aq.; d. s. eth.—Ignition w. CaO gives naphthalene (Test 915).—The anhyd. dissolves in conc. H_2SO_4 w. blue fluorescence, and boiled w. conc. NH_3 gives the imide of m. p. 300°.
274	148	**2, 4-Diphenylcyclobutanedicarbonic(1, 3), (α-Truxillic) Ac., $C_{18}H_{16}O_4$.**—Ndl. s. eth. or h. alc.—Dist. gives cinnamic ac. (Test 313).
276	99	**α-Resodicarbonic Ac., $(HO)_2.C_6H_2.(CO_2H)_2$.**—Cryst. v. d. s. h. aq.; s. eth.; gives blood-red color w. $FeCl_3$ sol.
277	97	**Hydrocinnamic-p-carbonic Ac., $CO_2H.C_6H_4.(CH_2)_2.CO_2H$.**—Sbl.—S. h. aq. or alc.—Gives nitro-deriv., m. p. 191°–2°.
278c.	196	**Cantharic Ac., $C_8H_{11}O.CO.CO_2H$.**—Cryst., s. 120 pt. c., or 12 pt. h. aq.; v. s. alc.; alm. i. eth.—$Ag\bar{A}$ ppt.—The imide, by heating w. 56 pt. alc. NH_3 at 150°, forms tbl. fr. alc., m. p. 187°.—Ignited w. CaO gives CO_2 and cantharene (C_8H_{12}).

Melting-point (C.°).	Neut. Equiv.	SOLID ACIDS.—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
278	166	**Triphenylmethanedicarbonic(2, 4) Ac., $Ph_2.CH.C_6H_3.(CO_2H)_2$.** —Ignited w. $Ba(OH)_2$ gives triphenylmethane.—$Ca\bar{A}+2H_2O$, ppt.
280–3	90	**Methylterephthalic Ac., $C_6H_3.(Me)(CO_2H)_2(1, 2, 5)$.**—Sbl. below 280°.—$Ba\bar{A}$ v. e. s. aq.
283	252	**β-Anthraquinonecarbonic Ac.**—Cf. Suborder 2.
285d.		**Cholanic Ac., $C_{20}H_{28}O_6$ (?).**—Pr. fr. alc., s. in 4000 pt. h. aq.—Sol. in conc. H_2SO_4 fluorescent. Opt. act.—$Ag\bar{A}$, curdy ppt., Ba salt s. aq.
287–8	90	**s-Uvitic Ac., $C_6H_3.(Me)(CO_2H)_2(1, 3, 5)$.**—Sbl.—Ndl. fr. h. aq., e. s. eth.—$Ba\bar{A}+H_2O$, e. s. aq.—Ignition w. CaO gives toluene (Test 918)!
288c.	91	**5-Oxyisophthalic(1, 3) Ac., $HO.C_6H_3.(CO_2H)_2$.**—(Cryst. w. $2H_2O$.)—Sbl.—E. s. eth. or h. aq.—Gives yellowish-brown color w. $FeCl_3$.—Ignition w. CaO gives phenol (Test 414).
290	128	**Diphenylmethanedicarbonic Ac., $CH_2.(C_6H_4.CO_2H)_2(1:4)_2$**
abt. 290 u. c. sblg.	58	† **Fumaric Ac., $CO_2H.CH:CH.CO_2H$.**—Cryst. s. 148.7 pt. aq. @ 16.5°. Reacts unsat. in Test 302; but adds Br_2 w. difficulty.—Above m. p. gives maleic anhyd. w. sl. decn.—$Me_2\bar{A}$: cryst. fr. dil. alc.; m. p. 102°; (fr. acid+MeOH+dry HCl).—$Ba\bar{A}.1\frac{1}{2}H_2O$: s. 100 pt. c. aq.
290d.	151	**m-Oxyuvitic Ac., $HO.C_6H_2(Me)(CO_2H)_2$.**—E. s. eth. or h. aq.—Gives reddish-violet color w. $FeCl_3$.—$Ba\bar{A}$, e. s. aq.
305	91	**4-Oxyisophthalic(1, 3) Ac., $HO.C_6H_3.(CO_2H)_2$.**—D. s. h. aq.; e. s. eth.—Aq sol. becomes cherry-red w. $FeCl_3$.—Destructive dist. gives phenol and salicylic ac. (Test 319).
d. abt. 320	71	**Muconic Ac., $CO_2H.CH:CH.CH:CH.CO_2H$.**—S. 5000 pt. c. aq.—$Me_2\bar{A}$, m. p. 154°.
320–30	90	**1-Methylisophthalic(2, 4) Ac., $Me.C_6H_3.(CO_2H)_2$.**—Sbl. in thick glassy cryst —D. s. h. aq.; s. h. alc.—Gives no anhyd.—$Ba\bar{A}+2H_2O$, e. s. aq. or alc.
a. 300	83	† **Isophthalic Ac., $m\text{-}C_6H_4(CO_2H)_2$.**—Sbl. undec. without forming an anhyd.—Hair-like ndl. fr. h. aq.—S. in 7800 pt. aq. at 25°, or 460 pt. h. aq.; s. alc.—$Ba\bar{A}+6H_2O$, triclinic cryst., *v. s. aq.* and efflorescent!—$Ag_2\bar{A}$ amorph. ppt., alm. i. h. aq.; swells like a zeolite on heating.—Apply Test 318–2!
a. 300	108	**β-Naphthalenedicarbonic Ac., $C_{10}H_6.(CO_2H)_2$.**—Alm. i. h. bz. or $\bar{A}$c.—Ca salt v. d. s. cryst. ppt.
much a. 300	108	**α-Naphthalenedicarbonic Ac., $C_{10}H_6.(CO_2H)_2$.**—Closely resembles β-acid (above).—Salts somewhat more soluble.
Sb. w. m.	83	† **Terephthalic Ac., $p\text{-}C_6H_4.(CO_2H)_2$.**—Powder.—S. in 67,000 pt. c. aq.; alm. i. alc. or h. aq.!—Alm. i. eth. or $CHCl_3$.—$Ba\bar{A}+4H_2O$, tbl. v. d. s. (1:355·4 at 5°)!—$Ag_2\bar{A}$ ppt.; $Ca\bar{A}+3H_2O$, alm. i. c. aq.—Apply Test 318–3!
345–50	70	**s-Trimesic Ac., $C_6H_3.(CO_2H)_3$.**—Solubility in aq. at 22·5°, 2·69%; at 16°, 0·38%; v. s. alc.—Sbl. at 300°.—BaA_2+H_2O (at 150°); alm. i. c. aq.; v. d. s. h. aq. (dif. fr. iso- and tere-phthalic acids).—$Me_3\bar{A}$ (fr. $Ag_3\bar{A}$ and CH_3I), m. p. 143°.
Sb. w. m.	78	**Furfuranedicarbonic (Dehydromucic) Ac., $C_6H_4O_5$.**—Ndl. fr. h. aq. (dif. fr. terephthalic ac.). V. d. s. alc.; d. s. eth.—Aq. sol. warmed w. $FeCl_3$ in absence of mineral acids gives a transparent jelly.—$Ba\bar{A}+2\frac{1}{2}H_2O$, s. h. aq.!—Dry dist. gives pyromucic ac.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I]

GENUS III, ACIDS.

DIVISION B, SECTION 1,—LIQUID ACIDS SOLUBLE IN COLD WATER.

Boiling-point (C.°).	Neut. Equiv.	**LIQUID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
32·3	60	† **Methyl Formate, H.CO_2Me.**—G. 0·9984$^0/_4$.—S. aq.—Saponified very easily and may be slowly titrated like a monobasic ac.—Test for methyl alc. by Test 819–1, and for formic ac. by boiling the neutral solution resulting from the titration for neut. eq. with $AgNO_3$ sol. Ag will be ppt'd.
100·8	46	† **Formic Ac., H.CO_2H.**—G. 1·2448$^0/_4$.—M. p. +8·6°.—Misc. w. aq.—Neutral salts all s. in aq.—Odor very sharp.—Gives Test 304.—Apply Test 315!
118·1c.	60	† **Acetic Ac., Me.CO_2H.**—G. 1·051$^{20}/_{20}$.—Solidifies at 16·7°. Misc. w. aq.; neutral salts all s. in aq.—Sharp odor.—Does not give Test 304. Apply Test 311!
137	51	† **Acetic Anhyd., (Me.CO)$_2$.O.**—G. 1·0969 at 0°.—Sharp and irritating odor. S. c. aq. and v. slowly decomposed by it.—For behavior on titration cf. p. 37! Identify by Tests 307 and 311!
139·6		**Acetylacetone, CH_3.CO.CH_2.CO.CH_3.**—Cf. IV, B. (A weak acid.)
140	36	**Acrylic Ac., CH_2:CH.CO_2H.**—G. 1·0621$^{16}/_4$.—M. p. +8°.—Sharp odor like Āc.—Gives Test 304.—$Pb\bar{A}_2$ lustrous ndl. s. in alc.—KOH fusion gives formic and acetic ac. (Tests 315 and 311).
140·7c.	74	† **Propionic Ac., C_2H_5.CO_2H.**—G. 0·996$^{19}/_{19}$.—M. p. −22°.—Odor like Āc.—Salts all soluble.—Does not give Test 304.—Apply Test 311!
144d.	70	**Propiolic Ac., CH⋮C.CO_2H.**—M. p. +6°.—S. aq., alc., or eth.—Strong acetic-acid odor.—Dec. by sunlight.—Gives Test 304. Addition product w. Br_2 has m. p. 85°.—Explosive brown ppt. w. ammon. CuCl sol. (Test 906)!—Reduces $AgNO_3$ sol.—Salts v. s. aq., but the solutions are dec. by boiling.
144·8		**Methyl Lactate, $C_4H_8O_3$.**—G. 1·118 at 0°.—Sapon. gives lactic acid (cf. p. 39), and methyl alc. (Test 819–1).
154·5		**Ethyl Lactate, $C_5H_{10}O_3$.**—G. 1·055 at 0°.—Sapon. gives lactic acid (cf. p. 39) and ethyl alc. (Test 814).
155	88	† **Isobutyric Ac., Me_2.CH.CO_2H.**—G. 0·9487$^{19·8}/_4$.—S. in 5 pt. aq. at 20°.—Unpleasant odor like rancid butter.—Aq. sol. of the v. s. Ca salt does not become turbid on boiling (dif. fr. normal Ca salt).—Salts are all more soluble than those of the normal acid.—May be oxid. by alkaline permanganate to acetonic ac. (a reaction used by V. Meyer to detect it in presence of much normal acid).—Identify by Test 311!
162–3	86	**Methacrylic Ac., CH_2:CMe.CO_2H.**—G. 1·0153$^{20}/_4$.—M. p. +14°.—S. aq.—Gives Test 304.—Heated for some time in tube at 130° polymerizes to a porcelain-like mass which dec. above 300°—$Ca\bar{A}_2$, e. s. aq.—Na amalgam gives odor of isobutyric ac.
162·5	88	† **n-Butyric Ac., C_3H_7.CO_2H.**—G. 0·9599$^{19·1}/_4$.—Miscible w. aq. (dif. fr. isobutyric ac.), alc., or eth.—M. p. −7·9°. Unpleasant and persistent odor of rancid butter.—Prepare a clear sat. sol. of the e. s. Ca salt by neutralizing a solution of the acid w. an x s of $CaCO_3$, concentrating, allowing to stand for some time in the cold, and filtering. The cold saturated sol. gives a white ppt. when warmed (dif. fr. isobutyric ac.).—Identify by Test 311!

(ORDER I, SUBORDER I.)

Boiling-point (C.°).	Neut. Equiv.	**LIQUID ACIDS.**—Colorless and generally soluble (cf. note, p. 38) in 50 parts of cold water.
165 s. d.	88	† **Pyruvic Ac., $Me.CO.CO_2H$.**—G. 1·288 at 18°.—Misc. w. aq., alc., or eth.—Sharp odor like $\bar{A}$c.—Readily attacked by Br or $KMnO_4$.—Mixed w. equivalent quantity of phenylhydrazine dissolved in 5 pt. ether gives a hydrazone, cryst. fr. alc., m. p. 192° (r. h.).—Mirror w. ammon. silver sol.—Salts fr. boiling solutions are gummy.—For color reaction w. sodium nitroprusside and ammonia, cf. Compt. rend. 125, 534.
168	86	**Buten(1)oic(4) Ac., $C_3H_5.CO_2H$.**—$Ca\bar{A}_2+H_2O$, lft. fr. h. aq.; cryst. fr. c. aq. w. $2H_2O$. —Gives Test 304.
169–9·3	86	† **Isocrotonic Ac., $Me.CH:HC.CO_2H$.**—G. $1·0312^{15}/_4$.—S. in 2·5 pt. aq.—Odor sharp! Gives Test 304.—$Ca\bar{A}_2$, s. aq.; $Ag\bar{A}$, curdy. ppt.—† Heat 0·5 cc. of the acid w. 5 mgr. iodine for 1 hour in a dry test-tube whose lower end is immersed in an oil-bath at 150°. Dissolve product in 1 cc. hot ligroïn. Cool w. ice-water. Drain crystals which separate on porous tile. Wash w. a few drops cold ligroïn, and dry. The crystals are crotonic acid, and melt at 72° (uncor.)!
176c.	102	**Isovalerianic Ac., $Me_2.CH.CH_2.CO_2H$.**—G. 0·9467 at 0°.—M. p. −51°.—S. 23·6 pt. aq. at 20°; misc. w. alc. or eth.—Odor offensive like decayed cheese!—Alkali salts give no ppt. w. $CaCl_2$; gelat. ppt. w. $ZnSO_4$ in the cold, or scales if hot; v. d. s. cryst. ppt. w. $AgNO_3$.
177 (th. i.)	102	**Methylethylacetic Ac., $Et.CHMe.CO_2H$.**—G. $0·938^{20}/_{20}$.—Feeble odor of isovalerianic ac.—Not solid at −80°.—$Ca\bar{A}_2$, s. aq.—$Zn\bar{A}_2$ more s. c. than h.
182	86	**Trimethylenecarbonic Ac., $C_3H_5.CO_2H$.**—G. $1·0879^{20}/_4$.—M. p. 17°.—"Somewhat" s. in aq.
186–6·4c.	102	**n-Valerianic Ac., $Me.(CH_2)_3.CO_2H$.**—G. 0·9577 at 0°.—M. p. −58·5°.—Odor and solubilities of ac. and its salts nearly the same as for isovalerianic ac. (cf. above).
186·1c.	146	† **Diethyl Oxalate, $C_2O_4.Et_2$.**—G. 1·0815 at 18·2°.—Titrates w. decinormal NaOH like monobasic ac.—Shaken w. conc. ammonia gives an immediate heavy cryst. ppt. of insol. oxamide!—Saponify (Test V), and test for ethyl alcohol (Test 814), and oxalic ac. (Test 317).
190	116	**Methylisopropylacetic Ac., $Me.CHPr.CO_2H$.**—G. 0·928 at 15°.—$Ca\bar{A}_2$ less s. in h. than in c. aq.
190 (th. i.)	116	**Diethylacetic Ac., $Et_2.CH.CO_2H$.**—G. 0·9355 at 0°.—$Ca\bar{A}_2$, e. s.; $Zn\bar{A}_2$ more s. c. than h.
191 (th. i.)	103	**1-Methyltrimethylenecarbonic(2) Ac., $C_4H_7.CO_2H$.**—G. $1·015^{18}/_4$.—S. in 12 pt. aq. at 15°.—$Ba\bar{A}_2+2H_2O$, ndl. v. s. c. aq.
193	116	**Methylpropylacetic Ac., $Me.CHPr.CO_2H$.**—G. 0·9414 at 0°.—$Ca\bar{A}_2$, s. aq.; $Fe\bar{A}_3$ flesh-red ppt. s. in x's $FeCl_3$.
194	100	**Pentene(2)-oic(1) Ac., $Me.CH_2.CH:CH.CO_2H$.**—G. 0·992 at 15°.—M. p. 9·5°–10·5°.—S. in 16 pt. c. aq.—Gives Test 304.—$Ca\bar{A}_2+H_2O$, e. s. aq., alc., or eth.; $Ag\bar{A}$ voluminous ppt.
195–8d.	118	**α-Ethoxypropionic Ac., $Me.CH(OEt).CO_2H$.**—E. s. aq., alc., or eth.—$Ca\bar{A}_2+2H_2O$, e. s. aq.; $Ag\bar{A}$ fine silky ndl. mod. s. c. aq.; v. e. s. h. aq.
200–1	100	**Penten(2)oic(1) Ac., $C_4H_7.CO_2H$.**—G. 1·0074 at 0°.—Lft., m. p. 10°.—Sharp odor.—Gives Test 304.—S. in 16 pt. aq.—Ba salt v. s. aq.
203	90	**Methoxyacetic Ac., $MeO.CH_2.CO_2H$.**—G. 1·18.—Misc. w. aq.—$Pb\bar{A}_2$, s. aq. and alc.
206–7	104	**Ethoxyacetic Ac., $EtO.CH_2.CO_2H$.**—S. aq.—$Ca\bar{A}_2+2H_2O$ v. s. aq. or alc.
213–20	132	**β-Ethoxybutyric Ac., $Me.CH(OEt).CH_2.CO_2H$.**
239 (sl. d.)	116	† **Lævulinic Ac., $Me.CO.(CH_2)_2.CO_2H$.**—M. p. 33°.—Gives iodoform in the cold in Test 801.—Cf. Div. A, Sect. 1.
275 (sl. d.)	130	**γ-Acetylbutyric Ac., $Me.CO.(CH_2)_3.CO_2H$.**—Deliquesces to hydrate w. m. p. 35°–36°.

GENUS III, ACIDS.

DIVISION B, SECTION 2,—LIQUID ACIDS NOT SOLUBLE IN COLD WATER.

Boiling-point (C.°).	Neut. Equiv.	**LIQUID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
168·6	65	† **Propionic Anhyd., $(Et.CO)_2O$.**—G. 1·0169 at 0°.—Sharp and irritating odor.—For behavior on titration cf. p. 37.—D. s. c. aq. and v. slowly dec. by it.—Identify by conversion into propion-p-toluide (cf. p. 81) either by heating w. p-toluidine directly or by methods of Tests 307 and 311 !
181	132	**α-Ethoxyisobutyric Ac., $Me_2.C(OEt).CO_2H$.**—G. 1·0211 at 0°.—D. s. c., e. s. h. aq.—$Ba\bar{A}_2+H_2O$, s. alc. or h. aq.—$Zn\bar{A}_2$, lft., e. s. alc. or eth.
182·5	79	**Isobutyric Anhyd., $(Me_2.CH_2.CO)_2.O$.**—G. 0·9574 at 16·5°.—For behavior on titration cf. p. 37.—Convert into isobutyr-p-toluide (cf. p. 81) either by heating directly w. p-toluidine or by methods of Tests 307 and 311 !
187	116	**Dimethylethylacetic Ac., $Me_2.CEt.CO_2H$.**—V. d. s. aq.—$Ba\bar{A}_2+5H_2O$, e. s. tbl.; $Ag\bar{A}$ ndl. fr. h. aq.; $Zn\bar{A}_2$, d. s. aq.
188 (th. i.)	100	**Allylacetic Ac., $CH_2:CH.(CH_2)_2.CO_2H$.**—G. 0·9842 at 15°.—Unpleasant valerianic odor.—D. s. aq.; e. s. alc. or eth.—Gives Test 304.—No ppt. w. $CaCl_2$.—$Ag\bar{A}$, ndl. fr. h. aq.
189–91	116	**Methylisopropylacetic Ac., $Me.CHPr.CO_2H$.**—Cf. Div. B, Sect. 1.
191–3	79	**n-Butyric Anhyd., $(Pr.CO)_2.O$.**—G. 0·978 at 15·5°.—For behavior on titration cf. p. 37. Identify by conversion into butyr-p-toluide (cf. p. 81) by methods indicated under anhydride of Iso-acid above !
195	100	**Tetramethylenecarbonic Ac., $C_4H_7.CO_2H$.**—G. $1{\cdot}0538^{20}/_4$.—D. s. aq.; misc. alc.—Odor penetrating, unpleasant.—Oxid. by alk. $KMnO_4$; Br_2 does *not* add.—$Ca\bar{A}_2+5H_2O$, v. e. s.; $Ag\bar{A}$ ppt
197 (th. i.)	116	[+]-**Caproic Ac., $Me.CHEt.CH_2.CO_2H$.**—G. 0·930 at 15°.
200–5		**Ethyl Diacetoacetate, $C_6H_7O_4.Et$.**—G. 1·101 at 15°.—D. s. aq.—$FeCl_3$ gives bright-red color to sol. !—"Expels acetic ac. fr. its salts."—$Cu\bar{A}_2+2H_2O$, sky-blue ppt. w. copper acetate.
202–4	114	**Hexen(1)oic(6) Ac., $C_6H_{10}O_2$.**—Ba salt, lft., e. s. aq. or alc.
205·7c.	116	† **n-Caproic Ac., $Me.(CH_2)_4.CO_2H$.**—G. 0·9449 at 0°.—M. p. −5·2°.—Unpleasant odor, like valerianic acid, but fainter.—V. d. s. aq.—$Ca\bar{A}_2+H_2O$, lft. s. in 37 pt. aq. at 18·5°; $Ag\bar{A}$ ppt.; $Zn\bar{A}_2+H_2O$ cryst. ppt. formed when ac. is poured into $Zn\bar{A}c_2$ sol.
206·5 (th. i.)	114	**Hexen(2)oic(6) Ac., $C_6H_{10}O_2$.**—Still liquid at −10°.—Ba salt alm. i. alc.
207–8	130	**Methyldiethylacetic Ac., $Me.CEt_2.CO_2H$.**—Oil, alm. i. c. aq.; still liquid at −20°.—$Ba\bar{A}_2+5H_2O$, ndl. e. s. aq.
207·7c.	116	**Isobutylacetic Ac., $Me_2.CH.(CH_2)_2.CO_2H$.**—G. 0·925 at 20°.—Odor unpleasant.—$Ca\bar{A}_2+5H_2O$, s. aq.
209	130	**Isoamylacetic Ac., $Me_2.CH.(CH_2)_3.CO_2H$.**—G. 0·9122 at 19°.—$Ca\bar{A}_2$, d. s. h. aq.
209·2c.	130	**Ethylpropylacetic Ac., $Me.(CH_2)_2.CHEt.CO_2H$.**—$Ca\bar{A}_2$, more s. in c. than in h. aq.
210	130	**2-Methylhexanoic(1) Ac., $C_5H_{11}.CHMe.CO_2H$.**—Alm. i. aq.—$Ca\bar{A}_2+6H_2O$, ndl., quickly efflorescing; c. saturated sol. becomes turbid on warming.

Boiling-point (C.°).	Neut. Equiv.	**LIQUID ACIDS.**—Colorless and generally not soluble (cf. note, p. 38) in 50 parts of cold water.
211–2	114	**2-Methylpenten(3)-oic(5) Ac., $C_6H_{10}O_2$.**—Oil of unpleasant odor.
213c.	114	**2-Methylpenten(2)-oic(1) Ac.**—Cf. m. p. 24·4°, Div. A, Sect. 2.
213–4c.	56	**Citraconic Anhyd., $C_5H_4O_3$.**—G. 1·262 at 4°.—M. p. +7° (tends to remain liq.).—(Citraconic ac. is v. s. aq., m. p. 80°.)
214–15	114	**Pentamethylenecarbonic Ac., $C_5H_9.CO_2H$.**—G. 1·0385 at 25°.—M. p. −4° to −3°.—Odor like perspiration.
215	93	**Valerianic Anhyd., $(C_5H_9O)_2.O$.**—(Prepared fr. fusel oil.)—G. $0.929^{27}/_4$.—Cf. Test 307.
218 (th. i.)	130	**Teracrylic Ac., $C_7H_{12}O_2$.**—Unpleasant valerianic odor.—Adds Br_2 easily.
219·5	144	**Dipropylacetic Ac., $Pr_2.CH.CO_2H$.**—G. $0·9215^0/_4$.—D. s. aq.—$Ca\bar{A}_2+2H_2O$, s. aq.
221	130	**Act. Amylacetic Ac., $(Me)(Et).CH.(CH_2)_2.CO_2H$.**—G. 0·9149 at 20°.
223	130	**n-Heptylic (Œnanthylic) Ac., $Me.(CH_2)_5.CO_2H$.**—G. 0·9313 at 0°.—"Faint tallow-like odor."—$Ca\bar{A}_2+H_2O$, s. 110 pt. aq. at 8·5°.—$Pb\bar{A}_2$, ppt. (lft. fr. h. aq.); $Zn\bar{A}_2$ easily cryst. fr. h. abs. alc., giving prisms (dried) w. m. p. 132°; $Ag\bar{A}$, ppt., ndl. fr. h. aq.
227c.	140	**Diallylacetic Ac., $(C_3H_5)_2.CH.CO_2H$.**—G. 0·9555 at 15°.—Unpleasant odor.—Alm. i. aq.—Gives Test 304.—$Ca\bar{A}_2+2H_2O$, less s. h. than c.
227 (th. i.)	128	**Hepten(3)oic(1) Ac., $Pr.CH{:}CH.CH_2.CO_2H$.**—Gives Test 304.—$Ba\bar{A}_2$, lft.
230	107	**Diethylacetic Anhyd., $(Et_2.CH.CO)_2.O$.**—Cf. Test 307.
235	144	**2-Methylhexamethylenecarbonic(1) Ac., $C_7H_{13}.CO_2H$.**—G. 1·0079 at 4°.—Odor unpleasant.
237·5c.	144	† **n-Caprylic Ac., $Me.(CH_2)_6.CO_2H$.**—G. $0·9100^{20}/_4$.—Lft., m. p. +16·5°.—S. in 400 pt. aq. at 100°; alm. i. c. aq.—$Ca\bar{A}_2+H_2O$, ndl. v. d. s. c. aq.; $Zn\bar{A}_2$, scales (m. p. 136°); $Ag\bar{A}$ curdy ppt.
238–40		**Diethyl Acetylmalonate, $Me.CO.CH(CO_2Et)_2$.**—Alc. sol. colored dark red by $FeCl_3$!—Cf. Genus IV.
240–2	154	**Cis-trans-Campholytic Ac., $C_9H_{14}O_2$.**—G. $1·017^{15}/_4$.—Unsat.—$Zn\bar{A}_2$, ppt. e. s. eth.
245–6	78	**s-Diethylsuccinic Anhyd., $[CO.(CHEt)_2.CO].O$.**—G. $1·086^{16·5}/_0$.—W. aq. gives mixture of para and anti acids which are d. s. aq.; former melts at 192°, latter at 129°.
245–6	116	† **Lævulinic Ac.**—Cf. Div. A, Sec. 1, M. p. 33°. (If slightly impure usually remains liquid at ordinary temperature after fusion.)
245–8	144	**Cycloheptanecarbonic Ac., $C_7H_{13}.CO_2H$.**—Sharp-smelling oil, remaining liq. at −20°.—$Ca\bar{A}_2$ (at 140°), silky ndl. fr. dil. alc.
253–4 (th. i.)	158	† **Nonylic (Pelargonic) Ac., $Me.(CH_2)_7.CO_2H$.**—G. $0·9068^{17·5}/_4$.—Odor faintly rancid but not very unpleasant.—Leafy cryst., m. p. 12·5°.—$Ba\bar{A}_2$, lft. v. d. s. c. aq.—$Ag\bar{A}$, ppt., v. d. s. h. aq.
257		**[+]-Citronellic Ac., $C_{10}H_{18}O_2$.**—Opt. active.—Odor like capric ac.—Unsat.
264–5	150	**α-Phenylpropionic (Hydratropic) Ac., $Me.CHPh.CO_2H$.**—Heavier than aq. and v. d. s.—$Ba\bar{A}_2+2H_2O$, ndl. s. aq.—$Ag\bar{A}$, scales, e. s. h. aq.—Amide, m. p. 92°.
265·5c.	168	**α-Campholenic Ac., $C_{10}H_{16}O_2$.**—G. 1·0092 at 0°.—I. aq.; e. s. alc. or eth.—Yellow viscous oil w. turpentine odor! Gives Test 304.
266–9		**Phenylacetylacetone, $Ph.CH_2.CO.CH_2.CO.Me$.**—Cf. IV, B.
268–71	121	**Œnanthylic Anhyd., $(C_7H_{13}O)_2.O$.**—G. 0·932 at 21°.—Cf. Test 307.
272	178	**Ethylbenzylacetic Ac., $Et.CH.C_7H_7.CO_2H$.**—$Ba\bar{A}_2$, s. aq.; $Ag\bar{A}$ curdy ppt.
275–80	184	**Umbelulic Ac., $C_{11}H$[illegible]O_2.**—M. p. 21°–23°.—Ag salt cryst. fr. h. aq.—Faint tallowy odor. (From California laurel.)
292 sl. d.	176	**2, 6-Dimethyloctanon(3)-oic(8)Ac., $C_{10}H_{18}O_3$.**—Yellow oil, v. d. s. aq.; e. s. alc. or eth.—Br (in $CHCl_3$) gives oily substitution product.—Ba salt, e. s. alc.
300–10	228	**Amylheptylacetic Ac., $C_5H_{11}.CH(C_7H_{15}).CO_2H$.**—Still liq. at −10°.

NUMBERED SPECIFIC AND SEMI-SPECIFIC TESTS FOR ACIDS.

[TESTS 301–400.]

301. Neutralization Equivalent (Neut. Eq.).

The neutralization equivalent of an acid is the number expressing in grams the quantity of the compound required for the neutralization of one liter of normal alkali. For monobasic acids it is identical with the number representing the molecular weight; for polybasic acids a simple submultiple of this number. In the tables the neutralization equivalent always follows the melting- or boiling-point of an acid in the next vertical column to the right. Its value in this genus ranges from 45 to above 400, and is a numerical constant of great analytical importance.

The determination of neutralization equivalent should be made with a portion of the acid which has been dried to constant weight at 105°–110°, in order to remove hygroscopic moisture or water of crystallization, — the equivalents in the tables having been calculated for the anhydrous acids whenever these are easily obtainable. The titration should be performed with a pure decinormal sodium hydroxide or baryta solution, using phenolphthaleïn as the indicator, and observing all the precautions noted in the observations on Generic Test III (p. 35). If the supply of the substance permits, it will, however, be better to weigh out 0.200 grm. of the acid instead of 0.100 grm., and also to double the quantities of phenolphthaleïn and water or alcohol prescribed. These changes in quantities will not affect the "sharpness limit" demanded in Test III, but will raise the minimum limit of decinormal alkali consumption set for all species of the genus from 2 cc. to 4 cc.

To calculate a neutralization equivalent from the results of a titration, it is only necessary to substitute the experimental data into the following formula:

$$\text{Neut. Eq.} = \frac{1000 \times \text{grams of acid taken}}{\text{cc. of alkali consumed} \times \text{normal strength of alkali}}.$$

If 0.200 grm. of benzoic acid, for example, neutralized 16.41 cc. of a 0.0999 baryta solution, the neutralization equivalent of benzoic acid would be

$$\frac{1000 \times 0.200}{16.41 \times 0.0999} = 122.0.$$

Titrations with decinormal acid and alkali are made with such frequency in organic analysis that it is almost imperative that every organic laboratory should have these solutions, each with its special burette, always ready for immediate use. One of the simplest and most satisfactory arrangements for this purpose is shown in Fig. 2. The bottles, even in small private laboratories, should have a capacity of not less than three liters, and the labels should be inscribed with the dates of standardization as well as the titres of the solutions. The bottle figured in the cut is fitted for use with caustic alkali, and its contents are protected from carbon dioxide by the small guard-tubes A and B, which are packed with granulated soda-lime. The arm C supporting the burette is a strip of wood two inches wide and an inch thick, through which three circular holes have been bored to admit the passage of the neck of the bottle, the tube D, and the burette. After boring the holes the strip is sawed longitudinally through the middle, and the two halves are then tightly clamped in position by the long screws whose heads are visible in the cut. Strips of rubber, leather, or canvas should be wrapped around the glass surfaces at the points of contact to ensure a firm hold on the bottle-neck and burette without risk of crushing them when the screws are tightened. The burette is filled by suction at E, or, if it is preferred, by the action of a pressure-bulb attached at F.

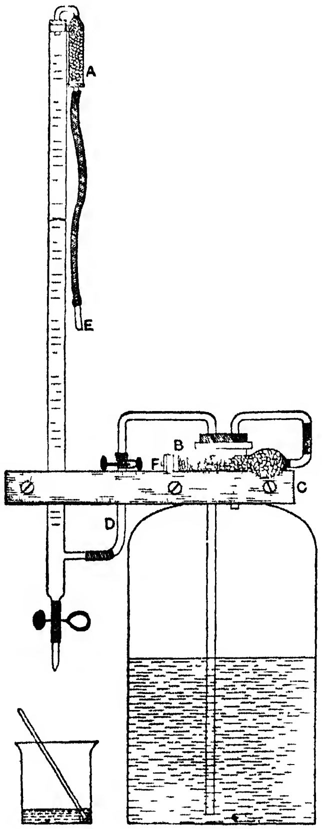

Fig. 2.

302. α-Hydroxy-acids.

Dissolve 0.1 grm. of the acid in 100 cc. of cold water. Place 20 cc. of this solution in a test-tube of about 20 mm. diameter; add one drop of a ten-per-cent aqueous solution of crystallized ferric chloride, and mix quickly. Hold the tube over a sheet of white paper side by side with another of like size, containing 20 cc. of a cold aqueous tartaric-acid solution of exactly the same concentration as that of the unknown acid, and with which one drop of the same ferric-chloride solution has also just been mixed. Compare the "hues" and "tints" of the colors in the two tubes with each other, and with the color standard (cf. p. 232), observing the color from above.

After a few seconds the color of the tartaric-acid solution will be a clear yellow (Y–YT1). If the hue of the solution of the unknown acid is nearly the same, while the intensity of its color equals or exceeds that of the standard, the substance is very likely to be an α-hydroxy-acid. If, on the other hand, the color is distinctly paler than the standard (i.e. lighter than YT1), or is a tint of yellow-orange or orange-yellow, the test has little significance.

This test can be used only with cold solutions; for heat alone develops a yellowish coloration in ferric-chloride solutions of the concentration employed. Nearly all hydroxyl derivatives, when in sufficiently concentrated solution, will give a slight coloration with dilute neutral ferric chloride. The test is therefore valuable only when made comparatively.

While it is not impossible that the hydroxyl group may produce identical color-effects in the case of some acids in which it does not occupy the alpha position with reference to carboxyl, in absence of any direct evidence that such acids exist, it may be assumed that the phenomena of this test are characteristic of the α-hydroxy-acids. Yellow colors approaching Tint 2 are likely to be given by almost any soluble acid. The colors given by the polybasic and keto-acids are much the most intense. Oxalic acid gives YT2–1—GYT2–1. Succinic and glutaric acids give slightly brownish colors, OYT1–2. Malonic acid gives no color. Pyruvic acid gives a Y–YO, and might almost be mistaken for an α-hydroxy-acid. Acetic acid and its homologues give a color that is YT2 or paler.

303. Acids Losing Carbon Dioxide at 200°.

Place 0.1 grm. of the acid in a piece of glass tubing 8 cm. long and 5 mm. in internal diameter, sealed at one end. Connect the open end by a bit of rubber tubing with a narrow gas delivery-tube that leads into a three-inch test-tube ("weighing-tube") containing clear baryta solution. Immerse the tube holding the acid for half its length in a bath of melted paraffin, or the sulphuric-acid mixture of page 219, contained in a small beaker. The bath must have been previously heated to 200° and be held constant at this temperature during the experiment. Continue the heating for two minutes. Acids that lose one or more molecules of carbon dioxide below 200° will give a heavy precipitate of barium carbonate.

This test is given by all acids having two or more carboxyl groups attached to the same carbon atom. Other acids, excepting only a few of unusual instability, do not give it. It is not given, for example, by oxalic, tartaric, citric, lactic, salicylic, tannic, or gallic acids, although none of these compounds are particularly stable substances. Whenever the reaction does take place with a polybasic acid, one product is an acid of lower basicity. Thus, malonic acid gives carbon dioxide and acetic acid: $CH_2.(CO_2H)_2 = CO_2 + CH_3.CO_2H$. By repeating the experiment on a somewhat larger scale, and continuing the heating as long as carbonic acid is given off, the organic acid formed may generally be isolated and identified.

304. Unsaturated Acids.

Dissolve 0.1 grm. of the acid in 3 cc. of sodium-carbonate solution (the ordinary laboratory reagent, about 1 : 10). Then add, drop by drop, a one-per-cent solution of potassium permanganate.

If the purple color of more than 1 cc. of the permanganate is instantly destroyed, and a brown precipitate of oxides of manganese appears, the acid may be unsaturated.

The essential phenomena in this test are very uniform, and easily observed. Several cubic centimeters of the permanganate are usually reduced, and the reaction is practically instantaneous. It is unsafe, however, to draw the conclusion that every acid which shows this behavior *must* be unsaturated. Formic acid, and most phenol acids like oxybenzoic acid and gallic acid, behave like the unsaturated compounds; but saturated acids are, as a rule, very slowly attacked, if at all.

As a confirmatory test for unsaturation in acids, Test 901 is often very useful. But as the addition of bromine at the multiple bonding, on which this reaction depends, takes place very slowly in the case of some of the double-bonded dibasic acids, the results (e.g. with fumaric acid) are occasionally a little difficult to interpret. Other cases in which unsaturated acids do not add bromine easily are discussed by Bauer (Ber. 37, 3317), and Sudborough and Thomas (Soc. 97, 715).

305. Use of Esters with Characteristic Odors.

The odors of many volatile esters are highly characteristic, though an adequate verbal description of their peculiarities can seldom be given. Ethyl cinnamate and ethyl benzoate may both be said to have an agreeable, sweet, aromatic odor; yet no one who is in the least familiar with these compounds would be in any danger of mistaking one for the other. The following procedure is occasionally referred to in the tables as a simple means for distinguishing between acids by differences in the odors of their esters. It is most satisfactory when it can be followed by a duplicate comparative experiment in which the organic acid used is known. The result requires confirmation by other more exact methods.

To a few centigrams of the dry acid in a test-tube, add 0.5 cc. of a mixture of one part of concentrated sulphuric acid and two parts of methyl or ethyl alcohol. Heat the mixture several minutes at about 100°, keeping the tube loosely stoppered and the upper portion cool. Pour off into 3–5 cc. of cold water in a watch-glass. Warm gently and note the odor.

An odor is much more easily observed in the open watch-glass than in a test-tube, and the dilution with water removes the sharp smell of sulphurous acid or alcohol that might otherwise mask the more delicate odor of the ester.

306. Precipitation of Metallic Salts.

The statement in the description of any acid, that its calcium salt is insoluble in water, does not justify the unqualified conclusion that it will appear as a precipitate when an aqueous solution of the acid is mixed with one of calcium chloride; for the salt will often be held in solution by the hydrochloric acid, which is the second product of the reaction. But a precipitate may usually be expected, whenever the neutral sodium salt of an organic acid is mixed with an equivalent quantity of any other neutral metallic salt which by a metathesis could yield a compound described in the tables as "insoluble."

In attempting to prepare an insoluble salt of an acid for analytical purposes, it is therefore a good general rule to start from an exactly neutral solution of its sodium salt, rather than from the free acid itself. To obtain such a solution quickly, a small quantity of the acid may be dissolved or suspended in about twenty parts of water, a trace of phenolphthaleïn added, and caustic-soda solution then dropped in until the first appearance of a pink color; or, when the acid is difficult to obtain in quantity, the solution left over from the determination of neutralization equivalent in Test 301 may be used, after being somewhat concentrated by evaporation.

When engaged in experiments of this kind, it is well to remember that some precipitates which, when once separated from solution, are very insoluble, do not appear *immediately* upon mixing the reagents; also, that some of the most characteristic salts of certain acids with the alkali earths, manganese, and zinc are more soluble in cold than in hot water, and hence do not begin to precipitate until the solutions containing them are heated or boiled.

307. Acid Anhydrides of Genus III.

All these anhydrides are soluble in dilute aqueous alkali to salts of the corresponding acids, though in many cases solution proceeds slowly. A general method for the identification of such compounds is, therefore, to exactly neutralize and dissolve them, while suspended in water, by the addition of an equivalent quantity of caustic-soda solution; to decompose the soluble sodium salts with an exactly equivalent quantity of normal sulphuric or hydrochloric acid; and then, finally, to isolate and examine the liberated organic acid.

A second important method is conversion into anilides or p-toluides. The anhydride is treated—heating above 100° for some minutes is occasionally necessary—with somewhat more than an "equivalent" weight of aniline or p-toluidine. The reaction product is crushed; washed with a little cold dilute acid, to remove the excess of base; and then purified by crystallization from hot water, dilute alcohol, or ligroïn. The anilides and toluides are distinguished for the ease with which they can be crystallized and purified. The melting-points for a very large number have been determined and will be given a place in Vol. II of this work.

311. Acetic, Propionic, Butyric, and Isobutyric Acids.

Whenever these acids have to be identified *in an aqueous solution*—and this is the problem which in actual practice will have to be solved more frequently than any other—the first step should always be to exactly neutralize with caustic soda, and then evaporate to dryness on a water-bath. The dry residue of sodium salt, from which it is not necessary that the water of crystallization should be removed, is then ready for use in the following tests. In very careful work, the result from the "Preliminary Test 1" should be accepted as final only when it is negative. If, on the contrary, it points to the probable presence of one of these acids, Test 2, which is trustworthy and specific, should be applied.

1. [Preliminary Test.]—Place 0.05 grm. of the dry salt in a three-inch test-tube. Add 0.1 cc. of concentrated sulphuric acid, and warm over a very small flame until the odor

of the vapors of the liberated organic acid can be easily recognized at the mouth of the tube. After noting whether the odor is simply sharp like acetic or propionic acid, or sharp and rancid like the butyric acids, cool; add 0.1–0.2 cc. of strong ethyl alcohol, and warm until vapors again begin to come off freely. Then pour into a watch-glass containing 5 cc. of cold water and carefully observe the odor of the ester that has been formed. (Cf. Test 305.) This is sensibly different for the different acids; but the differences are not great and the odors may all be described as ethereal and fruity. That given by acetic acid, and closely resembled by the ester from propionic acid, is often spoken of as "refreshing and agreeable." The test is rather delicate, and, if made comparatively, may *suggest* which of the four acids is present. More than this should not be expected from it.

2. [Identification as Toluides.]—Mix in a dry six-inch test-tube 1.0–1.2 grms. of para-toluidine, and 0.3–0.4 cc. of concentrated hydrochloric acid. Add 0.4 grm. of the powdered sodium salt of the fatty acid. Rest the lower end of the test-tube in a circular hole 1 cm. in diameter cut, by a cork-borer, in a piece of thick asbestos-paper or thin asbestos felt, to screen the side walls from overheating; and support the tube in a vertical position by a clamp on a lamp-stand. Boil gently over a very small gas-flame for one hour. During the first fifteen minutes steam should be allowed to escape slowly. After about twenty minutes, the water having all been removed by evaporation, the vapors of the condensing toluidine should be seen wetting the glass in a ring showing a clearly outlined upper margin and extending half way up the tube. Regulate the heat so that this appearance will continue unchanged to the end of the hour.

[The following treatment of the fused mixture is designed to separate the acid-toluide, the desired product of the reaction ($RCO.NH.C_7H_7$), from the excess of toluidine, and from a dark oily resinous substance, by which it is always accompanied. Resinous residues filtered off in the course of this treatment should never be thrown away until it is found that the yield of acid-toluide will be sufficient for the purpose of identification; for unless properly extracted, small quantities of the resin will hold back the greater part of the toluide. The separation depends on the solubility of the toluides and the insolubility of the resin in boiling water, and on the volatility of toluidine with steam. If the directions given are carefully followed, the yield of pure acid-toluide will be entirely satisfactory, although never large.]

Boil the cooled reaction product with 5 cc. of strong alcohol until nothing but white sodium chloride remains undissolved. Pour the solution, with stirring, into 50 cc. of hot water in a small beaker, and boil down quickly to 10–12 cc. Filter the boiling hot solution through a very small wet filter supported in a funnel that has been warmed by rapid rotation in a flame. Wash the filter with 2 cc. of boiling water. Unless the resin left on the filter forms only an exceedingly thin film, boil out filter and resin with 5 cc. of water, and filter hot into the first filtrate. Boil down the combined filtrates to a volume of about 10 cc. Cool well with running water; shake vigorously and filter. Dissolve the precipitate in 5 cc. of boiling water; or, if it will not dissolve in this volume of water, increase the quantity by successive additions of 1 cc. until all does dissolve. Filter hot through a very small wet filter in a hot funnel 2.5 cm. in diameter. Wash with 2 cc. of hot water. Cool well in running water. Shake and filter. This precipitate should be white and free from resin. If yellowish, another crystallization from 5 cc. of boiling water followed by hot filtration will be necessary. Dry the precipitate at 100°, if the odor of the acid was not rancid,—otherwise at a lower temperature,—and determine its melting-point.

Acetic Acid (properties tabulated on p. 73) gives acet-p-toluide, melting-point 146°–7° (uncor.). The corrected melting-point of the pure compound is 148.2°.

Propionic Acid (properties tabulated on p. 73) gives propion-p-toluide, melting-point 123.5°–124.5° (uncor.).

Isobutyric Acid (properties tabulated on p. 73) gives isobutyr-p-toluide, melting point 104°–5° (uncor.).

n-Butyric Acid (properties tabulated on p. 73) gives butyr-p-toluide, melting-point 72.5°–73.5° (uncor.).

By diminishing the quantities of reagents and solvents used, heating for two hours instead of one, and working very carefully, Test 2 may be carried out with one quarter of the weight of sodium salt recommended; but the yield is then so small that failures will sometimes occur.

The quantity of hydrochloric acid used in a test ought never to exceed greatly the quantity theoretically required to combine with the sodium of the organic salt, toluidine hydrochloride reacting upon the toluides at high temperatures. Hence, if the quantity of salt taken for any experiment is less than has been directed, the hydrochloric acid must be diminished proportionally. A moderate excess of para-toluidine will, however, do no harm, and the quantity should under no circumstances be reduced to less than 0.5 grm.

Test 2 may be used for the identification of acids containing slight admixtures of homologues. In the case of acetic acid it is still applicable when the impurity is quite considerable, if the first crop of impure acet-toluide crystals is recrystallized from hot benzene. The benzene gives at the same time a good separation both from the resin and from homologues. The other toluides are too soluble in benzene to be crystallized from it with advantage, but they may be recrystallized from a few cubic centimeters of hot petroelum ether, in which the resin will remain dissolved on cooling.

Whenever it is desired to separate the acids under consideration from a dilute aqueous solution containing salts, neutral compounds of any description, or non-volatile acids, proceed as follows: Distil over into a dish containing 3 cc. of normal caustic-soda solution, or 0.12 to 0.14 grm. of solid caustic soda dissolved in a little water, the solution being colored by the addition of a little phenolphthalein. As soon as enough acid has distilled over to discharge the pink color, evaporate to dryness, scrape together the residue of dry sodium salt, and use the whole of it for Test 2.

312. Benzoic Acid. (Properties tabulated on p. 60.)

1. To 0.1 grm. of the acid in a dry test-tube add 0.17–0.20 grm. of phosphorus pentachloride, and warm, stirring with a glass rod until a clear solution is obtained. Cool, and add, drop by drop, cooling, 1 cc. of cold water to destroy the excess of chlorides of phosphorus. Then add slowly 0.4–0.5 cc. of aniline. Dissolve the reaction product in 2 to 5 cc. boiling dilute alcohol (1 : 1). Cool. Filter off the white crystalline precipitate; dry at 100°, and determine the melting-point.

The *benzanilide* obtained from benzoic acid in this test is in the form of pearly-white scales melting at 159.5°–160.5° (uncor.).

2. Heat in a six-inch test-tube for one-half hour 0.1 grm. of the acid, 0.5–0.7 grm. of para-toluidine, and two or three drops of concentrated hydrochloric acid. The tube must be supported by a clamp, and its bottom made to rest in a circular hole 1 cm. in diameter, cut by a cork-borer in a piece of thick asbestos-paper which has been laid upon the small iron ring of a lamp-stand. Heat with a very small flame whose height is so regulated that the vapor of the boiling toluidine shall condense upon the walls of the tube for a distance of two to three inches from the lower end. Dissolve the reaction product in 10 cc. of dilute alcohol (1 : 1). Filter hot. Cool and filter. Wash the crystalline precipitate with 5 cc. of cold water. Repeat the crystallization with the same quantity of solvent, and wash as before with 5 cc. of water. Dry at 100°–105° and determine the melting-point.

p-Benztoluide, the product in this test, crystallizes in white or slightly yellowish plates melting at 155.5°–156.5° (uncor.).

313. Cinnamic Acid. (Properties tabulated on p. 61.)

1. Stir 0.05 grm. of the acid into 3 cc. of a cold ten-per-cent solution of potassium

permanganate on a watch-glass or in a small round-bottomed glass dish. A strong odor of bitter almonds (benzaldehyde) will immediately develop.

2. Stir 0.1 grm. of the powdered acid into 3 cc. of fuming nitric acid (sp. gr. 1.48–1.60), contained in a small round-bottomed dish. The substance will at first dissolve, but within two or three minutes a considerable light-colored precipitate will separate. Allow to stand for 7–10 minutes. Then mix with 30 cc. of cold water and stir for a minute. Filter off the bulky precipitate of nitro acids and wash with 10 cc. of cold water. Transfer the precipitate to a test-tube and boil with 5 cc. of strong alcohol. Cool well. Shake, and allow to stand a few minutes to insure complete precipitation. Filter, and wash with 5 cc. of cold alcohol. Boil up the precipitate in a test-tube with 5 cc. of ether. Cool. Shake and filter. Wash the rather scanty precipitate with 5 cc. of cold ether. Dry at 100°, and make a melting-point determination.

The final product in this test is *para-nitrocinnamic* acid. It is more or less distinctly crystalline, nearly white, and melts to a dark-brown liquid at 286°–287° (uncor.), after turning brown and beginning to soften at about 265°–270°.

[Ortho-nitrocinnamic acid, and possibly a little nitrobenzoic acid, are also formed during the nitration, but they are completely removed by the treatment with alcohol and ether.]

314. Color Reactions for Citric, Malic, and Tartaric Acids.

To 0.05 grm. of the finely powdered acid in a small porcelain evaporating-dish add 10–15 drops of a freshly prepared solution of 0.1 grm. β-naphthol in 5 cc. of pure concentrated sulphuric acid. Place the dish on a boiling water-bath and remove it at intervals of thirty seconds to one minute for the observation of the color changes which follow one another in quite rapid succession. When the maximum color intensity has been reached, dilute cautiously with four to five volumes of water and again note all the changes that occur.

Citric Acid (cf. p. 47) gives at first a pale greenish blue, soon turning to blue-green (BG), and finally, rather slowly on continued heating, to an *impure green of very slight intensity* and permanence. The color after dilution with water is similar in quality to that from tartaric acid, only very much paler.

Tartaric Acid (cf. p. 48), after exhibiting a momentary pale blue-green color changes very rapidly to *pure intense green* (G), which is rather persistent, even when heated on the water-bath. The dilution with water causes a change to a very distinct orange-yellow (YO–OY).

Malic Acid (cf. p. 43) at first gives a momentary greenish yellow (GY–Y) that changes rapidly to an *intense yellow* (Y) which is quite permanent. Dilution gives a yellow-orange (YO), which is distinctly more intense than the corresponding color from the two other acids.

These tests were first described by Pinerua (Compt. rend. 124, 291). While not conclusive unless supported by other specific tests, they are useful reactions. They are most satisfactory when used as "comparative tests."

315. Formic Acid. (Properties tabulated on p. 73.)

Formic acid has a very sharp penetrating odor much like that of acetic acid, but more irritating. Like other acids of its series, aqueous solutions of its neutral sodium salt show reddish or orange colorations with ferric chloride. Unlike its homologues it reduces alkaline permanganate in the cold in Test 304.

1. To 5 cc. of a 1–3 per cent aqueous solution of the acid, add one gram, or an excess, of powdered mercuric oxide. Warm to a temperature of 40°–50°. Close the mouth of the tube with the thumb and shake vigorously for about one minute. Filter off the

undissolved oxide, and boil the clear filtrate for at least half a minute. A dark gray precipitate of finely divided mercury will appear suddenly within a few seconds after boiling begins. $HgO + CH_2O_2 = Hg + CO_2 + H_2O$.

2. Place at least two drops of strong acid, or 0.1 grm. of the dry sodium salt in a small "weighing-tube" (a narrow three-inch test-tube). Add five drops of concentrated sulphuric acid and heat over a very small flame until a brisk effervescence begins. Ignite the escaping gas. [$H_2CO_2 = H_2O + CO$.] The carbon monoxide will burn at the mouth of the tube with a pale-blue flame for some seconds, if the heating is continued.

316. Glutaric Acid. (Properties tabulated on p. 42.)

In a dry test-tube fitted with a cork stopper and a 25 cm. length of glass tubing, to act as a return condenser, heat 0.1 grm. of the acid with 0.4–0.6 cc. of aniline at 175°–190° for one hour. Boil with 10 cc. dilute alcohol (1 : 1). Cool and filter. Wash with 2 cc. cold dilute alcohol (1 : 1). Crystallize from 5 cc. boiling strong alcohol. Cool, shaking if no precipitate appears at once. Filter. Wash with 1 cc. cold strong alcohol. Recrystallize from 4 cc. boiling strong alcohol. Filter. Wash with 1 cc. cold alcohol. Dry at 100°, and determine the melting-point.

The product, *glutaranilide*, crystallizes in white needles and melts at 221°–222°. It begins to sublime slightly at 214°–218°.

317. Oxalic Acid. (Properties tabulated on p. 42.)

1. Dissolve a few centigrams of the acid in water. Add ammonia in excess, and then a few drops of calcium-chloride solution. A white pulverulent precipitate of calcium oxalate will at once make its appearance. The precipitate is insoluble in ammonia or acetic acid, but dissolves readily in dilute hydrochloric acid.

2. In a dry three-inch test-tube (small "weighing-tube") place 0.1 grm. of the acid and five drops of concentrated sulphuric acid. Heat over a very small flame so as to obtain a brisk effervescence. Ignite the gas that issues from the tube—(a mixture of carbon monoxide and dioxide). The carbon monoxide will burn with a pale-blue flame for several seconds, if the application of heat is continued.

3. Heat in a six-inch test-tube for fifteen minutes 0.1 grm. of the acid and 0.5–0.7 grm. of para-toluidine. The bottom of the test-tube should be made to rest in a circular hole 1 cm. in diameter cut by a cork-borer through a piece of heavy asbestos-paper. The tube should be supported in an upright position by a clamp, and the asbestos-screen rested upon the small iron ring of a lamp-stand. Heat with a very small flame protected from drafts, and so regulated that the toluidine vapors shall be seen to condense and flow back along the walls of the lower third or half of the tube. Boil out the reaction product with 10 cc. of dilute alcohol (1 : 1). Cool and filter. Wash the residue of oxaltoluide on the filter with 5 cc. of cold water. Transfer to a test-tube and boil up with 10 cc. of strong alcohol. Cool and filter. Wash with 2 cc. of strong alcohol. Dry at 100°–110°, and determine the melting-point.

Oxal-para-toluide crystallizes in white plates melting at 266.5°–267.5° (uncor.).

318. The Phthalic Acids.

The different behavior of these isomers towards heat is an important distinguishing characteristic. Phthalic acid melts with loss of water at 184°, giving a sublimate of thin flat needles of its anhydride. Isophthalic acid also melts and then sublimes; but this occurs above 300°, and the sublimate is the unchanged acid. Terephthalic acid sublimes unchanged above 300°, but without previously melting.

Phthalic Acid. (Properties tabulated on p. 67.)

1. Mix 0.05 grm. of the powdered acid with an equal quantity of resorcin. Place in a dry test-tube and moisten with one drop of concentrated sulphuric acid. Stand the

test-tube in a small beaker containing a liquid bath (cf. p. 152), that is, at a temperature of 160°, and heat for three minutes. Cool. Treat the fused mass with 2 cc. dilute sodium-hydroxide solution. Pour off into 500 cc. of cold water. The water will show a very intense yellow-green fluorescence due to fluoresceïn (cf. Test 402). The isomers of phthalic acid do not give this reaction, though similar colorations are given by some other dibasic acids, like succinic and glutaric. The test is extremely delicate.

2. Heat in a six-inch test-tube for fifteen minutes 0.1 grm. of the acid and 0.4–0.6 cc. of aniline. The tube must be supported by a clamp, and its lower end rest in a circular hole 1 cm. in diameter cut by a cork-borer through a square piece of thick asbestos-paper that is supported on the iron ring of a lamp-stand. Heat with a very small flame whose height is so regulated that the boiling aniline vapor shall be seen to condense upon the walls of the tube for a distance of two or three inches from its bottom. Boil the reaction product with 10 cc. dilute alcohol (1 : 1). Cool and filter. Wash the precipitate with 5 cc. of cold water. Recrystallize from 10 cc. of boiling strong alcohol. Cool and filter. Dry at 100°, and determine the melting-point.

o-Phthalanil, the product in this test, crystallizes in white plates which melt at 204°–205°.

Isophthalic Acid. (Properties tabulated on p. 72.)

Mix in a dry test-tube 0.1 grm. of the acid and 0.3 grm. of phosphorus pentachloride. Heat cautiously over a very small flame until the mixture fuses to a clear liquid. Cool. Dissolve in 2 cc. of pure methyl alcohol.

Precipitate out the dimethyl isophthalate formed, by adding 5 cc. of cold water, cooling and shaking. Filter. Wash the flocculent crystalline precipitate with 2 cc. of cold water. Recrystallize from 4 cc. of boiling dilute methyl alcohol (1 : 1). Cool well. Shake. Filter, and wash with 2 cc. of cold water. Press the precipitate between dry filter-paper. Dry at a temperature not exceeding 50°, and determine the melting-point. *Dimethyl isophthalate* melts at 64° (uncor.). It is very much more soluble in dilute methyl alcohol than the corresponding terephthalate.

Terephthalic Acid. (Properties tabulated on p. 72.)

Follow the direction given in the test for isophthalic acid, as far as the close of the first paragraph. Then precipitate the dimethyl ester from the methyl-alcohol solution by the addition of 10 cc. of cold water. Filter, and wash the precipitate with 5 cc. of water. Recrystallize from a boiling mixture of 4 cc. strong methyl alcohol and 1 cc. of water. Filter off the heavy precipitate of thin, white, lustrous crystals that separates when the solution cools, and wash with 3 cc. of dilute methyl alcohol (1 : 1).—[*Dimethyl terephthalate* melts at 140°. This test might be successfully conducted, if it were necessary, with much smaller quantities of acid and reagents than are here recommended.]

319. Salicylic Acid. (Properties tabulated on p. 64.)

(1) Prepare the methyl ester from methyl alcohol and 0.05 grm. of the acid or one of its salts by the method of Test 305.

Methyl salicylate has the agreeable odor of oil of wintergreen. There are a few rare phenol-acids that are said to have a somewhat similar odor; but it is one that is not given by the isomers of salicylic acid, or by any acid of commercial importance.

(2) Dissolve 0.1 grm. of the acid in 5 cc. of boiling water. Add 1 cc. of nitric acid (sp. gr. 1.2) and boil gently for five minutes. Pour into 20 cc. of cold water. Filter off the precipitate. Wash with 2 cc. of cold water. Recrystallize twice—the first time from 5 cc. of boiling water; the second time from 3 cc. Dry, and determine the melting-point.

5-Nitrosalicylic acid, the product in this test, crystallizes in white needles which begin to sinter together at 220°–222°, and then melt sharply to a brown liquid at 226°–227° (uncor.).

[The purple coloration (RV–VR), which will be observed in a 1 : 10000 aqueous solution of the acid while applying Generic Test IV with ferric chloride, is a simple and favorite reaction. It is said to be sufficiently delicate to show the presence of the acid in solutions containing only one part in 500,000 parts of water. It is also given by neutral solutions of salicylates of the alkalies, but is prevented by the presence of free acids, alkalies, or salts of strongly alkaline reaction, like the alkaline carbonates or borax. The isomers of salicylic acid do not give it.

Calcium and barium chlorides do not give a precipitate in neutral solutions of sodium salicylate, even after dilution with an equal volume of alcohol, or after adding ammonia and warming. Sharply ignited above its melting-point, salicylic acid emits a faint odor of phenol.]

320. Succinic Acid. (Properties tabulated on p. 49.)

Place in a dry test-tube 0.1 grm. of the acid and 0.5 grm. of para-toluidine. Immerse the lower part of the tube in a small beaker containing one of the liquid baths mentioned on page 152. Insert a cork stopper fitted with a 25 cm. length of glass tubing to serve as a return cooler, and heat for one half hour at 200°–220°. After the tube has been removed from the bath and allowed to partially cool, add 10 cc. of dilute alcohol (1 : 1), and boil. Cool well and filter off the crystalline precipitate of succintoluide. Wash with 2 cc. cold dilute alcohol (1 : 1). Crystallize from 5 cc. of boiling strong alcohol. Filter. Wash the crystals with 1 cc. cold strong alcohol. Dry at 100°, and take the melting-point.

The *succintoluide* thus obtained forms white needles melting at 254.5°–255.5° (uncor.).

CHAPTER VI.

GENUS IV. PHENOLIC COMPOUNDS

OF

SUBORDER I, ORDER I.

(Colorless Compounds of Carbon, Hydrogen, and Oxygen.)

To this genus belong all the true phenols of the suborder not included in the foregoing genera, and many non-aromatic "enols."

GENERIC TEST IV.

APPLY PROCEDURE 1 OF THIS TEST FIRST TO EVERY COMPOUND, SOLID OR LIQUID. APPLY PROCEDURE 2 TO EVERY SOLID COMPOUND THAT FAILS TO GIVE A COLORATION IN PROCEDURE 1; BUT NOT TO LIQUIDS. COMPOUNDS THAT SHOW A PHENOLIC BEHAVIOR IN THE FIRST PART OF THE TEST ARE CLASSIFIED AS PHENOLS IRRESPECTIVE OF THEIR BEHAVIOR IN PROCEDURE 2.

PROCEDURE 1.

(The Test with Ferric Chloride.)

Dissolve about 0.05 grm. of the substance in 1 cc. of cold water; or, if this should be found impossible prepare a hot saturated aqueous solution; cool; filter, and use 1 cc. of the cold saturated filtrate. To this solution, in a narrow three-inch test-tube (small weighing-tube), held in front of a sheet of white paper, add three drops of the ferric-chloride reagent described below,* pausing for a few seconds after the addition of each drop to note whether any color change occurs. If no coloration is noticed, repeat the test in the same way as before, except that alcohol is substituted for water as the solvent.

If any coloration, transient or permanent, other than a tone of yellow or orange-yellow (Y or OY), is observed, the substance is probably a phenol or an enol.

PROCEDURE 2.

(The Test with Alkali.)

a. Place 0.10 grm. of the *finely powdered* substance in a narrow three-inch test-tube with 1 cc. of cold water, and ascertain by shaking and stirring whether it will dissolve. If it dissolves *completely* in the cold, and gave no color with ferric chloride in Procedure 1, it is not a phenol.

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* **The Ferric-chloride Reagent.**—Prepare the reagent as required for use by diluting three drops of the 10 per cent stock solution of ferric chloride with 1 cc. of water.

b. If the substance did not dissolve appreciably in experiment a, add 1 cc. of a cold aqueous sodium-hydroxide solution (1 : 10) to the mixture. Shake or stir well for about one minute, and notice whether solution is effected, and whether any strong coloration is produced. If the compound now dissolves completely, or if it dissolves completely after diluting the alkaline mixture with an additional cubic centimeter of cold water, the compound should be sought among the phenols. The appearance of any pronounced coloration in the alkaline solution, also shows the compound to be a phenol, though most of the phenols give colorless solutions in alkali.

If a considerable part of the substance, though not all, dissolves in experiment *a*, add a little more of it to the solution, so that an undissolved residue of about 0.10 grm. shall remain. Treat this mixture with sodium hydroxide just as directed in the last paragraph, except that the subsequent dilution with water should be omitted in this case, unless a change in the appearance of the powder should indicate strongly that the formation of a sodium salt insoluble in concentrated alkali has taken place. The phenomena observed are to be interpreted as in the last paragraph.

OBSERVATIONS ON GENERIC TEST IV.

In "the test with ferric chloride" yellow and orange-yellow colorations have to be disregarded, because tones of these hues are produced by many polyatomic alcohols belonging to subsequent genera. A strong yellow also appears whenever alcohol is substituted for water as the solvent. Fortunately the colorations given by phenols, although varying widely in hue, intensity, and permanence, are not very often yellow, or either of the two adjacent hues in the color standard. The colorations characteristic of some phenols appear in extremely dilute solutions, others only in concentrated solutions. Some remain unchanged in quality for many hours; others appear and disappear within a second. A trifling excess of the reagent is sometimes sufficient to destroy the color; in other cases it is beneficial or necessary. It is for this reason, that it is desirable to observe the color after the addition of each drop of the chloride. The ferric-chloride test is applicable to cold solutions only. For further information concerning this reaction see numbered Tests 302 and 401.

In "the test with alkali" several distinct principles are involved. The first and most important of these is, that, with the exception of some polyatomic phenols like resorcin and pyrogallol, the species of this genus as a class are not "easily soluble" in cold water, although they do dissolve readily in cold sodium-hydroxide solutions of certain concentrations. For the larger number of species a "normal" concentration of the alkali has been found to be the best. But since the sodium salts of some phenols (e.g. sodium-methyl salicylate) are much less soluble in strong caustic soda than in water, they occasionally appear as precipitates even when the alkali used is only normal. It is to provide for this contingency that it is directed to dilute with about one volume of water whenever a precipitate (an insoluble sodium phenolate) is found to form. The use of a weaker alkali at the start is not advisable, because the salts of many phenols are so completely hydrolyzed in solution, unless a considerable excess of alkali is present, that their solubility in decinormal soda may appear to be no greater than in pure water. Finally, it should be mentioned that a few compounds having phenolic structure will not dissolve unless the alkali is much stronger than normal. But their number is so small that it has been considered better to treat them as exceptions than to complicate the test for the sake of assuring them a position with the other phenols.

The production of a colored solution in the test with alkali is not a general reaction of the phenols, but whenever a coloration does appear at this point, or in the titration in Test III, in the examination of an unknown substance, it is a very significant phenomenon, and is alone sufficient to indicate that the body should be sought among the phenols. The colors are sometimes very brilliant, as with the phthaleïns, but often yellow, and sometimes dark brown, appearing gradually on stirring. Brown colorations are characteristic of phenols like pyrogallol, whose alkaline solutions are rapidly oxidized by the absorption of atmospheric oxygen.

It is necessary to restrict "the test with alkali" to solid phenols, because it has been found that a considerable number of liquid species in Genus V and VI (e.g. diethyl succinate), which react neutral in Test III with very dilute alkali, are saponified by short shaking with a 1 : 20 aqueous soda solution. Since the liquid phenols, so far as is certainly known, all give colorations with ferric chloride, this limitation placed on the application of the alkali test is accompanied by no serious disadvantages.

General Physical and Chemical Characteristics of the Phenols and Enols.

Many of the phenols, like ordinary phenol, eugenol, and methyl salicylate, possess intense and characteristic odors and tastes; but many solid species are odorless and tasteless. All except a few of the simpler phenols, such as ordinary phenol, resorcin, and pyrogallol, are nearly insoluble in cold water, though soluble in solutions of the caustic alkalies. All the water-soluble species either give colorations in the test with ferric chloride, or else solutions in dilute sodium hydroxide that rapidly turn brown through oxidation upon exposure to the air. In alkaline solution many phenols reduce potassium permanganate in the cold in Test 304, and a smaller number, including many of the polyatomic phenols, reduce metallic silver from Tollen's reagent in Test 101. The phenols are as a rule readily soluble in cold concentrated sulphuric acid, being very easily sulphonated, and are not reprecipitated upon dilution with water. In Test VIII they evolve hydrogen when treated with sodium, and are sometimes acetylated in the treatment with acetic anhydride. The color reactions of the phenols are numerous. Those depending upon fusion with phthalic anhydride (cf. Test 402), treatment with sulphuric acid containing oxides of nitrogen, or with aromatic diazonium salts, all have analytical application. Colorations obtained with ferric chloride, as in Test IV, have been described for about half the solid species mentioned in this volume, and for nearly every liquid species. These colorations are ascribed to the formation of unstable iron salts. Some phenols, like α-naphthol, whose dilute aqueous solutions are little or not at all colored by ferric chloride, are oxidized by it, and then separate from the solutions as precipitates of insoluble condensation products (like dinaphthol). A portion of the aromatic hydrogen in phenols is very easily substituted by halogens or by nitro groups, poly-halogen, or poly-nitro derivatives being formed. Even very dilute aqueous phenol solutions consequently give precipitates upon treatment with an excess of bromine water (cf. Test 414-3). Test 901 may also be applied when evidence as to ease of substitution by bromine is desired. The nitro derivatives are readily prepared on the small scale, and are very often useful in completing identifications (cf. Tests 414-(2), 415, 418-(2), and 419). A few phenols, like guiacol (cf. p. 91), give characteristic crystalline derivatives with picric acid.

One of the most important reactions of the *enols* is their behavior upon saponification. The saponification may be conducted, and the saponification products identified, by the method of Part 2 of Test V, as described on pp. 113 *et seq.* The following are examples of such reactions:

$$\underset{\text{(Acetyl acetone)}}{CH_3.CO.CH_2.CO.CH_3,\ (\text{or, } CH_3.C(OH):CH.CH_3)} + KOH = \underset{\text{(Acetone)}}{CH_3.CO.CH_3} + \underset{\text{(Potassium acetate)}}{CH_3.CO_2K.}$$

$$\underset{\text{(Acetoacetic ether)}}{CH_3.CO.CH_2.CO_2Et,\ (\text{or, } CH_3.C(OH):CH.CO_2Et)} + 2KOH = K_2CO_3 + \underset{\text{(Acetone)}}{CH_3.CO.CH_3} + \underset{\text{(Alcohol)}}{EtOH.}$$

The names usually applied to the enols in the tables of this volume, and in the illustrations here given, are those properly belonging to the ketones with the corresponding desmotropic formulæ. This keto nomenclature, while open to criticism, is used, because, besides being probably the one in more general use at the time of writing, it also more quickly suggests the names of the saponification products that are to be expected. The enols, like the phenols, are soluble in cold dilute alkalies, give colorations with ferric chloride, and are attacked by sodium or bromine. When shaken with a saturated solution of copper acetate in water or dilute alcohol, some enols give precipitates of stable and characteristic blue or green copper salts.

GENUS IV, PHENOLIC COMPOUNDS.

DIVISION A,—SOLID PHENOLIC COMPOUNDS.

Melting-point (C.°).	Boiling-point (C.°).	PHENOLIC COMPOUNDS.—Colorless and Solid.
26	211·5c.	† **1, 3-Xylenol(4), $Me_2.C_6H_3.OH$.** — V. d. s. aq.; miscible w. alc. or eth.—In Test 401 w. $FeCl_3$, the 1% alc. sol. gives a GB color, very quickly fading through G to YT2, while the aq. sol. (1:100) gives a BV color, which fades in 2 min. to a white turbidity.
26	228	**m-Propylphenol, $Pr.C_6H_4.OH$.**—V. d. s. aq.—Aq. sol. pale blue w. $FeCl_3$; alc. sol. green.
30	190·8	† **o-Cresol, $Me.C_6H_4.OH$.**—1% aq. sol. w. $FeCl_3$ in Test 401 gives a VB color on mixing, changing to Y in 5 min. and later to a turbid brown —The picrate, prepared by mixing a sol. of the cresol in a little 50% alc. with a concentrated solution of picric acid in 50% alc., forms orange-yellow ndl. w. m. p. 88° (m- and p-cresols give no picrates).—Unlike phenol, not dissolved by 5 pt. conc. NH_4OH!
31–2	205	† **Guiacol, o-$MeO.C_6H_4.OH$.**—S. in 60 vols. aq. at 15°.—The 1% aq. sol. gives w. $FeCl_3$ in Test 401 a ROR color which slowly fades, the sol. becoming turbid. The 1% alc. sol. gives a GB w. $FeCl_3$, which very rapidly fades to a YT2.—The alkaline sol. fr. the fusion w. phthalic anhydride in Test 402 has a VB–BV color, and an absorption spectrum not easily distinguishable from that of thymol (IV, A, m. p 49·6°).—† To a mixture of 0·1 grm. guiacol and 1 cc. aq., add a hot sol. of 0·2 grm. picric acid in 5 cc. aq.; shake well and allow to cool slowly. A brilliant O–YO cryst. ppt. of the picrate compound, w. m. p. 86°, appears within a minute or two!
35		**Diacetylbenzoyl Methane, $Ph.CO.CH.(COMe)_2$.**—E. s. alc.; s. w. yellow color in Na_2CO_3.—Alc. sol. blood-red w. $FeCl_3$.—Cu salt dark blue tbl. w. m. p. 224°–5°, s. $CHCl_3$.—Saponification by Test V–2 gives acetophenone and acetic ac. (Tests 712 and 311).
36	201·8	† **p-Cresol, $Me.C_6H_4.OH$.**—Is not dissolved by 5 pt. conc. NH_4OH.—Aq. sol. (1:100) in Test 401a gives BVT1–BT1–2 on mixing; the sol. then finally becomes turbid.
40–1	250 (560 mm.)	**o-Oxybenzophenone, $Ph.CO.C_6H_4.OH$.**—M. p. oxime 133°–4°.
42·5	172–3 (12 mm.)	† **Phenyl Salicylate (Salol), o-$HO.C_6H_4.CO_2Ph$.**—Odor faintly aromatic.—Alm. i. h. aq. (dif. fr. phenol); e. s. alc. or eth.—Dil. alc. sol. colored violet-red w. $FeCl_3$.—Saponification by Test V–2 gives salicylic acid and phenol (Tests 319 and 414).
42·5–3	183	† **Phenol, $C_6H_5.OH$.**—S. in 15 pt. aq. at 16°; alm. i. Na_2CO_3; miscible w. alc. or eth. Is dissolved by less than 5 pt. conc. ammonia (dif. fr. cresols).—An aq. sol. (1:100) w. $FeCl_3$ (Test 401) gives a violet color (V), permanent for more than 15 min.—Identify by Test 414!
43		**Ethyl Benzoylpyruvate, $Ph.CO.CH_2.CO.CO_2Et$.**—Dec. on dist.—Pr. fr. lgr., e. s. alc.—Alc. sol. blood-red w. $FeCl_3$.—Saponification by Test V–2 gives acetophenone (Test 712), sodium oxalate, and ethyl alcohol.

Melting-point (C.°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
46	218·5	**p-Ethylphenol, $Et.C_6H_4.OH$.**—V. s. alc. or eth.—Aq. sol. gray-blue w. $FeCl_3$.—Warmed w. P_2O_5 gives phenol and ethylene.
47	239d.	**Isohomopyrocatechin, $Me.C_6H_3.(OH)_2(1, 2, 3)$.**—E. s. aq., alc., or eth.—Aq. sol. gives a transient green w. $FeCl_3$.
49	211–2	**1, 3-Xylenol(2), $Me_2.C_6H_3.OH$.**—S. h. aq.—Tribrom-derivative, m. p. 175°.
49		**Diacetylacetone, $CO.(CH_2.COMe)_2$.**—Decomposes spontaneously.—Lustrous lft. e. s. eth. or h. alc.; sol. in alkalies w. yellow color! Gives dark-red color w. $FeCl_3$.—Gives a leaf-green Cu salt and light-yellow Ba salt i. aq.—With NH_3 gives lutidone.
49·6	231·8	† **Thymol, $Me.C_6H_3.(Me_2CH)(OH)(1, 4, 3)$.**—Strong odor of thyme!—S. at 15° in 1200 pt. aq., or in 900 pt. at 100°.—Gives no color w. $FeCl_3$ except in conc. alc. sol. (1:2), when a trace of the very dil. reagent gives a transient green color (G). (Dif. fr. guiacol.)—Test 402 w. phthalic anhyd. is very striking though similar to that given by guiacol. The fused mass, which has a very intense VR–R color, dissolves to an intense blue (B) in dilute NaOH. This sol. shows an absorption band, when viewed through the spectroscope, extending fr. E to the orange. It narrows on cautious dilution until it finally appears as a thick line almost exactly at D!—Identify by Test 419!
50		**Paönol, $Me.CO.C_6H_3OH.OMe$.**—Ndl. e s. alc. or eth.; vol. w. st.—Alc. sol. colored dark red-violet by $FeCl_3$.—Oxime, ndl., e. s. alc.; d. s. aq.
51	251–2	**Homopyrocatechin, $Me.C_6H_3.(OH)_2(1, 3, 4)$.**—V. s. aq. alc. or eth.—W. $FeCl_3$ gives green color, which changes to red-violet w. Na_2CO_3.—Reduces $AgNO_3$ or Fehling's sol.
51–2	253	**Pyrogalloldimethylether, $HO.C_6H_3.(OMe)_2$.**—$FeCl_3$ gives cörulignon (s. in conc. H_2SO_4 w. intense corn-flower color).—Conc. HCl at 100° gives pyrogallol.
53	243	**Hydroquinone Methyl Ether, $p\text{-}HO.C_6H_4.OMe$.**—Not vol. w. st.—E. s. c. bz.—Reduces h. ammon. Ag. sol.
57	239	**Iridol, $Me.C_6H_2.(OMe)_2(OH)(3, 4, 5, 1)$.**—E. s. alc., eth., or bz.
59–60	330–40d.	**Dioxybenzophenone, $(C_6H_4OH)_2.CO$.**—Pale-yellow pr. fr. lgr.; alm. i. aq.; v. s. alc. or eth.; s. in K_2CO_3 sol., but ppt'd by CO_2.—Dil. alc. sol. colored brown-red by $FeCl_3$.—Warming w. conc. H_2SO_4 or boiling w. KOH sol. gives carbonyldiphenyleneoxide, i. aq., m. p. 173°–4°.
60		**1, 2 ($\alpha\beta$)-Hydronaphthoquinoue, $C_{10}H_6.(OH)_2$.**—Silvery lft., s. in NaOH w. yellow color, which changes to an intense green.—Diacetate melts at 105°.
60–1	260–2	**Benzoylacetone, $Ph.CO.CH_2.COMe$.**—D. s. c. aq.; v. s. alc. or eth.; e. s. NaOH; d. s. Na_2CO_3; i. $NaHCO_3$.—Intense red color w. $FeCl_3$!—Saponification by Test V–2 gives acetophenone (Test 712).—Cu salt, pale-green ppt. by $Cu\bar{A}c_2$ fr. dil. alc. sol.! Ag salt i. ppt.
61	229c	**p-Isopropylphenol, $Me_2.CH.C_6H_4.OH$.**—Aq. sol. becomes pale blue w. $FeCl_3$; alc. sol. green.
63–6		**Dioxytoluene, $Me.C_6H_3.(OH)_2(1, 2, 6)$.**—E. s. aq. or alc.—W. $Ca(OCl)_2$ quickly turns to a fuchsine-red color that changes to yellowish brown.
65	225c.	† **1, 2-Xylenol(4), $Me_2.C_6H_3.OH$.**—Long ndl. fr. h. aq.—Odor like phenol. Cold saturated aq. sol. becomes B on mixing with $FeCl_3$ (Test 401); the color rapidly fades, however, and is replaced by a white turbidity.—Tribrom-derivative melts at 169°.

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Boiling-point (C.°).	PHENOLIC COMPOUNDS.—Colorless and Solid.
66	246–7	**Hydroquinone Ethyl Ether, p-$HO.C_6H_4.OEt$.**—Thin lft. e. s. h. aq. or eth.; d. s. c. aq.
64 or 68	219·5	**1, 3-Xylenol(5), $Me_2.C_6H_3.OH$.**—V. d. s. c. NaOH.—No color w. $FeCl_3$.—M. p. of tribrom-derivative 162·5°.
67		**m-Oxybenzyl Alc., $HO.C_6H_4.CH_2OH$.**—Cryst., e. s. alc., eth., or h. aq.; d. s. $CHCl_3$.—Aq. sol. gives violet-blue color w. a little $FeCl_3$.
68–9	219·5c.	**Mesitol, $Me_3.C_6H_2.OH$(1, 3, 5, 2).**—V. s. alc. or eth.; i. NH_4OH or Na_2CO_3.—No color w. $FeCl_3$.
71–2	234–5	**Pseudocumenol, $C_6H_2.(Me_3)(OH)$(1, 2, 4, 5).**—Alm. i. c. aq.; v. s. alc. or eth.—No color w. $FeCl_3$.—Very vol. w. st.—Acetic ac. sol. with Br gives Br deriv. m. p. 35°.
73–4		**Coniferyl Alc., $MeO.C_6H_3:(OH)(C_3H_4.OH)$.(3, 4, 1).**—D. s. h. aq.; e. s. eth.; s. alkalies.—Dil. mineral acids change quickly to amorphous isomer, alm. i. eth.—Na amalgam reduces to eugenol, Div. B, b. p. 247°.—CrO_3 mixture oxid. to vaniline, etc.
74·5	211·5 (th. i.)	**1, 4-Xylenol(2), $Me_2.C_6H_3.OH$.**—Odor like phenol.—Gives no pronounced color reac. w. $FeCl_3$ in aq. or alc.!
75	218c.	**1, 2-Xylenol(3), $Me_2.C_6H_3.OH$.**—Odor like phenol.—Aq. sol. blue w. $FeCl_3$!—M. p. of tribrom-derivative 184° (ndl. fr. alc.).
76·5		**Diethyl Ketipate, $EtCO_2.CH_2.CO.CH_2.CO_2Et$.**—Flat pr. fr. alc.—I. c. aq., e. s. eth.—Gives intense-red color w. $FeCl_3$.—Boiling w. dil. H_2SO_4 gives diacetyl!—Substitutes Br_2 easily.—The free acid is unstable.
79	262	**Pyrogalloldiethylether, $HO.C_6H_3.(OEt)_2$.**—V. s. c. bz.; d. s. c. dil. alc.—Vol. w. st.
79–80		**Propylpyrogallol, $Pr.C_6H_2.(OH)_3$(1, 3, 4, 5).**—V. s. aq., alc. or eth.—Aq. sol. indigo-blue w. $FeSO_4$.
81		**1, 2, 3-Trimethylphenol(5), $Me_3.C_6H_2.OH$.**—No color w. $FeCl_3$.
81	a. 200	**Dibenzoylmethane, $CH_2.(COPh)_2$.**—Tbl. fr. methyl alc.; e. s. alc. or eth.; i. Na_2CO_3; v. e. s. NaOH.—Alc. sol. intense red-violet w. $FeCl_3$!—Monobrom-derivative formed fr. 1·8 grm. Br and 2·24 grm. substance, each dissolved in 3 pt. $CHCl_3$ at 0°, (silky ndl., m. p. 93°).
80–5		**(α)-Dibenzoylacetone, $(PhCO)_2.C:COH.Me$.**—Pr. fr. lgr.; dec. at 270°.—Sol. in Na_2CO_3 w. yellow color.—Alc. sol. blood-red w. $FeCl_3$.—Quite a strong acid.—Heated for 1 hour at 85° gives (β)-dibenzoyl acetone of m. p. 107°–10°, i. in Na_2CO_3 sol., and giving no color in alc. sol. w. $FeCl_3$.
84		**Dipyrocatechin, $[C_6H_3.(OH)_2]_2$.**—Ndl.—Sbl.—Unstable.—Aq. sol pale green w. $FeCl_3$, becoming dark blue w. a little Na_2CO_3.
84	abt. 325	**p-Benzylphenol, $Ph.CH_2.C_6H_4.OH$.**—Cryst. fr. alc.—S. in NaOH, but not in NH_4OH.—Dist. w. P_2O_5 gives benzene, anthracene, and phenol. (Tests 913, 912, and 414.)—Dibrom-derivative, fr. excess of Br in CS_2 sol., m. p. 175°.
86		† **Saligenin, o-$HO.C_6H_4.CH_2.OH$.**—Rhombic tbl.—Sbl. fr. 100°—E. s. c. aq.; v. s. h. aq.; v. s. alc. or eth.—Test 401 w. a 0·5% alc. sol. and $FeCl_3$ gives a RV color, soon changing to YOT_2.—The powder stirred w. a little conc. H_2SO_4 gives a red color (RT1–VRT1).—Boiled for a short time w. 5 pts. aniline gives oxybenzyl-aniline, m. p. 108°; ndl. fr. alc.
86	266 (th. i.)	**1, 2, 3-Tetramethylphenol (4), $Me_4.C_6H.OH$.**—E. s. alc. or eth.—Gives no color w. $FeCl_3$.

Melting-point (C.°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
88		† **Diethyl Diacetylsuccinate, $C_8H_8O_6.Et_2$.**—Tbl., e. s. alc. or eth. —Sat. aq. sol. w. $FeCl_3$ gives, in Test 401, a very pale but rather permanent violet-red (VRT2).—† To 5 cgrms. ester in a test-tube add 1 cc. conc. NH_4OH, 1 cc. glacial acetic acid and 10 cc. dilute H_2SO_4. Place a pine splinter in the mixture and boil for 2 min.—The splinter becomes colored deep red (pyrrol reaction)!—Saponification gives acetonylacetone, C_2H_5OH, and CO_2.
89		**2-Methylnaphthol(1), $Me.C_{10}H_6.OH$.**—Ndl. fr. aq.—Gives white ppt. w. $FeCl_3$; green ppt. w. $Ca(OCl)_2$.—Ignition w. Zn dust gives β-methylnaphthalene.
92		**2-Methylnaphthol(4), $Me.C_{10}H_6.OH$.**—Gives same reactions as preceding, except that Zn dust gives α-methylnaphthalene.
92–3	255	**p-Isoamylphenol, $C_5H_{11}.C_6H_4.OH$.**—Ndl. fr. h. aq.
93	250d.	**p-Anol, $Me.CH:CH.C_6H_4.OH$.**—S. in alkalies.—Exposure to air or h. dil. acids gives a brown oil.
94	278–80	† **α-Naphthol, $C_{10}H_7.OH$.**—Monoclinic.—Odor phenolic.—D. s. h. aq.; i. c. aq.; e. s. alc., eth., bz., or alkalies.—Aq. sol. gives scanty white ppt. w. $FeCl_3$. Identify by Test 412!
95		**Pyrogallol Ethyl Ether, $(OH)_2.C_6H_3.OEt$.**—Ndl. vol. w. st.—S. c. aq.; e. s. h. aq.; v. d. s. c. bz.—Gives blue-violet color w. $FeSO_4$.
95	230–1 (th. i.)	**Trimethylphenol, $C_6H_2.(Me_3)(OH)(1, 2, 4, 6)$.**
95–7		**Ethyl Oxalylacetate, $CO_2H.CO.CH_2.CO_2Et$.**—$FeCl_3$ + aq. sol. gives deep-red color.
96–7		**β-Hydrojuglon, $C_{10}H_5.(OH)_3$.**—Silvery 6-sided ndl. fr. alc.—S. 1000 pt. c. aq.; d. s. alc. or eth.; e. s. $CHCl_3$ and bz.—Gives an intense-yellow color w. NaOH, changing to red.—Boiled w. $FeCl_3$ gives juglon.
98		**Benzocotoïn, $C_{15}H_{14}O_4$.**—Pale-yellow ndl., e. s. eth. or dil. NaOH. —$FeCl_3$ gives dark-brown color.—Ammon. sol. gives amorphous yellow ppt. w. $Pb\bar{A}c_2$.
99	237	**p-tert.-Butylphenol, $Me_3.C.C_6H_4.OH$.**—Ndl. fr. aq.—Heated w. P_2O_5 gives isobutylene and phenol.
99		**o-Oxyhydroanthranol, $C_{14}H_{12}O_2$.**—Yellowish lft. fr. alc.—S. alc. or eth.—The alc. sol. is colored green by $FeCl_3$.—Solutions show a pronounced green-yellow fluorescence.
103	325 sl. d.	**Methyl Oxynaphthyl Ketone, $Me.CO.C_{10}H_6.OH$.**—6-sided pale-green pr. fr. bz.; i. aq., d. s. alc.; s. alkalies, but ppt'd by CO_2.—Oxime, m. p. 168°–9°.
103–4	267–70	**1, 2-Dioxytoluene(4), $(OH)_2.C_6H_3.Me$.**—E. s. aq., alc., or eth.; d. s. bz.—Aq. sol. colored green-blue by $FeCl_3$; gives ppts. w. Br or $Pb\bar{A}c_2$; gives yellow color w. $Ca(OCl)_2$ sol.—Phthalic anhyd. fusion (Test 402) gives a fluoresceïn.
104	240–5	† **Pyrocatechin, $o\text{-}C_6H_4.(OH)_2$.**—Lft. fr. bz.; e. s. aq., alc., or eth.; s. c. bz. (Separation fr. hydroquinone.)—Aq. sol. (1:250) gives w. $FeCl_3$ a green (G) color, which, on addition of Na_2CO_3, changes to R, becoming OR within 15 min.!—Alkaline sol. browns in the air.—$Pb\bar{A}c_2$ gives white ppt. (dif. fr. hydroquinone).—Easily reduces sol. of noble metals and Fehling's sol. on warming.—Apply Test 416!
105		**Homosaligenin, $Me.C_6H_3.(CH_2OH)(OH)(1, 2, 4)$.**—Lft. s. 15 pt. c. aq.—Sol. gives deep-blue color w. $FeCl_3$.—Dec. by heating w. dil. HCl to i. homosaliretin, m. p. 200°–5°.
104–6		**Dihydroresorcin, $C_6H_8O_2$.**—Pr. e. s. aq. or alc.; v. d. s. abs. eth. —Aq. sol. reacts strongly acid.—Aq. sol gives intense violet color with $FeCl_3$. Reduces Ag sol.—Gives a phenylhydrazone w. m. p. 176°.

Melting-point (C.°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
105–6	298	**Dimethylapionol, $C_6H_2.(OH)_2(OMe)_2$(1, 2, 3, 4).**—S. h. aq., alc., eth., bz., and alkalies.
106·5–108	287–90	† **Orcin, $Me.C_6H_3.(OH)_2$(1, 3, 5).**—Cryst. w. $1H_2O$ (m. p. 58°).—Sweet taste.—E. s. aq., alc., or eth.; d. s. $CHCl_3$.—A 1% aq. sol. gives a VBT1–BVT1 color w. $FeCl_3$ in Test 401, which slowly fades to a light tint of the same hue.—Reduces ammon. Ag sol.—Sol. in ammonia absorbs O from air, becoming red.—Br aq. ppts. tribrom-derivative (ndl. fr. dil. alc., m. p. 98°).—† Bring to a boil a sol. of 5 cgrm. orcin in 5 cc. of a 1% NaOH sol. to which 5 drops of $CHCl_3$ have been added. An O–OR color is produced. Dilute the solution to 50 cc. and view with a black background. An intense YG fluorescence appears!—The phthalic anhyd. fusion (Test 402) gives a pure OR solution.
108		**1, 2, 3-Tetramethylphenol(5), $Me_4.C_6H.OH$.**—Alc. sol. becomes yellow-green w. $FeCl_3$.
108–9		**Phloridzin.**—Cf. m. p. abt. 170°, at which temp. it remelts after losing aq.
110		**Ethyl Isocarbopyrotritarate.** — Alc. sol. blue w. $FeCl_3$. — Cf. Genus III (A, 2).
110		**p-Oxybenzyl Alc., $HO.C_6H_4.CH_2.OH$.**—Fine ndl., e. s. aq., alc., or eth.—Sol. in conc. H_2SO_4 is red-violet.
112		**Phenanthrol, $C_{14}H_9.OH$.**—Lft. w. blue fluorescence.—D. s. aq.; e. s. alc. or eth
114	255	**Pentamethylphloroglucin, $C_{11}H_{16}O_3$.**—E. s. in sol. of NaOH or Na_2CO_3.—Reduces $KMnO_4$ immediately. Abs. methyl alc. sol. with Br gives Br deriv., ndl., m. p. 75°–6°.
115	d.	**Vanillyl Alc., $C_6H_3.(MeO)(OH)(CH_2OH)$,(3:4:1).** — Ndl. E. s. alc., eth., or warm aq.—S. in conc. H_2SO_4 w. red-violet color.—Gentle oxidation w. a little CrO_3 mixture gives vanilline (odor like vanilla)!
115	295–300	**Acetovanillon, $MeO.C_6H_3.OH.COMe$.**—Pr. s. in 200 pt. c. aq.—Cu salt a yellowish-green ppt.—Oxime melts at 95°.
116	276·5	† **Resorcin, m-$C_6H_4.(OH)_2$.**—Tbl. fr. aq., alc., or eth.—Taste sweet.—V. s. c. aq., alc., or eth.; i. $CHCl_3$ or CS_2.—A 1% aq. sol. gives a strong clear BV with $FeCl_3$ (Test 401), permanent for more than 15 min.—Identify by Test 418!
116	297–8	**Ethyl p-Oxybenzoate, $HO.C_6H_4.CO_2Et$.**—Saponification by Test V-2 gives p-oxybenzoic ac. and C_2H_5OH.
116		**m-Oxybenzophenone, $Ph.CO.C_6H_4.OH$.**—Lft. e. s. alc. or eth.—Gives two oximes w. m. p. 76° and 126°; fusion of first gives second.
117	227–8 (th. i.)	**Pyromeconic Ac., $C_5H_4O_3$.**—Sbl. at 100°.—4-sided pr. fr. h. aq.—V. s. alc., $CHCl_3$, and h. aq.—Gives a cherry-red color w. $FeCl_3$.—Boiling w. alkalies gives formic ac. and CO_2.—Salts very unstable.
117	249–50c.	**1, 2, 4-Tetramethylphenol(5), $Me_4.C_6H.OH$.**—Flat pr. fr. alc.—E. vol. w. st.
120		**2, 6-Dioxy-1, 3-xylol, $Me_2.C_6H_2.(OH)_2$.**—S. aq.; v. s. alc. or eth.—Aq. sol. reddish w. $FeCl_3$.
120–1		**1, 3-Trioxynaphthalene, $C_{10}H_5.(OH)_3$.**—Sbl. in scales.—V. s. eth., $CHCl_3$, or bz.
120–1		**Oxalyldiacetone, $C_2H_3O.CH_2.CO.CO.CH_2.COMe$.**—Cryst. d. s. aq.; s alc., eth., or NaOH(Na comp. yellow).—Alc. sol. is colored dark brownish-red by $FeCl_3$.

Melting-point (C.°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
122		**p-Diphenolethane, Me.CH.$(C_6H_4OH)_2$.**—Cryst. fr. bz.; i. lgr.—Aq. sol. gives yellow-brown ppt. w. $FeCl_3$.—Gives Ag mirror w. h. dil. ammon. $AgNO_3$ sol., evolving aldehyde.
122	285–6	† **β-Naphthol, $C_{10}H_7.OH$.**—D. s. h. aq.; e. s. alc., eth., or bz.—$FeCl_3$ gives a white opalescence w. the c. aq. sol.—Identify by Test 413!
124		**2, 5-Dioxytoluene(1), Me.$C_6H_3.(OH)_2$.**—Sbl. partially. — V. s. aq., alc., or eth.; less s. bz.; s. alkalies.—Aq. sol. w. $FeCl_3$ gives brownish-red color.—Sol. in NaOH is blue-green, soon turning brown.—Boiled w. aniline gives compound (lft. fr. aq.) w. m. p. 82°–85°.
125	276–9	**m-Xylorcin, $C_6H_2.(Me_2)(OH)_2$(1, 3, 4, 6).**—Tbl. e. s. aq. or eth.
125		**Cubebin, $CH_2.O_2.C_6H_3.C_3H_4OH$.**—Ndl., alm. i. aq.; d. s. alc.; s. eth.—Conc. H_2SO_4 quickly produces a purple-red color.—HNO_3 gives picric and oxalic acids.
126–7		**Diethyl Succinylosuccinate, $C_8H_6O_6.Et_2$.**—Pale-greenish cryst. w. bluish fluorescence fr. eth.; v. d. s. h. aq.—$FeCl_3$ colors alc. sol. deep cherry-red.—The sol. in NaOH is deep yellow.—The alc. sol. shows intense light-blue fluorescence.
128		**Ethylsuccinylosuccinic Ac., $C_6H_8O_3$.**—Ndl. or tbl.—Sbl.—S. c. aq.; e. s. alc.—$FeCl_3$ gives cherry-red color w. aq. sol.—Fusion w. KOH gives formic and butyric acids.—$Ba\bar{A} + 2H_2O$, or $4H_2O$, pale rose-colored crystals.
129		**Methylpyrogallol, $CH_3.C_6H_2(OH)_3$.**—Sbl. in ndl.—W. $FeSO_4$ gives same bluish color as pyrogallol.
129·5		**9, 10-Dihydroanthrol(2), $C_6H_4:(CH_2)_2:C_6H_3OH$.**—E. s. alc. w. blue fluorescence.
129–31		**Diketohydrinden, $C_6H_4:(CO)_2:CH_2$.**—Cryst. fr. lgr.; v. d. s. c. aq.; e. s. h. alc. or bz. S. w. intense yellow color in dil. NaOH or Na_2CO_3!—Boiled w. aq. or alkali gives an acidic body, m. p. 206°–8°, whose alkaline salts are intensely red-violet, and whose Ag salt is dark red!
133	293 (sl. d.)	† **Pyrogallol, $C_6H_3.(OH)_3$(1, 2, 3).**—V. s. c. aq.; s. alc. or eth.—Taste bitter (poisonous).—Alkaline sol. absorbs O rapidly, turning brown.—A 1% aq. sol. gives w. $FeCl_3$ an OYS1 color, changing within 15 min. to OYS2.—V. dil. $FeCl_3$ gives bluish color.—Reduces $AgNO_3$ sol. in the cold.—Apply Test 417!
133–3·5		**Diethyl Hydroquinonedicarbonate, $C_8H_4O_6.Et_2$.** — Sbl. in flat greenish lft. w. bluish fluorescence.—D. s. c. alc.; sol. fluoresces blue in reflected light, pale greenish yellow by transmitted light.—S. in dil. NaOH w. deep-yellow color.—With a trace of $FeCl_3$ gives a blue-green color.
134		**p-Benzoylphenyl, $C_{13}H_{10}O_2$.**—Dist.—Lft. d. s. c.aq., more s. h. aq.; e. s. alc., eth., and Ac.; s. in alkalies, but reppt'd by acids.—Dec. by conc. H_2SO_4 at 200°, giving phenol and benzoic acid.
134–5		**1, 6-Dioxynaphthalene, $C_{10}H_6.(OH)_2$.**—D. s. c. alc.; e. s. eth.—$FeCl_3$ gives a transient blue color, then a copper-red ppr.
135		† **Furoïn, $C_4H_3O.CO.CH(OH).C_4H_3O$.**—Nearly colorless (about YT3) cryst., d. c. alc.; i. aq.—Sol. in c. conc. H_2SO_4 is deep blue-green!—$FeCl_3$ gives no coloration.—E. s. c. NaOH to deep bluish-green sol., very deep violet-red by transmitted light; color discharged on dilution, after first changing to green! The violet-red sol. diluted as much as practicable shows heavy absorption bands between D and C in orange, and between D and D½E!—The m. p. of oxime is 160°–1°; of the phenylhydrazone 79°–80°.
135–6		**1, 4-Dimethylnaphthol(2), $Me_2.C_{10}H_5.OH$.**—Sbl. fr. 100°.—D. s. aq.; s. alc.; e. s. eth.—Zn dust ignition gives dimethylnaphthalene.—Acetate, m. p. 77°–78°.

Melting-point (C°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
135–6		**o-Oxystilbene, $HO.C_6H_4.CH:CH.Ph$.**—Alm. i. h. aq.; d. s. c. alc.; e. s. h. alc.
139		**Butenylonphenol(2), $C_{10}H_{10}O_2$.**—Ndl. d. s. aq.; e. s. alc.—Aq. sol. deep blue-violet w. $FeCl_3$.—M. p. of oxime 84°–5°.
139·5		**Oxythymol, $Me.C_6H_2.(Me_2.CH)(OH)_2(1, 4, 2, 5)$.**—B. p. 290°.—Sbl. undecomposed.—V. d. s. c. aq.; s. h. aq.; e. s. alc. or eth.—Oxid. gives thymoquinone.—Occurs in oil fr. root of Arnica Montana.
140		**1, 8-Dioxynaphthalene, $C_{10}H_6.(OH)_2$.**—D. s. h. aq.; e. s. eth. or bz.—Dust provokes sneezing.—Aq. sol. w. $FeCl_3$ gives flocculent white ppt. which soon becomes dark green.—Easily oxidized.—Diacetate, silvery lfts. fr. alc. (m. p. 147°–8°).
abt 140		† **Hæmatoxylin.**—Sol. in alkalies intense purple-red.—Cf. Suborder II, A, 1, p. 207.
140·5		**Oxyhydroquinone, $C_6H_3.(OH)_3(1, 2, 4)$.**—V. s. aq., alc., or eth.; alm. i. $CHCl_3$, CS_2, or bz.—Aq. sol. exposed to air soon browns.—Aq. sol. w. v. dil. $FeCl_3$ gives transient green which changes w. Na_2CO_3, first to dark blue and then to wine-red.—A conc. aq. sol. gives dark floc. ppt. w. $FeCl_3$.—M. p. of triacetate 96·5°.
141–2		**Protocotoïn, $C_{16}H_{14}O_6$.**—Pr. fr. alc.—Gives blue-green color w. c. conc. HNO_3.—Dibrom-deriv. fr. Br in CS_2 sol., scales, m. p. 170°.
142		**Resacetophenone, $Me.CO.C_6H_3.(OH)_2(1, 2, 4)$.**—Cryst. d. s. aq.—Aq. sol. colored wine-red by $FeCl_3$.—M. p. of oxime, 198°–200° d.
143		**Dioxyphenanthrene, $C_{14}H_8.(OH)_2$.**—E. s. NaOH w. green color, quickly changing to red.—S. in conc. H_2SO_4 + trace of HNO_3 w. red color.—V. e. oxidized.—Diacetate, m. p. 159°.
144		**Benzoresorcin, $Ph.CO.O_6H_3.(OH)_2$.**—Ndl. fr. h. aq.; d. s. c. aq.; e. s. alc. or eth.—Alc. sol. becomes brown-red w. $FeCl_3$.—M. p. of dibenzoate 141°.
145		**Benzopyrocatechin, $Ph.CO.C_6H_3.(OH)_2$.**—V. d. s. c. aq.—Alc. sol. w. $FeCl_3$ gives rich green coloration, changing to red on addition of a drop of ammonium carbonate.—Reduces Tollen's reagent (cf. Test 101).
144–6		**Arbutin, $C_{25}H_{34}O_{14}$ (?) (substance dried in vacuo at 100°).**—(Statements concerning symbol and m. p. are conflicting; m. p. 165° and 170° are also recorded.)—Taste bitter.—Lustrous ndl. e. s. h. aq. or alc.; i. eth.; more s. in dil. NaOH than in aq.—A 1% aq. sol. gives a transient VB-BV color w. $FeCl_3$.—Boiled w. x's of $FeCl_3$ sol. gives pungent odor of quinone!—(A glucoside hydrolyzed by dil. H_2SO_4 to dextrose and hydroquinone.)
146		**Orcacetophenone, $(Me)(OH)_2.C_6H_2.CO.Me$.**—Silky ndl. v. s. alc. or eth.; e. s. NaOH or NH_4OH.—Aq. sol. black w. $FeCl_3$.
149		**Dioxyxylene, $C_6H_2.(Me_2)(OH)_2(1, 3, 2, 4)$.**—Sbl. in ndl.; v. s. aq., alc., or eth.—Gives intense violet color w. $FeCl_3$.
149–50		**1, 3, 5-Trimethylphendiol, $Me_3.C_6H.(OH)_2$.** — B. p. 275° c.—Sbl. in lft.—D. s. c. aq.; e. s. alc. or eth.—Aq. sol. gives transient green color and gray ppt. w. $FeCl_3$.—Reduces ammon. $AgNO_3$ sol.
151–2		**p-Diphenylol-dimethyl-methane, $(C_6H_4.OH)_2.C.Me_2$.**—I. c. aq.; d. s. h. aq.; e. s. alc. or eth.
152		**Dimethyl Succinylosuccinate, $C_8H_6O_6.Me_2$.**—$FeCl_3$ gives red color w. alc. sol.—The free acid is unstable.

Melting-point (C.°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
154		**Bicarvacrol, $C_{20}H_{26}O_2$.**—Silky ndl.; i. aq.; e. s. alc., eth., or bz.
156		**1, 2, 4-Trimethylphendiol(3, 5), $Me_3.C_6H.(OH)_2$.**
156		**Anemonin, $C_{10}H_8O_4$.**—Vol. w. st.—Lustrous ndl. fr. alc., or plates fr. $CHCl_3$.—D. s. h. aq. or c. alc.; i. eth.—Alc. sol. reacts neutral.—E. s. alkalies w. yellow-red to blood-red color.—A few degrees above m. p. solidifies to yellow compound which decomposes at 290°.—Combines w. phenylhydrazine.
158		**p-Dioxydiphenylmethane, $CH_2.(C_6H_4OH)_2$.**—Sbl.—Not vol. w. st.—E. s. alc.; v. s. eth.; s. $CHCl_3$; i. CS_2; s. in NaOH and ppt'd by CO_2.—Aq. sol. colored brown-yellow by $FeCl_3$.—Aq. sol. of disodium salt is green.—Fusion w. KOH gives p-oxybenzoic ac. and phenol (Test 414).
158		† **Convolvulin, $C_{32}H_{62}O_{16}$ (?).**—Amorphous.—Alm. i. aq. or eth.; e. s. alc.—Mix a few mgr. w. a drop of c. conc. H_2SO_4 After 5 min. a VR color appears, changing after ½ hr. to R.—Warm a little w. x's of conc. H_2SO_4; disagreeable odor of rancid butter, changing to sharp odor if temp. is increased. —S. NaOH w. dec.—A glucoside fr. jalap root (Convolvulus purga), yielding dextrose, etc., on hydrolysis by h. baryta water.
159		**Maltol, $C_6H_4O.(OH)_2$.**—Sbl. in lft.—D. s. bz. or c. aq.; v. s $CHCl_3$ or h. aq.; s. NaOH, but reppt'd by CO_2.—Aq. sol. colored an intense violet by $FeCl_3$.—Reduces ammon., Ag sol. c., or Fehling's sol. when hot
159		**2, 3-Dioxynaphthalene, $C_{10}H_6.(OH)_2$.**—Rhombic lft. fr. aq.—S. h. aq.; e. s. alc. or eth.—Gives intense dark-blue color w. $FeCl_3$.
160		† **Æsculin, $C_{15}H_{16}O_9$.**—White lustrous odorless ndl, slightly bitter taste.—Loses cryst. aq. at 120°-130°.—S in 600 pt. c., or 12·5 pt. h. aq.; d. s. c. alc. or eth.; e. s NaOH—The cold supersaturated aq. sol. gives blue-green color (BG) w. $FeCl_3$.—V. dil. aq. sol., especially in presence of a trace of alkali, shows a magnificent light-blue (BT2) fluorescence! Shaken w. little HNO_3 gives yellow sol., which becomes deep blood-red upon addition of NH_4OH!—Hydrolysis by h. dil. HCl gives dextrose and æsculetin—Gives the Molisch color reaction in Test II w. *α*-naphthol.—(In bark of the horse-chestnut)
161		**4, 4-Dioxytriphenylmethane, $Ph.CH.(C_6H_4OH)_2$.**—Ndl. fr dil. alc.; i. c., d. s. h. aq.; e s alc. or eth.—Diacetate melts at 109°-111°.
161		**o-Bicresol, $(Me.C_6H_3.OH)_2$.**—D. s. h. aq.; e. s. alc. or eth.—Diacetate m. p. 131°.
161		**Benzyhydroxylphenol, $Ph.CHOH.C_6H_4.OH$.**—D. s. c aq.; e. s. alc. or eth.; s. alkalies—Aq. sol colored red by $FeCl_3$.
161		**δ-Biphenol, $(C_6H_4.OH)_2$.**—B p 342° Ndl., v. d s h aq.; v. s. alc. or eth.—Aq. sol. gives ppt w $Pb\bar{A}c_2$—Diacetate melts at 94°.
162-3		**3, 3′-Dioxybenzophenone, $(C_6H_4OH)_2 \cdot CO$.**—E s. KOH but reprecipitated by CO_2.—Fusion w. KOH gives phenol and oxybenzoic ac.
163		**β-Orcin, $C_6H_2.(Me_2)(OH)_2(1, 4, 3, 5)$.**—B. p. 277°-80°—Much less s. aq. than orcin—NH_4OH sol w. $Ca(OCl)_2$ gives clear carmine-red color.—Boiled w. dil. NaOH and $CHCl_3$ gives deep-red sol. w. green fluorescence like orcin!—Tetrabrom-derivative, ppt'd by Br aq., cryst. fr. lgr. w. m. p. 101°.—Phthalic anhyd. fusion gives no color.

Melting-point (C.°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
160–70d.		† **Anthranol, $C_6H_4:C_2H(OH):C_6H_4$.**—Lustrous v. pale-yellow (about YT3) ndl.—E. s. h. bz. Does not dissolve fully in c. alkali, but becomes bright yellow and gives a yellow filtrate; reppt'd by CO_2.—The alkaline sol. when boiled in presence of air absorbs O, giving much anthraquinone!—Dissolve a small quantity in *cold* fuming HNO_3; dilute w. aq. and dissolve orange ppt. in alc. containing 1 drop NaOH sol.; an intense violet-red color is produced!—Ignition w. Zn dust gives anthracene (Test 912).
165·5		**Bithymol, $C_{20}H_{26}O_2 + H_2O$.**—I. aq.; e. s. alc., eth., or bz.; s. in alkalies w. orange color.
168		**Arbutin,** cf. IV, A, m. p. 144°–6°.
168		**Trioxyacetophenone (Gallacetophenone), $(HO)_3.C_6H_2.CO.Me$.**—Pearly lft., e. s. h. aq.—S. in NaOH w. brownish color; in conc. H_2SO_4 w. clear yellow color.—Picrate, yellow ndl., w. m. p. 133°.—Oxime, ndl. fr. toluene w. m. p. 162°–3°.
168–70		**α-Hydrojuglon, $C_{10}H_5.(OH)_3$(1, 4, 5)** (fr. the walnut-tree, Juglans regia).—Cryst., s. in 200 pt. aq. at 25°; v. s. alc. or eth.; i. $CHCl_3$ or bz.; e. s. alkalies w. intense yellow color which changes in air to red.—Br or $FeCl_3$ gives juglon.
169		† **Hydroquinone, p-$C_6H_4.(OH)_2$.**—Sbl. in lft.—Taste slightly sweetish.—S. in 17 pts. aq. at 15°; e. s. alc. or eth.—The cold saturated aq. sol. gives a YO colored sol. w. $FeCl_3$ in Test 401.—Boiled w. excess $FeCl_3$ gives pungent odor of quinone.—Alkaline sol. browns in air.—Reduces $AgNO_3$ on warming, and Fehling's sol. in the cold.—Identify by Test 411!
169		**1, 2, 4-Trimethylphendiol(3, 6), $Me_3.C_6H.(OH)_2$.**—D. s. c. aq.; e. s. h. aq., alc., eth., or bz. Diacetate, m. p. 112°.
abt. 170		**Phloridzin, $C_{21}H_{24}O_{10}$.**—Taste bitter!—Silky ndl. wh. first melt at 108°–9°, losing $2H_2O$ of cryst., and then solidifying at 130°.—S. in 1000 pt. c. aq.; e. s. h. aq. or alc.; alm. i. eth.; sol. in NaOH absorbs O, becoming red-brown.—Sol. dark violet w. $FeCl_3$.—A glucoside readily hydrolyzed by boiling w. dil. H_2SO_4 to phloretin and dextrose.
171		**Tetraoxytriphenylmethane, $Ph.CH.[C_6H_3.(OH)_2]_2$.**—D. s. aq.; e. s. alc. or eth.—Easily oxid. to resorcinbenzein.
173–4		**2-Acetylnaphthol(4), $Me.CO.C_{10}H_6.OH$.**—Ndl. e. s. alc.—$FeCl_3$ gives floc. ppt. w. aq. sol.—Ppt'd fr. sol. in alkali by CO_2.—$KMnO_4$ oxid to phthalic ac. (Test 318).
175		**1, 4-Hydronaphthoquinone, $C_1H_6.(OH)_2$.**—Long ndl. s. h. aq.; e. s. h. alc. or eth.; alm. i. CS_2.—CrO_3 oxid. to α-naphthoquinone.—Diacetate melts at 128°–30°.
176		**Phenyl p-Oxybenzoate, $HO.C_6H_4.CO_2Ph$.**—Saponification by Test V very easily gives p-oxybenzoic ac. and phenol (Test 414).
178		**1, 7-Dioxynaphthalene, $C_{10}H_6.(OH)_2$.**—S. aq.; e. s. alc. or eth.—Aq. sol. gives deep-blue ppt. w. $FeCl_3$.—Alkaline sol. blackens in the air.—Diacetate melts at 108°.
180		**Benzoylsalicin (Populin), $C_{20}H_{22}O_8$.**—Cryst. w. $2H_2O$ (lost at 100°).—Taste sweetish.—S. in abt. 2000 pt. c. aq.; s. conc. KOH.—Conc. H_2SO_4 colors amethyst-red.—Saponified by h. $Ba(OH)_2$ to salicin and benzoic ac. (Test 412).
184		**1, 3, 5-Trimethylphloroglucin, $Me_3.C_6.(OH)_3$.**—S. alkali carbonates.—Br gives derivative w. m. p. 90°.
184·5		**Filixic Ac., $C_{14}H_{16}O_5$** (fr. Aspidium Filix mas.).—Mic. lft. fr. eth.—I. aq.; alm. i. alc.; s. eth.—Reduces ammon. $AgNO_3$.—Fusion w. KOH gives phloroglucin (cf. Test 415).

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Boiling-point (C.°).	PHENOLIC COMPOUNDS.—Colorless and Solid.
185		**Dithymolethane, Me.CH.$(C_{10}H_{12}OH)_2$.**—Dist. undecomposed.—Ndl. fr. bz., plates fr. alc.—Oxid. by MnO_2 and dil. H_2SO_4 gives thymoquinone (Suborder 2, m. p. 45·5°).
185		† **Coniferine, $C_{16}H_{22}O_8 + 2H_2O$.**—I. c. aq.; v. s. h. aq. or dil. alkalies.—Warmed with conc. HCl turns cobalt-blue.—Warmed w. conc. H_2SO_4 gives violet sol. changing to violet-red.—Gives no ppt. w. $Pb\bar{A}c_2$.—Gives no color w. $FeCl_3$.
186		**Iretol, $C_6H_2.(MeO)(OH)_3(2, 1, 3, 5)$.**—Ndl. e. s. aq., alc., or eth.—Br aq. gives hexabromacetone.—HNO_3 oxid. to oxalic ac. (Test 317).
186		**Irigenin, $C_{18}H_{16}O_8$.**—Rhombohedra fr. dil. alc.; d. s. aq.; i. eth. or lgr.—Aq. sol. deep violet w. $FeCl_3$.
190		**Phenolphthalol, $(HO.C_6H_4)_2.CH.C_6H_4.CH_2OH$.**—Pr. d. s. h. aq.; e. s. alc. or eth.; i. bz. or $CHCl_3$.—Becomes red w. conc. H_2SO_4.—Alkaline potassium ferricyanide oxid. to deep-red solution of phenolphthaleïn.
190		**2, 7-Dioxynaphthalene, $C_{10}H_6(OH)_2$.**—Ndl., sbl. w. dec.—E. s. h. aq., alc., or eth.; alm. i. CS_2.—Transient dark-red color w. $Ca(OCl)_2$.—Alkaline sol. darkened by air.—M. p. of diacetate 129°–30°.
190		**Hydrocœrulignon, $(MeO)_4.C_{12}O_4.(OH)_2$.**—Monoclinic pr. fr. alc.—V. d. s. aq. or eth.; s. h. alc. or bz.—Reduces c. ammon. Ag sol.—$FeCl_3$ on exposure to air causes separation of cœrulignon.
194d.		**Methylene-di-β-Naphthol, $CH_2.(C_{10}H_6OH)_2$.**—Mic. ndl., e. s. alc.; alm. i. CS_2.—M. p. of diacetate 211° (i. alc.; e. s. bz.).—Picrate melts at 178°–9°.
198–200		**Diethyl-p-diphenol-methane, $Et_2.C.(C_6H_4.OH)_2$.**—Pr. fr. alc.; i. h. aq.; e. s. alc. or eth.
200		**Resorcinphthaleïn.**—Yellowish crystals.—Cf. Suborder 2.
200		† **Picrotoxin,** $C_{30}H_{34}O_{13}$ (from Menispermum Cocculus).—Cryst. s. 300–400 pt. c. aq.; e. s. alc. or h. aq.; e. s. in NaOH, the sol. soon becoming golden yellow.—The color of a sol. obtained by dissolving a few crystals in conc. H_2SO_4 on crucible cover is a strong orange-yellow (OY)!—*Taste of aq. sol.* (1:10,000) *intensely bitter!*—No pronounced color w. $FeCl_3$.—Gives ppt. w. Br aq.—Reduces $AgNO_3$ sol. when warmed. (Very poisonous.)
200d.		**Daphnin, $C_{15}H_{16}O_9$.**—(Loses $2H_2O$ of cryst. at 100°.)—Colorless pr. w. bitter astringent taste!—D. s. c. aq.; e. s. h. aq. or h. alc.; i. eth.; s. NaOH or Na_2CO_3 w. yellow color.—$FeCl_3$ colors the solution bluish.—HNO_3 gives red color in the cold.—Hydrolyzed by dil. acids to dextrose and daphnetin. (In bark of Daphne Mezereum.)
200 or 210d.		**Tannic Ac., $C_{14}H_{10}O_9$.**—See III, A, 1, m. p. 210°. Taste astringent.
200·5		**Phenoglucin, $C_6H_6O_3 + 2H_2O$.**—Taste very sweet.—Pr. fr. aq.—Gives pale-violet color w. $FeCl_3$.
201		† **Salicin, $C_{13}H_{18}O_7$.**—Taste bitter.—A glucoside.—Hydrolyzed by h. dil. H_2SO_4 gives dextrose and saliretin; by emulsin gives dextrose and saligenin.—Cryst. s. 28 pt. aq. (15°); more s. in NaOH; i. eth.—Gives no color w. $FeCl_3$.—The powder stirred into conc. H_2SO_4 on crucible cover gives bright scarlet (OR) color!
202–3		**Hydroquinonphthalin, $C_{20}H_{14}O_5$.**—Oxid. agents give hydroquinonphthaleïn.
200–9 (s. h.)		**Phloroglucin.**—See m. p. 217°–19°.

Melting-point (C.°).	Boiling-point (C.°).	PHENOLIC COMPOUNDS.—Colorless and Solid.
206		**4-4′-p-(or α)-Dioxybenzophenone, $CO.(C_6H_4OH)_2$.**—Dist. undecomposed.—Cryst. fr. h. aq., e. s. alc., eth., or alkalies.—Ppt'd fr. $Ba(OH)_2$ sol. by CO_2.—No color w. $FeCl_3$.—Fusion w. KOH gives CO_2 and phenol.—Tetrabrom substitution product fr. alc. sol. of compound w. $\bar{A}c$ sol. of Br in cold, m. p. 213°–14°.
206–8d		**Anhydrobisdiketohydrindene, $C_{18}H_{10}O_3$.**—Sol. in alkalies intense red to violet; ppt'd by CO_2.—Oxime d. at 210° without melting.
212		**Phenolphthalideïn, $C_{20}H_{14}O_4$.**—S. alc. or eth.; s. alk. w. pale yellow and in conc. H_2SO_4 w. intense violet color.
212		**Hydrophloron, $C_6H_2.(Me_2)(OH)_2$(1, 4, 2, 5).**—Sbl. in lft., s. h. aq.; v. s. alc. or eth.; d. s. CS_2.—Boiled w. $FeCl_3$ or dil. HNO_3 gives phloron.—Reduces Ag sol.
212–13		**Acetonresorcin, $Me.CO.(C_6H_4OH)_2+H_2O$.**—I. aq., $CHCl_3$, bz., or abs. eth.; s. NaOH.—Resorcin and acetone are among the products of decomposition by heat.
210–20		**α-Tribenzoylmethane, $(Ph.CO)_2.C:(HO)C.(Ph)$.**—S. in $CHCl_3$ or aq.—Freshly prepared gives pale-yellow sol. in 1% Na_2CO_3, and a deep-red color w. $FeCl_3$. After fusion or keeping goes over to neutral β-modification, w. m. p. 225°–6°.
215–16		**2, 6-Dioxynaphthalene, $C_{10}H_6.(OH)_2$.**—Sbl. in pearly lft.—D. s. c. aq.; e. s. alc. or eth.—Aq. sol. gives yellowish-white color w. $FeCl_3$.—M. p. of diacetate 175°.
215–20		**1, 2, 4, 5-Tetroxybenzene, $C_6H_2.(OH)_4$.**—Silvery lft. fr. $\bar{A}c$.—E. s. aq., eth., or alc.—Quickly oxid. by $FeCl_3$ or by air in alkaline sol. to dioxyquinone.
217–19 (r. h.)		† **Phloroglucin, $C_6H_3.(OH)_3$.(1, 3, 5).**—Loses $2H_2O$ cryst. on heating to 100°.—Sbl. w. sl. decomposition.—Taste sweetish.—E. s. aq., alc., or eth.—A 1% aq. sol. in Test 401 w. $FeCl_3$ gives BV–V coloration, which fades rapidly.—Sol. in NaOH absorbs O, but less rapidly than pyrogallol.—A pine splinter first well soaked w. conc. HCl assumes a deep-red coloration (R–VR) when dipped in a dilute aqueous sol. of phloroglucin!—The aq. sol. gives a heavy ppt. of tribromphloroglucin, which when purified melts at 151°.—Identify by Test 415!
218c		**β-Binaphthol, $(HO.C_{10}H_6)_2$.**—Distillation gives β-naphthol (Test 413).—Flat ndl. fr. alc.; i. aq.; s. alc.; e. s. eth. Gives greenish color w. $FeCl_3$, becoming bright red on heating.—Picrate, e. s. alc., has m. p. 174°.
218–19d.		**Fustin, $C_{58}H_{46}O_{23}$ (?).**—White lustrous ndl., e. s. h. aq. or c. dil. NaOH; d. s. eth.—$FeCl_3$ gives green coloration changed to blue-violet and red by Na_2CO_3!—$Pb\bar{A}c_2$ gives yellow ppt.—(A glucoside; hydrolyzed by dil. H_2SO_4 giving fisetin and a carbohydrate.)
220d.		**Methylenedipyrocatechin, $CH_2.[C_6H_3.(OH)_2]_2$.**—D. s. alc. or eth.
222		**Di-p-Oxyhydrobenzoïn, $C_{14}H_{14}O_4$.**—Cryst., e. s. h. aq.; less s. alc.; i. eth.—(Forms a Na salt.)
223–4		**Umbelliferon, $C_9H_6O_3$.**—I. c. aq.; s. alc. and h. aq.—S. w. intense blue fluorescence in conc. H_2SO_4.—When warmed has odor like coumarin.—S. in cold KOH, but on heating the sol. to 60° gives umbelliferic ac.
224		**4-Oxyxanthone, $C_{13}H_8O_3$.**—Sbl. easily.—White ndl. fr. alc.—Acetyl derivative, mic. cryst. fr. dil. alc., m. p. 137°–8°.
223–6 (r. h.)		**β-Tribenzoylmethane, $(C_6H_5.CO)_3CH$.**—Small ndl.; d. s. alc. $CHCl_3$ or bz.; i. NaOH.
226–7		**Hydroquinonephthaleïn, $C_{20}H_{10}O_3.(OH)_2$.**—Ndl. fr. eth.—S. in alkalies w. deep-violet color.

(ORDER I, SUBORDER I.)

Melting point (C.°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
222–40d.		† **Gallic Ac., $(HO)_3.C_6H_2.CO_2H$(3, 4, 5, 1).**—Cryst. w. $1H_2O$ (lost at 120°) in silky ndl.; s. 130 pts. aq. at 12·5°.—Aq. sol. absorbs O from air and turns brown during titration; gives no ppt. w. sol. of gelatine (dif. fr. tannic ac.).
d. 230		**Orcinphthaleïn, $C_{22}H_{14}O_3.(OH)_2$.**—Pr. i. aq.; e. s. alc. or eth. S. in alkalies w. intense dark-red color without fluorescence.
231		**2-Oxyxanthone, $C_{13}H_8O_3$.**—Lustrous yellowish ndl. fr. alc.—Acetyl derivative, ndl. fr. dil. alc., m. p. 161°.
235d.		**β-Quinovin, $C_{38}H_{62}O_{11}$** (?).—(A glucoside of quinovic ac. and quinovase-ethylether found in Cuprea bark.)—Cryst. scales fr. dil. alc.; alm. i. aq. or abs. eth.; s. alkalies.—Sol. in conc. H_2SO_4 is yellow, becoming cherry-red on exposure to air.
237 sl. d.		**Bihydroquinone, $[C_6H_3.(OH)_2]_2$.**—Taste very sweet.—Lft. e. s. aq.; v. s. alc. or eth.—Aq. s. w. little $FeCl_3$ gives red color; x's of reagent gives biquinone.
241d.		**Methylenedipyrogallol, $CH_2.[C_6H_2(OH)_3]_2$.**—Cryst. powd.
242		**3, (β)-Oxyxanthone, $C_{13}H_8O_3$.**—Colorless ndl., e. s. NaOH sol.—$FeCl_3$ added to alc. sol. gives brown color.
d. w. m. 245		**Diresorcinphthaleïn, $C_{20}H_{12}O_6+3\frac{1}{2}H_2O$.**—Silvery lft. fr. aq.—S. in alkalies w. indigo-blue color.
248		**Tetraoxytetraphenyl-ethane, $C_{20}H_{18}.(OH)_4$.**—Scales i. aq.; e. s. alc. or eth.
abt. 250		† **Brazilin, $C_{16}H_{14}O_5$.**—Cryst. in colorless ndl. w. $1\frac{1}{2}H_2O$, soon assuming a broken orange-red color on exposure.—Taste at first faintly bitter, then *very sweet!*—Sol. in NaOH intense carmine-red (R); in conc. H_2SO_4 YO.—† Boil gently in a test-tube resting on a perforated asbestos screen, as described in Test 311–2, for 15 min., 0·1 grm. brazilin, 0·15 grm. fused sodium acetate, and 2·0 cc. acetic anhydride. Cool. Add 10 cc. water to residue, and boil. Cool. Filter. Dissolve cryst. in 10 cc. boiling dil. alc. (1:1). Cool. Filter. Repeat cryst. and filtration twice more as above directed. Dry crystals at 100° and determine melting-point.—The product, tetraacetylbrazilin, melts at 149° (uncor).
250		**1, 5-Dioxynaphthalene, $C_{10}H_6.(OH)_2$.**—D. s. aq.; e. s. eth.—Reduces Fehling's or ammon. Ag sol.—CrO_3 oxid. to the quinone.—Diacetyl compound has m. p. 159°–60°.
d. w. m. 250		**Methylenediresorcin, $CH_2.[C_6H_3.(OH)_2]_2$.**—The alkaline sol. absorbs O from the air and reddens.
251d.		**Hesperidin, $C_{22}H_{26}O_{12}$** (?).—Odorless, tasteless cryst. powder, s. 5000 pt. h. aq.; i. eth.; d. s. alc.; s. NaOH but reppt'd by CO_2.—The sol in NaOH on evaporating to dryness and treating w. x's H_2SO_4 and warming gives red to violet color!—[A glucoside hydrolyzed by boiling w. dil. acids to glucose and hesperitin (latter melts at 224°–6°, and is s. in alkalies and colored brown-red by $FeCl_3$).]
250–3		† **Phenolphthaleïn, $C_{20}H_{14}O_4$.**—When amorphous e. s. eth.; when cryst. d. s. eth.; s. alc.; i. aq.—S. in NaOH or Na_2CO_3 w. intense red color, approximately RV, but much purer than color of the standard. The color is discharged by large x's of NaOH or by warming w. Zn dust.
252d.		**Tetraoxydinaphthylmethane, $CH_2.[C_{10}H_5.(OH)_2]_2$.**—E. s. alc. or eth.—S. in conc. H_2SO_4 w. yellow color, changing to deep red.
252–4		**Thymolphthaleïn, $C_{28}H_{30}O_4$.**—Ndl., e. s. alc.; s. eth.; alm. i. aq.—NaOH gives intense blue sol. (purple by transmitted light).

Melting-point (C.°).	Boiling-point (C.°).	**PHENOLIC COMPOUNDS.**—Colorless and Solid.
253-5d.		**Phloretin, $C_{15}H_{14}O_5$.**—Lft. v. d. s. h. aq. or eth.; v. s. alc.—Sol. in alkalies absorbs O fr. air.—Boiled w. KOH gives phloretic ac. and phloroglucin.—Heated w. aniline at 170° gives scarlet sol.—Anilide, alm. i. aq. or eth., but s. in alc. w. deep-orange color.
253-6		† **Daphnetin, $C_9H_4O_2.(OH)_2$.**—Yellowish ndl. w. coumarin-like odor when warmed!—Sbl.—S. h. aq.; v. d. s. eth.; s. Na_2CO_3 w. orange color.—Aq. sol. gives green color w. $FeCl_3$, becoming red w. Na_2CO_3.—Gives yellow ppt. w. $Pb\bar{A}c_2$.—Diacetyl deriv., m. p. 129°-30°.
a. 270d.		† **Æsculetin, $C_9H_4O_2.(OH)_2+H_2O$.**—(After loss of cryst. aq. becomes yellow.)—Lustrous ndl. v. d. s. c. aq.; s. h. aq.; alm. i. eth.; s. in NaOH w. yellow color.—$FeCl_3$ gives intense green color w. aq. sol.!—$Pb\bar{A}c_2$ gives yellow ppt. fr. sol.!
272		**γ-(p)-Biphenol, $[C_6H_4.OH]_2$.**—Sbl. in scales.—D. s. aq.; e. s. alc. or eth.—Aq. sol. gives no color w. $FeCl_3$ and very transient violet w. $Ca(OCl)_2$.—Sol. in H_2SO_4 and trace of HNO_3 becomes blue.—Ignition w. Zn dust gives biphenyl.—Diacetate, m. p. 159°-160°.
d w. m. 275		**Arabinose-resorcin, $C_{11}H_{14}O_6$.**—Amorph. powder, v. s. aq.; v. d. s. alc. or eth.—Aq. sol. blue-violet w. $FeCl_3$; intense red-violet w. Fehling's sol.
280d.		**p-Dioxystilbene, $(HO.C_6H_4.CH:)_2$.**—E. s. eth.—Diacetate, d. s. h. alc.; m. p. 213°.
300		**α-Binaphthol, $[C_{10}H_6.OH]_2$.**—Sbl.—I. aq.; s. alc.; more s. eth.—Alc. sol. gives violet-red color w. $FeCl_3$ and ppt. of same color.
310		**Biresorcin, $C_{12}H_{10}O_4+2H_2O$.**—Cryst. s. h. aq.—$FeCl_3$ gives pale-blue color.—Heated at 100° for 10 min. w. 1 cc. H_2SO_4 + 1 cc. acetic anhyd. gives blue-violet sol.—M. p. of tetraacetate 158°.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I]

GENUS IV, PHENOLIC COMPOUNDS.

DIVISION B,—LIQUID PHENOLIC COMPOUNDS.

Boiling-point (C.°).	Specific Gravity.	PHENOLIC COMPOUNDS.—Colorless and Liquid.
139·6	0·987 (15°)	† **Acetylacetone, $Me.CO.CH_2.CO.Me$.**—Odor like acetone and acetic acid.—S. in 8 pt. aq.—The color of aq. sol. (1:100) w. $FeCl_3$ (Test 401) is a very permanent OR–RO.—Distinctly acid!—The aq. sol. gives heavy light-blue ppt. w. sol. of $Cu\bar{A}c_2$.—Saponification by Test V gives acetone and acetic ac. (Tests 711 and 311).
158	0·954 (15°)	**Hexanedione(2, 4), $Me.CO.CH_2.CO.Et$.**—Has acid properties.—Cu salt obtained by ppt'n of sol. in dil. alc. w. $Cu\bar{A}c_2$ sol., blue ndl. fr. alc., m. p. 197°–8°.
167–70		**3-Methylhexanedione(2, 4), $Me.CO.CHMe.CO.Et$.**—Blue ppt. w. ammon. CuCl sol., m. p. 192°.
169	0·994 (4°)	**3-Methylpentanedione(2, 4), $Me.CO.CHMe.CO.Me$.**
169–70c.	1·037 (9°)	**Methyl Acetoacetate, $Me.CO.CH_2.CO_2Me$.**—E. s. aq!—Sol. dark cherry-red w. $FeCl_3$!—Saponification by Test V–2 gives acetone and CH_3OH.
174–5	0·941 (15°)	**2, 4-Heptanedione, $Me.CO.CH_2.CO.Pr$.**—Gives a Cu salt, m. p. 160°–1°.
180·5	$1·046^0/_4$	† **Ethyl Acetoacetate, $Me.CO.CH_2.CO_2Et$.**—An aq. sol. (1:100) gives a clear and very permanent RT1 color w. $FeCl_3$ (Test 401).—Saponification by Test V–2 gives acetone, C_2H_5OH and CO_2 (cf. Tests 711 and 814).
183		† **Phenol** (cf. IV, A, m. p. 42·5°).
186·8	1·009 (6°)	**Ethyl Methylacetoacetate, $Me.CO.CHMe.CO_2Et$.**—Sol. colored blue by $FeCl_3$.—Saponification by Test V gives methyl ethyl ketone, C_2H_5OH and CO_2.
189·7c.	0·995 (14°)	**Methyl Ethylacetoacetate, $Me.CO.CHEt.CO_2Me$.** — Violet-red color w. $FeCl_3$.—Saponification by Test V gives methyl propyl ketone and CO_2.
191		**o-Cresol** (cf. Genus IV, A, m. p. 30°).
196		**Caffeol, $HO.C_6H_4.CH_2.O.Me$.**—Odor like coffee.—D. s. h. aq.; e s. alc. or eth.—Aq. sol. colored red by $FeCl_3$.—Fusion w. KOH gives salicylic ac. (Test 319).
198c.	0·998 (12°)	**Ethyl Ethylacetoacetate, $Me.CO.CHEt.CO_2Et$.**—Sol. colored blue by $FeCl_3$.—Saponification by Test V gives methyl propyl ketone, C_2H_5OH, and CO_2.
201	0·981 (0°)	**Ethyl Isopropylacetoacetate, $Me.CO.CHPr.CO_2Et$.**—Sol. colored pale red-violet by $FeCl_3$.—Saponification by Test V gives methyl isobutyl ketone, C_2H_5OH, and CO_2.
201·8		† **p-Cresol** (cf. IV, A, m. p. 36°).
202·8	1·050 (0°)	† **m-Cresol, $Me.C_6H_4.OH$.**—Does not solidify at 0°.—The color w. a 1% aq. sol. and $FeCl_3$ (cf. Test 401) is BV–BVT1 (on mixing).—Odor like phenol.—Not sol. in 5 pt. conc. ammonia.—† Nitrate and purify the product, 2, 4, 6-trinitrocresol, by the procedure given in Test 414–2 for phenol. This trinitrocresol is a cryst. compound resembling picric acid in most of its properties, but melting at 106·5° (uncor.).

(ORDER I, SUBORDER I.)

Boiling-point (C.°).	Specific Gravity.	**PHENOLIC COMPOUNDS.**—Colorless and Liquid.
204–6		**Acetylmesityloxide, Me.CO.CH_2.CO.C_4H_7.**—S. in alkalies.—Alc. sol. is colored intensely red by $FeCl_3$.—Olive-green Cu salt, m. p. 123°.
205		† **Guiacol** (cf. IV, A, m. p. 31°–2°).
205–6	1·086 (15°)	**Veratrol, o-$C_6H_4(OMe)_2$.**—Solid at +15°.
206	0·982$^{20}/_{17}$	**Ethyl Allylacetoacetate, Me.CO.CHC_3H_5.CO_2Et.**—Sol. colored carmine-red by $FeCl_3$.—Saponification by Test V gives allylacetone, C_2H_5OH, and CO_2.
207c.	1·037 (0°)	**Phlorol, o-Et.C_6H_4.OH.**—Not solid at −18°.—Violet color w. little $FeCl_3$.—Fusion w. KOH gives salicylic ac. (Test 319).
208·5	0·981$^0/_4$	**Ethyl Propylacetoacetate, Me.CO.CHPr.CO_2Et.**—Saponification by Test V gives methyl butyl ketone, C_2H_5OH, and CO_2.
211·5		**1, 3-Xylenol(1)** (cf. IV, A, m. p. 26°).
213c.	1·012$^0/_4$	**o-Isopropylphenol, Me_2.CH.C_6H_4OH.**—M. p. 15°.—Aq. sol. violet and then green w. $FeCl_3$.
214	1·025 (0°)	**m-Ethylphenol, Et.C_6H_4OH.**—M. p. abt. −4°.—Violet w. $FeCl_3$.
217·5	0·951 (17·5°)	**Ethyl Isobutylacetoacetate, Me.CO.CH(C_4H_9).CO_2Et.**—Saponification by Test V gives isobutylacetone, C_2H_5OH, and CO_2.
221–2	1·111 (0°)	**Homopyrocatechinmethylether, Kreosol, C_6H_3.(Me)(MeO)(OH)(1, 3, 4).**—Miscible w. alc. or eth.—Alc. sol. emerald-green w. $FeCl_3$.—M. p. of picrate 96°.
224c.	1·197 (0°)	† **Methyl Salicylate, o-HO.C_6H_4.CO_2Me.**—Odor of oil of wintergreen.—The color of the cold saturated aq. sol. w. $FeCl_3$ (Test 401) is RV, permanent for more than 15 minutes.—Saponification by Test V gives salicylic ac. and CH_3OH (Tests 319 and 819).
225c.	1·015 (0°)	**o-Propylphenol, HO.C_6H_4.Pr.**
227·5		**Ethyl Isoamylacetoacetate, Me.CO.CH(C_5H_{11}).CO_2Et.**—Saponification by Test V-2 gives isoamylacetone, C_2H_5OH, and CO_2.
231c.	1·009 (0°)	**p-Propylphenol, HO.C_6H_4.Pr.**
231		**Isocymophenol, C_6H_3.(Me)(Pr)(OH)(1, 3, 6).**—Not solid at −25°.—S. aq.—Aq. sol. pale-violet w. $FeCl_3$.—Vapor induces coughing.
231·5		† **Ethyl Salicylate, o-HO.C_6H_4.CO_2Et.**—Odor of oil of wintergreen.—The color of the cold saturated aq. sol. w. $FeCl_3$ (Test 401) is RV (on mixing); VRT2–RVT1 after 15 minutes.—Saponification by Test V-2 gives salicylic ac. and C_2H_5OH (Tests 319 and 814).
236·5–7	0·986 (15°)	† **Carvacrol, Me.C_6H_3.(Pr)(OH)(1, 4, 2).**—Viscous oil which solidifies at −20°.—$FeCl_3$ gives a coloration, but only in *very conc. alc. sol.;* the color is then an impure green, which changes and fades rapidly.—M. p. of the phenylcarbamate 140°.—(Cf. Ber. 26, 2086.)
238–40d.	1·098 (15°)	**Diethyl Acetylmalonate, C_2H_3O.CH.(CO_2Et)$_2$.**—Has a strong ac. reaction! Alc. sol. dark red w. $FeCl_3$.—Phenylhydrazine derivative melts at 120°.—Saponification by Test V-2 gives acetone, acetic ac., and C_2H_5OH (Tests 711, 311).
238–40	1·098 (15°)	**Propyl Salicylate, PrCO_2.C_6H_4.OH.**—Saponification by Test V-2 gives salicylic ac. and C_3H_7OH (Tests 319 and 820).
240–41c.	1·056 (15°)	**Cœrulignol, HO.C_9H_{10}.OMe.**—Odor like creosote.—V. d. s. c. aq.; miscible w. alc. or eth.—Aq. sol. gives carmine ppt. w. $FeCl_3$.—Alc. sol. green w. $FeCl_3$ and blue w. $Ba(OH)_2$.
242	1·144 (23°)	**Methyl 4-Oxy-m-toluate, HO.C_6H_3(Me).CO_2Me.**—Oil of wintergreen odor.—Saponification by Test V gives 4-oxy-m-toluic ac. and CH_3OH (Test 819-1).
243	1·140 (23°)	**Methyl 3-Oxy-p-toluate, HO.C_6H_3Me.CO_2Me.**—Saponification by Test V-2 gives 3-oxy-p-toluic ac. and CH_3OH (Test 819-1).

Boiling-point (C.°).	Specific Gravity.	PHENOLIC COMPOUNDS.—Colorless and Liquid.
243–4		**Methylresorcin Ether, m-HO.C_6H_4.OMe.**—S. c. aq.; miscible w. alc. or eth.—Aq. sol. pale violet w. $FeCl_3$.
247·5 sl. d.	1·063 (18·5°)	† **Eugenol, C_6H_3.(CH_2.CH:CH_2)$(OH)_2$(1, 3, 4).**—Odor of cloves.—V. d. s. aq.; e. s. alc., eth., or Ac.—Cold saturated *aq.* sol. gives a turbid YGT2 color in Test 401, w. $FeCl_3$; the *alc.* sol. (1:50) gives a B color fading in 15 min to GYT2.
248	1·102 (23°)	**Ethyl 1-Methyl-2-oxybenzoate(3), Me.C_6H_3(OH).CO_2Et.**—Sapon equiv. 178.—The corresponding ac. gives violet color w $FeCl_3$.—Saponification by Test V–2 gives 1-methyl-2-oxybenzoic ac. and C_2H_5OH (Test 814).
254	1·097 (23°)	**Ethyl 3-Oxy-p-toluate, HO.C_6H_3(Me).CO_2Et.**—Saponification by Test V–2 gives 3-oxy-p-toluic ac. and C_2H_5OH (Test 814).
254–5	1·067 (15°)	**Betelphenol, (CH_2.CH:CH_2).C_6H_3.$(OH)_2$(OMe)(1, 3, 4).**—Alc sol. intense blue-green w. alc. $FeCl_3$. (In ethereal oil from Piper betle.)
254–6	1·088 (15°)	**Diethyl Acetylsuccinate, $C_{10}H_{16}O_5$.**—Red-violet color w. $FeCl_3$.—Saponification by Test V–2 gives acetic and succinic acids and C_2H_5OH (Tests 311, 320, and 814).
258–62	1·080 (16°)	**Isoeugenol, (CH:CH.Me).C_6H_3.$(OH)_2$(1, 3, 4).**—Solidifies in freezing mixture.—Alc. sol. green w. $FeCl_3$.
265–70d.	1·122 (15°)	† **Ethyl Benzoylacetate, C_6H_5.CO.CH_2.CO_2Et.**—S. without decomposition in c. dil. NaOH.—Alc. sol. gives red-violet color w. $FeCl_3$.—Saponification by Test V–2 gives acetophenone, C_2H_5OH and CO_2 (Tests 712 and 814).
266–9		**Phenylacetylacetone, Ph.CH_2.CO.CH_2.CO.Me.**—D. s. c. aq.; e. s. dil. alkalies.—$AgC_{11}H_{11}O_2$, flocculent ppt.
270		**Isoamyl Salicylate, o-HO.C_6H_4.$CO_2C_5H_{11}$.**—Saponification by Test V gives salicylic ac. and $C_5H_{11}OH$ (Test 319).
273		**Methyl Orcinyl Ether, MeO.C_7H_6.OH.**—D. s. aq.; e. s. alc. or eth.—Browns on exposure to air.
283–4	1·036$^{15}/_{16}$	**Ethyl Benzylacetoacetate, C_2H_3O.CH(C_7H_7).CO_2Et.**—Saponification by Test V–2 gives Me.CO.$(CH_2)_2$.Ph, C_2H_5OH, and CO_2.

NUMBERED SPECIFIC AND SEMI-SPECIFIC TESTS FOR PHENOLIC COMPOUNDS.

[TESTS 401–500.]

401. Ferric-chloride Colorations.

The test with ferric chloride, forming the first part of Generic Test IV, is designed rather to favor the development of a maximum color effect in the largest possible number of cases than to secure the most characteristic results for individual species. To obtain the ferric-chloride coloration attributed to any phenol in the description given in the tables, it is necessary to pay attention both to certain principles that will be now stated, and to the special supplementary directions concerning dilution, etc., that form part of many of the individual specific descriptions.

The most desirable concentration for the phenol solution is one that will give a color of such quality and intensity that, when viewed horizontally in a six-inch test-tube, it will nearly match a spectrum color or "tint", rather than a "shade" or a "broken color" of the color standard. This concentration varies greatly with the phenol, but in aqueous solutions is often met in a 1 per cent solution. Alcohol is usually a much less satisfactory solvent in these tests than water, but is sometimes to be preferred. The same phenol often gives different colorations in the two solvents. Hot solutions must never be used with either solvent. The colors from some phenols are permanent for hours; but more often are very transitory, the first coloration sometimes undergoing a complete change in hue, or entirely fading away within a few seconds or minutes. The coloration is occasionally accompanied by a precipitate. The appearance of a color is prevented by the presence of either free acid or alkali, or else its character is essentially modified (cf. pyrocatechin). An excess of ferric chloride may destroy the coloring matter that is first formed, or obscure the proper coloration by blending it with yellow.

The usual procedure in the specific test with ferric chloride is as follows:

Place 5 cc. of the clear, cold solution of the phenol, which has the concentration specified in the tables, in a six-inch test-tube. Add one or more drops of a ferric-chloride solution (1 : 40) prepared by diluting one volume of the 10 per cent stock solution of the salt with three volumes of water. Use no more of the reagent than is required to produce a color suitable for comparison. Shake; and then, without delay, make a careful comparison of the color produced with the color standard. Repeat the comparison after the mixture has stood for five and for fifteen minutes. Comparisons should be made in clear diffused daylight, looking horizontally through the tube towards a white wall or card immediately behind it (cf. p. 232).

402. The Phthaleïn Fusion.

Mix about 0.05 grm. of the phenol with an equal bulk of powdered phthalic anhydride in a dry test-tube. Moisten with one drop of concentrated sulphuric acid. Stand the tube in a small beaker containing an inch or two of sulphuric acid, oil, or molten paraffin, which has been heated up to a nearly constant temperature of 160°. Heat for three minutes. Cool. Add 2 cc. of cold water, and 1–2 cc. of sodium-hydroxide solution (1 : 10); i.e.

enough to give the solution quite a strong permanent alkaline reaction. Stir the fused mass at the bottom of the tube until most of it has dissolved. Dilute with an equal volume of water and filter. Compare the color of the filtrate with the color standard (cf. p. 232), using such a dilution that the comparison can be conveniently made in a six-inch test-tube held before a white background. If the solution shows a fluorescence, examine its color with a black background.

The colors observed in this test are frequently intense and characteristic. When the coloration given by a phenol has been compared with the color standard, it will usually be found mentioned among the tabulated properties and reactions of the species.

411. Hydroquinone. (Properties tabulated on p. 99.)

1. Dissolve 0.1 grm. of the substance in 3 cc. of warm water. Cool, and slowly add 2-3 cc. of a 10 per cent ferric-chloride solution. Shake. Filter off the precipitate of green-black glistening quinhydrone. Collect the filtrate in a small graduate and wash with cold water until the total filtrate measures 10 cc. Rinse the precipitate into a test-tube, using 6 cc. of water. Warm to just 40°, so as to partly dissolve the crystals. (Boiling would decompose the quinhydrone to quinone.) Cool to below 20°. Filter into a small graduate, and wash with cold water until the filtrate measures 10 cc. Dry the precipitate on a piece of porous tile supported over a drying-oven where the temperature will be 35° to 40° for twenty minutes, and determine its melting-point. *Quinhydrone* is obtained in this test in slender needles of a peculiar greenish-black color and beautiful metallic luster. Rapidly heated it begins to sublime at 145°-50°; gradually softens; and, finally, not far from 170° (uncor.) melts completely to a dark orange-red liquid. Even when cold it emits a faint pungent odor of quinone.

412. α-Naphthol. (Properties tabulated on p. 94.)

1. Dissolve 0.05 grm. of the naphthol in 10 cc. of a 1 per cent caustic-soda solution. Add five drops of chloroform, and boil 20 seconds. Compare the color immediately with the standard (cf. p. 232).

α-Naphthol gives at first a clear blue (B). In 15 minutes the color changes to a bluish-green (GB-BG); in 4½ hours to yellow-green (YG).

2. Dissolve 0.10 grm. of the substance, and 0.15 grm. of picric acid, in 10 cc. of boiling dilute alcohol (1 : 1). Allow to cool slowly. Filter off the orange (O) needles of picrate, which separate after short standing and shaking, and wash with 2 cc. of dilute alcohol (1 : 1). Dry in a warm place on a bit of porous tile. Determine the melting-point in a bath whose temperature is rising somewhat rapidly.

The picrate, ($C_{10}H_8O.C_6H_3(NO_2)_3O$), melts at 188.5°-189.5° (uncor.).

413. β-Naphthol. (Properties tabulated on p. 96.)

1. Apply Test 412, 1.—The first coloration is blue (B); but unlike that from α-naphthol it fades rapidly, passing through GB and YT_2 of the color standard to colorlessness in 10 minutes.

2. Dissolve 0.10 grm. of the substance, and 0.15 grm. of picric acid, in 6 cc. of boiling dilute alcohol (1 : 1). Then proceed as in Test 412, 2.

The picrate, ($C_{10}H_8O.C_6H_3(NO_2)_3O$), crystallizes in long thin needles of an orange-yellow color (YO) which melt, when somewhat rapidly heated, at 155.5°-156.8° (uncor.).

414. Phenol. (Properties tabulated on p. 91.)

1. The "phthaleïn fusion" (Test 402) gives a bright violet-red (VR) solution after adding alkali due to formation of phenolphthaleïn.

2. Dissolve 0.05 grm. of the substance in 1 cc. of concentrated sulphuric acid. Pour with stirring into a mixture of 1 cc. of concentrated sulphuric acid and 1 cc. of concentrated nitric acid. Heat on a water-bath for 5 to 10 minutes. Pour slowly into 10 cc.

of cold water. Cool thoroughly. Filter. Wash the precipitate with a cold mixture of 2 cc. of water and 0.5 cc. concentrated hydrochloric acid. Recrystallize from a boiling mixture of 4 cc. of water and 1 cc. of concentrated hydrochloric acid. Cool well and filter. Wash as before with a cold mixture of 2 cc. of water and 0.5 cc. concentrated hydrochloric acid. Dry at 100°, and determine the melting-point.

The product in this test is *picric acid* (trinitrophenol) melting at 122.5° (cor.). Picric acid crystallizes from the dilute hydrochloric acid in plates, that are at first nearly colorless, but which gradually become yellow on exposure to the air. It deflagrates when heated on platinum foil. A dilute aqueous solution of the compound stains the skin and dyes wool an intense yellow; and its taste is very bitter. The test is simple, and very satisfactory when the result is corroborated by other evidence; but it should be remembered that picric acid is also formed, though usually not with the same ease, by the nitration of some other compounds. Since picric acid can be dried at 100°, this test may be completed more quickly than Test 3. It is, nevertheless, at least equally reliable.

3. Dissolve 0.05 grm. of the substance in 2 cc. of water, and add a saturated aqueous solution of bromine until the reagent is present in excess, the color of the liquid then remaining permanently yellow. Filter off the bulky, curdy yellowish-white precipitate. Transfer to a small beaker. Cover the precipitate with water, and add acid sodium-sulphite solution gradually until a strong odor of sulphur dioxide remains after stirring and warming to 40°. Filter. Wash well with cold water. Dissolve in 15 cc. of boiling 40 per cent alcohol. Filter off the precipitate which separates on cooling. Transfer to a piece of porous tile; allow to become thoroughly air dry, and determine the melting-point.

The white, crystalline 2, 4, 6-*tribromphenol* obtained as the final product by this procedure is very insoluble in cold water and melts at 92.5°–93.5° (uncor.). The precipitate with bromine water contains at first an excess of bromine, and consists of the compound $C_6H_2Br_4O$, which loses one atom of bromine and is converted into the tribrom-derivative during the treatment with the sulphite solution. Salicylic acid also gives tribromphenol when treated with bromine water. The bromine-water test is most useful when phenol is present in small quantity in a dilute aqueous solution.

415. Phloroglucin. (Properties tabulated on p. 101.)

Dissolve 0.1 grm in. 1 cc. of concentrated sulphuric acid by stirring. Pour the clear solution into a mixture of 1 cc. of concentrated sulphuric, and 1 cc. of concentrated nitric acids, cooling with cold water, and stirring until a precipitate appears. Allow to stand for five or six minutes; then pour into 10 cc. of cold water. Cool well and filter. Wash the precipitate with 2 cc. of water containing 0.5 cc. of concentrated hydrochloric acid. Recrystallize from a boiling mixture of 3 cc. of water and 1 cc. of concentrated hydrochloric acid. Cool and filter. Wash with 2 cc. of water containing 0.5 cc. of concentrated hydrochloric acid. Dry at 100°–105°.

The product, *trinitrophloroglucin*, crystallizes easily in pale-yellow needles melting at 165°–166° (uncor.). It stains the skin yellow, and deflagrates when heated on platinum foil like picric acid.

416. Pyrocatechin. (Properties tabulated on p. 94.)

1. Always apply the ferric-chloride color reaction as directed in the tables, adding 1 cc. of the ordinary laboratory sodium-carbonate solution in the latter part of the test. This test requires very little substance, and is one of the most satisfactory of its class.

2. Dissolve 0.05 grm. of the substance in 2.5 cc. of warm chloroform. Add 0.4 cc. of bromine. Evaporate to dryness on a water-bath. Dissolve the residue in 5 cc. of cold alcohol. Add 20 cc. of cold water. Shake, and then filter. Wash the precipitate with a little cold water. Redissolve in 5 cc. of alcohol, and reprecipitate with 20 cc. of cold water. Allow the precipitate to become air dry on a piece of porous tile, and determine its melting-point.

The product, *tetrabrompyrocatechin*, crystallizes in white needles. As obtained in this test, the crystals are often tinged with violet, and melt (not very sharply) at about 192°–3° (uncor.) after beginning to shrink and soften at 185°–187°.

417. Pyrogallol. (Properties tabulated on p. 96.)

1. To 2 cc. of water in a 6-inch test-tube add 1 drop of glycerine and 5 drops of a solution of 0.01 grm. of the substance in 1 cc. of water. Next add 2 cc. of concentrated sulphuric acid and boil for 20–25 seconds. Then, *without delay*, compare the color of the hot solution with the color standard (cf. p. 232). Use a white background behind the tube.

The color given by pyrogallol in this test is a clear tint of violet-red (VRT 1–2). On continued boiling or standing, the color intensifies rapidly, but soon becomes impure and unsuited for purposes of comparison.

2. In a dry test-tube place 0.1 grm. of pyrogallol, 0.5 grm. of powdered anhydrous sodium acetate, and 1.0 cc. of acetic anhydride. Boil for one and one-half to two minutes. Add 10 cc. of water, and boil for fifteen or twenty seconds till the oily liquid solidifies. Cool. Filter, and wash with 10 cc. of cold water. Dry at 100°–105°.

The product obtained in this test, *pyrogallol triacetate*, is in the form of white crystals which soften at about 155° and melt at 160.5°–161.5° (uncor.) when heated rather rapidly. Recrystallization from 4 cc. of strong alcohol raises the melting-point about 0.5°

418. Resorcin. (Properties tabulated on p. 95.)

1. One of the simplest, most delicate, and rapid of the tests for resorcin is the fluoresceïn fusion, which is fully described under Test 318–1. If more convenient, substitute phthalic anhydride for the phthalic acid.

Color reaction 114 with formic aldehyde furnishes another simple resorcin test.

2. Dissolve 0.1 grm. in 1 cc. concentrated sulphuric acid. Pour slowly with constant stirring into a cold mixture of 1 cc. concentrated nitric acid and 1 cc. concentrated sulphuric acid. (It is well to place the mixed acids in a small round-bottomed dish resting on the top of a small beaker filled to the brim with very cold tap water.) Do not run in the resorcin solution fast enough to cause a *permanent* brown coloration in the acid. When all has been added, remove the dish from the cold water and allow to stand on the table for two or three minutes. Then pour the mixture of liquid and yellow crystals that have separated slowly into 10 cc. of cold water, keeping well cooled with running water. Filter. Wash with 5 cc. of cold water. Recrystallize from a boiling mixture of 10 cc. of cold water, 4 cc. strong alcohol, and 0.4 cc. concentrated hydrochloric acid. Cool well and shake. Filter. Wash with 5 cc. of cold water and dry at 100°.

The product in this test, *trinitroresorcin*, consists of slightly yellowish crystals of melting-point 175° (uncor.). It stains the skin yellow like picric acid. The yield is good.

419. Thymol. (Properties tabulated on p. 92.)

1. The colors obtained in the phthaleïn fusion (Test 402), and described in the tables, are quite characteristic. This test should always be applied.

2. Dissolve 0.1 grm. of the powdered substance in 1 cc. of concentrated sulphuric acid. Add with stirring to a mixture of 1 cc. of concentrated nitric, and 1 cc. of concentrated sulphuric acids contained in a very small dish. Allow to stand on the cover of a boiling water-bath for three or four minutes. Pour into 20 cc. of cold water. Cool well and shake vigorously. Filter. Wash the precipitate with 10 cc. of cold water. Crystallize from a boiling mixture of 10 cc. water, 4 cc. alcohol, and 0.4–0.6 cc. concentrated hydrochloric acid. Filter. Wash with 5 cc. of cold water. Dry on a piece of porous tile in the air, or in a drying-oven below 50°.

The product in this test is *trinitrothymol*, melting at 109°–110° (uncor.). The crystals, which are at first nearly colorless, like those of many other nitrophenols, turn lemon-yellow after a few hours' exposure to the air.

CHAPTER VII.

GENUS V. ESTERS

OF

SUBORDER I, ORDER I.

(Colorless Compounds of Carbon, Hydrogen, and Oxygen.)

The tables of this genus contain only the most important esters derived from the well-known volatile alcoholic compounds enumerated in the table on p. 116. Other esters are to be identified through their alcoholic and acidic saponification products by a method which will be given in connection with "Procedure 2" of the generic test. Esters that are rapidly saponified by cold alkali, the ester-acids, ester-phenols, and the enolic esters, show a behavior with reagents which places them in Genus III or IV with the acids or phenols. Finally, a few esters like those of the aromatic diortho-substituted carbonic acids, which offer extraordinary resistance to the action of hot alkali, fall in later genera.

GENERIC TEST V.

APPLY PROCEDURE 1.—IF THE RESULT IS NEGATIVE, THE COMPOUND DOES NOT BELONG TO EITHER GENUS V OR VI. IF IT SHOWS THAT THE COMPOUND MAY BE AN ESTER OR ACID ANHYDRIDE, BUT FAILS TO POSITIVELY IDENTIFY IT WITH ANY SPECIES DESCRIBED IN GENUS V OR VI, PROCEDURE 2 SHOULD, IF POSSIBLE, THEN BE APPLIED.—[PROCEDURE 2 MAY LEAD TO THE IDENTIFICATION OF ANY ESTER THAT SAPONIFIES TO AN ALCOHOL AND ACID DESCRIBED IN THESE TABLES, WHETHER THE ESTER IS ITSELF MENTIONED OR NOT, BUT IS LONGER THAN PROCEDURE 1.]

PROCEDURE 1.

Weigh out very carefully in a 3-inch lipped weighing tube about 0.1 grm. of the substance. Add 2 cc. of a nearly colorless and approximately normal solution of sodium or potassium hydroxide in pure strong alcohol from a thin-stemmed pipette. The pipette need not be accurately calibrated, but must be used with such precautions to ensure *uniformity* in delivery that the volume of liquid discharged by it in two successive experiments shall not differ by more than about 0.005 cc. Stopper the weighing tube tightly with a sound soft cork, which must be wired down with a thin copper wire in the manner shown in Figure 3. [The wire, after being first doubled, is twisted so as to form a small eye at A. It is then drawn tightly around the tube by twisting with pliers at B, and the free ends passed over the cork and through the eye. The ends are then seized with the pliers and drawn back with sufficient force to slightly imbed the wire at the edges of the cork. If the wire is now bent sharply back upon itself, as is shown at C, the stopper will be securely held during the subsequent heating.] Place 2 cc. of the same normal alkali that was added to the substance in a second tube stoppered like the first.

Hang the two tubes from a glass rod by their wires, side by side, in a beaker of boiling water, and heat for thirty minutes. Or, better still, thrust the tubes through perforated cork stoppers, and heat half an hour at 100° in a bath of the kind described on p. 152 and shown in Figure 4. Then wash the contents of each tube into a separate small beaker, and titrate carefully with *decinormal* acid and phenolphthaleïn. From the results of the titrations calculate the "saponification equivalent" * of the compound by use of the following formula, in which the number of cubic centimeters of standard acid consumed in neutralizing the alkali used for the blank experiment is represented by a; and the quantity consumed by the alkali after being heated with the substance, by b. Then—

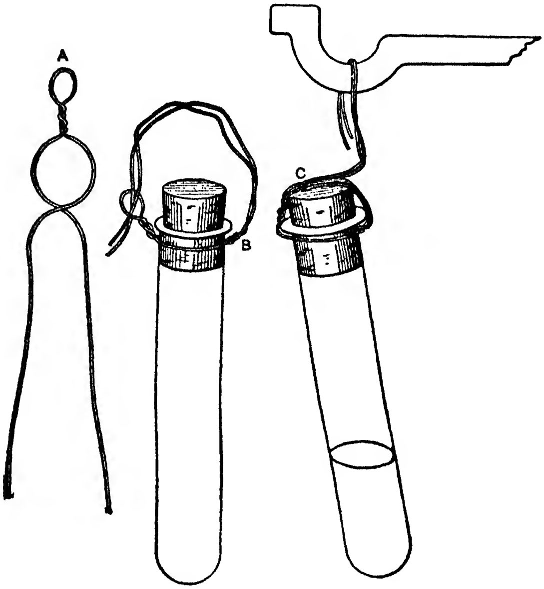

Fig. 3.

$$\text{Sap. Eq.} = \frac{1000 \times \text{grm. of ester taken}}{(a\text{-}b) \times \text{normal strength of the standard acid}}.$$

If this equivalent is found to have a value greater than 500, pass on to Genus VII; for in this case the compound can not be a species described in either Genus V or VI. If, on the contrary, the equivalent has a value less than 500, a search must be made through the proper divisions of the tables of Genera V and VI for a species whose physical constants and saponification equivalent correspond to those found for the substance. If this search leads to the discovery of an apparently corresponding species, the identification may sometimes be satisfactorily completed by the application of special tests suggested in the text. In all other cases, provided the supply of substance remaining permits, it is best to saponify a larger quantity,

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* By "saponification equivalent" is here meant the number expressing how many grams of a compound would be required to just neutralize 1000 cc. of normal sodium hydroxide solution in a saponification experiment.

and isolate and identify its acid,* or alcohol, or both, by the methods given under Procedure 2.

PROCEDURE 2.

Saponify with aqueous alkali as directed below under **A.** Identify any neutral saponification products (alcohols, phenols, or ketones) as directed under **B,** below, and any acid saponification products according to **C,** p 116.

A (Saponification).

Fit a 250-cc. round-bottomed flask with a clean, sound cork stopper perforated to receive the lower end of a return-flow condenser that has been mounted vertically on a heavy iron stand.

Introduce about 2 grm. of the substance, accurately weighed, into the flask; and then, from a pipette, exactly 50 cc. of an aqueous normal solution of pure sodium hydroxide. Next drop in an ebullator-tube to prevent bumping (cf. p. 223) and boil briskly for about two hours, or even longer if the odor or appearance of the mixture gives indication that, while the substance has been attacked by the treatment, a portion of it remains unchanged. The flask should rest lightly on a square of iron gauze during the boiling, and the burner flame should be shielded from drafts of air; for any pause in the boiling that is more than momentary will cause the ebullator capillary to fill, after which such violent bumping may occur as to shatter the flask.

The saponification completed, cool; add two drops of phenolphthaleïn solution, and titrate with normal sulphuric acid without removing from the flask. The saponification equivalent may now be calculated from the experimental data by substituting in the equation—

$$\text{Sap. Eq.} = \frac{1000 \times \text{no. grm. ester saponified}}{\text{no.cc. alkali neutralized in saponific.} \times \text{normal strength of alkali}}.$$

B (Examination of the Neutral Saponification Products).

Drop a fresh ebullator-tube into the flask whose contents have been neutralized in the titration mentioned in the last paragraph, and rapidly distil off 40 cc. of liquid through an inclined condenser, collecting the distillate in a tall narrow graduated cylinder or test-tube:

During the first part of the distillation, observe whether the distillate is turbid, separating into two layers in the recipient, or is clear and apparently homogeneous. At the same time make careful note of the odor. (The greater part of the volatile alcohols, phenols, and ketones will be contained in the first few cubic centimeters of the distillate.) After the distillate has all been collected, if two layers are still

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* The quantity of acid present as sodium salt in the neutral solution after the titration in Procedure 1 is so small that its direct identification is only occasionally possible. In such cases the procedure, after evaporating the solution to a very small volume and filtering, is identical with that described in Section C (p. 116) of Procedure 2.

present, close the mouth of the test-tube with the thumb and shake, in order to ascertain whether the smaller layer, which will usually have a volume considerably less than 1.0 cc., can be dissolved in the water present. If a clear solution is not obtained, separate the two layers by the aid of a long and very thin-stemmed pipette. The aqueous solution is at once used for the lettered tests (**a**) to (**i**) which follow. The smaller layer, consisting of compounds not readily soluble in cold water, is dried, and its boiling-point later determined by the procedure given towards the end of paragraph (**i**).

(**a**) **Phenol.**—If the odor of the distillate suggests the presence of phenol, remove 1 cc. of the clear aqueous solution to a 3-inch test-tube and add bromine water in excess. If a voluminous white precipitate appears, add to a second 1 cc. portion of the distillate one drop of a ferric-chloride solution (1:200). Then, if a violet coloration is obtained, phenol is probably present. If more conclusive evidence is wished for, apply Specific Test 414–3 to the remaining portion of the distillate.

(**b**) **Allyl Alcohol.**—If the odor of the distillate is purely pungent, like horseradish or mustard-oil, allyl alcohol may be present. In this case 1 cc. of the distillate will instantly decolorize two or three drops of a saturated aqueous solution of bromine. (Allyl alcohol is miscible with water.)

(**c**) **Isobutyl and the Amyl Alcohols.**—If the vapors from the first part of the distillate are disagreeable and suffocating, tending to produce coughing when deeply inhaled, isobutyl alcohol or an amyl alcohol is likely to be present. These alcohols always rise to the surface of the distillate as distinct layers during the *first part* of the distillation, but are miscible on shaking,—isobutyl alcohol easily, the amyl alcohols with more or less difficulty. Isolate, dry, and determine the boiling-point of the alcohol in the distillate by the method described under test (**i**).

(**d**) **Benzyl Alcohol.**—If the odor of the distillate is faintly aromatic, and some of the oily drops that separate from it sink to the bottom of the recipient but dissolve later upon being shaken, benzyl alcohol may be present. Separate from the solution by the method of paragraph (**i**). Determine the boiling-point and finally apply Test 812.

(**e**) **Higher Volatile Fatty Alcohols.**—If the distillate contains an upper layer whose odor is milder, less suffocating, and more aromatic than that of amyl alcohol, and does not dissolve in the aqueous layer after shaking, one of the volatile fatty alcohols higher in the homologous series than amyl alcohol should be looked for. In this case "salt out" the organic compound directly, by adding 40 grm. of dry potassium carbonate; mix it with the smaller insoluble layer which separated from the original distillate; and then dry and determine the boiling-point as in paragraph (**i**).

(**f**) **Methyl Alcohol and other Lower Fatty Alcohols and Ketones.**—If the distillate is a clear solution without layers, and is odorless, or has a mild alcoholic odor, remove 2 cc., oxidize with a hot copper spiral, and examine for methyl alcohol by Specific Test 819. If no colored ring whatever appears in this test, the distillate does not contain any volatile alcohol provided for in this method, or acetone; and unless some non-volatile alcohol can be separated from the salts remaining in the distilling-flask, the compound under examination must next be sought among the species of Genus VI.

(g) Acetone and Isopropyl Alcohol.—If no satisfactory reaction for methyl alcohol was obtained in (f), but a reddish, yellowish, or brownish ring was noticed, remove 1 cc. of the original distillate to a 3-inch test-tube and add; first, two drops of the iodine solution (described in Test 801); and then barely enough sodium hydroxide (1 : 10) to just destroy the brown color of the iodine. The immediate appearance of a yellowish-white precipitate of iodoform will indicate the possible presence of acetone or isopropyl alcohol.* In case such a precipitate does appear, separate out the alcohol or acetone contained in the remaining portion of the distillate by the method of paragraph (i), and determine its boiling-point.

(h) Ethyl Alcohol.—If no iodoform was obtained in (g), heat the same portion of solution used in the test to 60°, and add another drop of caustic soda and just enough more iodine to give a very faint permanent coloration. If a good precipitate of iodoform appears within one minute, and the colored ring in test (f) was a deep impure greenish or amber yellow, ethyl alcohol is very probably present. If no iodoform separates within a minute, normal propyl and butyl alcohols remain to be looked for. In any case, proceed as directed in the following paragraph.

(i) Identification of n-Propyl and n-Butyl, or other Soluble Alcohols, by Boiling-point Determination.—Transfer the remainder of the distillate, which will now measure at least 30 cc., to a 100-cc. distilling-flask containing 30 grm. of dry potassium carbonate. Connect with a condenser, and, when the carbonate has dissolved, drop in a fresh ebullator-tube and distil over 15 cc. of liquid, collecting in a narrow graduated cylinder or test-tube. Dissolve 15 grm. of dry potassium carbonate in the distillate by stirring, cooling with running water to prevent loss of alcohol by heating and evaporation. Stopper, and allow to stand for at least ten minutes. Insert a thin-stemmed pipette of about 25 cc. capacity into the liquid, so that its almost capillary point shall rest lightly on the bottom of the tube. Suck the solution, to the last drop, into the pipette. After waiting a few seconds for all the small globules of alcohol to rise to the surface and unite, allow the lower layer, consisting of carbonate solution, to run out slowly into a beaker. Collect the upper layer of alcohol, which may measure less than 0.5 cc., by itself, in a narrow weighing-tube just wide enough to admit the stem of the pipette. Drop in a granule of dry potassium carbonate having a bulk one-third as great as that of the liquid. Stopper, and allow to stand for half an hour or more. Then incline the tube; remove the clear alcohol by a thin capillary pipette, and determine the boiling-point by Siwoloboff's method, following the directions for manipulation given on p. 222. *Do not neglect the precaution to boil off half the liquid before allowing it to recede into the capillary for the final observation of temperature.* This method requires no complicated apparatus, and gives useful results with as little as 0.1 cc. of an alcohol. Enough alcohol will often be left after the boiling-point determination to permit its identification by other special confirmatory tests.

The accompanying table contains a list of all the neutral volatile products that are formed from the saponification of the ester species described in the tables of Genus V. With the exception of phenol, they are all liquids at the ordinary temperature; and with the exception of phenol and acetone, all are alcohols.

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* See Test 801, p. 166.

Neutral Saponification Product.	Boiling-point (C.°).	Number of Specific Test.	Neutral Saponification Product.	Boiling-point (C.°).	Number of Specific Test.
Acetone	56·5c.	711	Act. Amyl Alcohol.	128·7	
Methyl Alcohol	66	819	Isoamyl Alcohol	130	
Ethyl Alcohol	78·4	814	n-Amyl Alcohol	137·8 (th. i.)	
Isopropyl Alcohol	82·8	818	n-Hexyl Alcohol	157c.	
Tert. Butyl Alcohol	82·9c.		n-Heptyl Alcohol	175·8 (th. i.)	
Allyl Alcohol	96·6	811	n-Octyl Alcohol	195·5 (th. i.)	
Propyl Alcohol	97·4c.	820	Phenol	183	414
Sec. Butyl Alcohol	99·8		Benzyl Alcohol	204·7c.	812
Isobutyl Alcohol	106·5	817	Glycerine	290 (very little volatile with steam)	816
n-Butyl Alcohol	117c.	813			

(j) **Non-volatile Alcohols.**—Esters of alcohols not volatile with steam forming, with the exception of the natural fats, a comparatively unimportant class, are omitted from the tables. The alcohols from such esters remain behind in the flask with the neutral sodium salts after the distillation in **B**. They may usually be separated from these salts by extraction with ether or other organic solvent, and identified, after purification, by application of the usual systematic procedure used for the species of Genera IV, VII, and VIII. But unless the alcohol in such cases is very easily purified, a much larger quantity of substance will have to be used in the saponification than would otherwise be necessary.

For the identification of glycerine, after saponification, evaporate the neutral salt solution to dryness on the water-bath, extract with ether-alcohol, and then proceed as directed in Test 816.

C (Examination of the Acid Saponification Products).

The acid radicals of esters are identified through an examination of the sodium salts remaining in the neutral solution obtained from the saponification equivalent determination of **A** (p. 113) after the alcoholic saponification products have been removed by the methods described under **B** (p. 113).

This neutral saline solution, if not clear, must first be filtered. Then add to it, in the cold, a quantity of normal sulphuric or hydrochloric acid exactly equivalent * to the alkali *consumed* during the saponification; i.e. just enough to unite with that portion of the sodium present which is in combination with the organic acid. Shake vigorously, and then proceed as directed in paragraphs (**a**), (**b**), and (**c**) below.

(**a**) **Insoluble Acids.**—If a precipitate of an insoluble acid appears upon acidification and shaking, filter it off; purify it by recrystallization or other means; and identify it by reference to the tables of Genus III.

(**b**) **Soluble Acids Volatile with Steam.**—If no precipitate appears upon acidification, place the solution in a distilling-flask, drop in an ebullator capillary (cf. page 223), to prevent bumping, and rapidly distil over all but about 20 cc. (It may be necessary to add more water to the flask and to again distil, if the acid should be one that is only slowly volatile with steam.) Examine the distillate for soluble volatile acids.

To identify acetic acid or any of its immediate higher homologues in the same

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* If the mineral acid added at this point, and the alkali used for the saponification, both have the same normality, the volume of the standard acid here required will be identical with the "cc-alkali neutralized" which appears as a term in the denominator of the equation for the calculation of the saponification equivalent on p. 113.

series, neutralize the distillate exactly with caustic soda, evaporate to dryness, and apply Test 311 to the residue. The presence of formic acid in the distillate may be established by Test 315.

(c) Soluble Acids not Volatile with Steam.—Pour the mixture remaining in the distilling-flask after the removal of the volatile acids in (**b**) into an evaporating-dish, and evaporate to dryness on the water-bath. Extract the residue with ether or other volatile organic solvent. Purify the extracted acid, and identify it by the tables of Genus III.

Observations on Generic Test V.

The ease with which esters are saponified differs with the species and the method of saponification. Species soluble in water are all readily saponified by either Procedure 1 or 2; and some of them, like methyl formate, so rapidly that they may be slowly titrated, and are therefore described in Genus III instead of V. Among the liquid esters there are some slightly soluble species, like diethyl succinate, which appear perfectly neutral in the titration test for acids, but which are dissolved with saponification when shaken with cold aqueous normal alkali. Compounds of this class escape being classified with the phenols only because of the provision that Test IV-2, with alkali, shall not be applied to liquid species.

With increasing insolubility of the ester in water, saponification by Procedure 2 becomes slower and more difficult; but as most esters are quite soluble in hot alcohol, the rate of saponification of different species by Procedure 1 is comparatively uniform, so that the reaction is usually completed within half an hour. Procedure 1 is on this account an indispensable preliminary generic test for difficultly soluble esters. Some insoluble esters of high molecular weight would escape recognition as species of Genus V if examined by Procedure 2 only.

As regards really "non-saponifiable esters," there is no positive evidence that such species exist in Order I; and it has been shown by Mr. J. R. Odell, in the writer's laboratory, that even the esters of diortho-substituted aromatic acids, which V. Meyer has pointed out are exceptionally alkali resistant, are measurably attacked by the treatment of Procedure 1. Methyl 2, 4, 6-Trimethylbenzoate, for example, is 7 per cent saponified in the procedure at the end of half an hour, or 18 per cent when the salting-out effect* of the normal alkali is counteracted by previous dilution with an equal volume of alcohol. The velocity of saponification with esters of this class is not great enough, however, to bring them into Genus V.

The most serious limitation of Procedure 1 as a complete generic test is, that the use of ethyl alcohol as a solvent renders the direct identification of the lower boiling alcohols, when they are formed as saponification products, impracticable.

The possibilities for experimental error in the determination of a "saponification equivalent" by either of these procedures are more numerous than in the determination of the "neutralization equivalent" for acids. Differences of 5 per cent between the values found by these methods, and calculated from the theory, should not be considered serious discrepancies. The main object of the saponification is to ascertain quickly whether a compound really belongs to Genus V or VI or not.

*** Caustic soda appears to produce a "salting-out" effect upon some esters in alcoholic solution even when its concentration is only normal. In such cases the addition of one or two volumes of alcohol will give a clear solution and accelerate the saponification.**

GENUS V, ESTERS.

DIVISION A,—SOLID ESTERS WHOSE NEUTRAL SAPONIFICATION PRODUCTS, METHYL, ETHYL, PROPYL, BUTYL, AND ISOBUTYL ALCOHOLS, AND PHENOL, ARE SOLUBLE IN COLD WATER AND READILY VOLATILE WITH STEAM.

Melting-point (C.°).	Sapon. Equiv.	Boiling-point (C.°).	ESTERS.—Solid Esters whose Neutral Saponification Products are Soluble in Cold Water and Readily Volatile with Steam.
			Generic Position and Properties of the Acidic Saponification Products.
20	150	211c	**Phenyl Propionate**, $C_9H_{10}O_2$.— (III, B, 1), b. p. 140·7°; Test 311.
22	350		**Methyl Behenolate**, $C_{23}H_{42}O_2$.— (III, A, 2), m. p. 57·5°.
24·2	284		**Ethyl Palmitate**, $C_{18}H_{36}O_2$.— “ “ 62·6° c.
27–8		176° d. (13 mm.)	“ **Benzoylacetoacetate**, $C_{1}H_{14}O_4$.
28	270		**Methyl Palmitate**, $C_{17}H_{34}O_2$.— (III, A, 2), “ 62·6° c.
29		253°	**Triethyl Methanetricarbonate**, $C_{10}H_{16}O_6$. —Cf. Genus III, A, 2, m. p. 29°.
29–30	366	a. 360	**Ethyl Brassidate**, $C_{24}H_{46}O_2$.— (III, A, 2), m. p. 60°.
30			“ **Tetrinate**, $C_7H_{10}O_3$.— “ “ 189°.
32			**Diethyl Benzalmalonate**, $C_{14}H_{16}O_4$.—“ “ 195°; also cinnamic and malonic acids.
33·7	312	224d.	**Ethyl Stearate**, $C_{20}H_{40}O_2$.— “ “ 69·3° c.
34	180	254	“ **Mandelate**, $C_{10}H_{12}O_3$.— (III, A, 1), “ 118°.
34	194	273	“ **o-Hydrocoumarate**, $C_{11}H_{14}O_3$.—(III, A, 1), m. p. 82°–3°.
34	256		“ **Benzilate**, $C_{16}H_{16}O_3$.— (III, A, 2), m. p. 150°.
34	140	197c.	“ **Pyromucate**, $C_7H_8O_3$.— (III, A, 1), “ 132°–4°.
36	162	260c.	**Methyl Cinnamate**, $C_{10}H_{10}O_2$.— (III, A, 2), “ 133°; Test 313.
38	115	288d	**Dimethyl Sebacate**, $C_{12}H_{22}O_4$.— (III, A, 1), “ 133°.
38			**Methyl Stearate**, $C_{19}H_{88}O_2$.— (III, A, 2), “ 69·3° c.
42	149		**Diethyl Diphenate**, $C_{18}H_{18}O_4$.— “ “ 229°.
43·4	210	295°	**Ethyl Veratrate**, $C_{11}H_{14}O_4$.— “ “ 181°.
44	196	292	“ **Vanillate**, $C_{10}H_{12}O_4$.— “ “ 207°.
44	111		**Diethyl Terephthalate**, $C_{12}H_{14}O_4$.— “ sbl. a. 300°; Test 318.
45·5	166	255°	**Methyl Anisate**, $C_9H_{10}O_3$.— “ m. p. 184·2°.
48	89	280	**Dimethyl Tartrate**, $C_6H_{10}O_6$.— (III, A, 1), “ 168°; Test 314.
51	204	290	**Ethyl β-Methylcoumarilate**, $C_{12}H_{12}O_3$.—(III, A, 2), m. p. 188°–9°.
52	166		**Methyl Mandelate**, $C_9H_{10}O_3$.— (III, A, 1), m. p. 118°.
52	119		**Diethyl 4-Oxyisophthalate**, $C_{12}H_{14}O_5$.— (III, A, 2), m. p. 305°
54	59	163·3c.	† **Dimethyl Oxalate**, $C_4H_6O_4$.— Belongs to Genus III, A, 1.
57	96	abt. 200	**Diethyl Mesoxalate**, $C_7H_{12}O_6$.— (III, A, 1), m. p. 119°–20°.
57			**Ethyl Dibenzylacetoacetate**, $C_{20}H_{22}O_3$.—(III, A, 2), m. p. 89°.
56–8		325–8d.	**Tetraethyl Ethylenetetracarbonate** $C_{14}H_{20}O_8$.—Acid unstable.
59	228		**Phenyl Methylethersalicylate**, $C_{14}H_{12}O_3$.—(III, A, 2), m. p. 98·5°.
59	196	283	**Methyl Veratrate**, $C_{10}H_{12}O_4$.— “ “ 181°.
59·5		295–297d.	**Ethyl Benzalacetoacetate**, $C_{13}H_{14}O_3$. —Benzoic, acetic, and acetone.

Melting-point (C.°).	Sapon. Equiv.	Boiling-point (C.°).	ESTERS.—Solid Esters whose Neutral Saponification Products are Soluble in Cold Water and Readily Volatile with Steam.
			Generic Position and Properties of the Acidic Saponification Products.
61·5	127	207 (16·5 mm.)	**Dimethyl Hemipinate, $C_{12}H_{14}O_6$.**—(III, A, 2), m. p. 161°.
62·5	182	285–7	**Methyl Vanillate, $C_9H_{10}O_4$.**— “ “ 207°.
68	131	324	**Diisobutyl Tartrate, $C_{12}H_{22}O_6$.**— (III, A, 1), “ 168°; Test 314.
64·5	97		**Dimethyl Isophthalate, $C_{10}H_{10}O_4$.**—(III, A, 2), m. p. a. 300°; Test 318–2.
68–9	198	314c.	**Phenyl Benzoate, $C_{13}H_{10}O_2$.**— (III, A, 2), m. p. 121°; Test 312.
70	159		**Diphenyl Phthalate, $C_{20}H_{14}O_4$.**— “ “ 184°; Test 318–1.
72	166	282	**Ethyl m-Oxybenzoate, $C_9H_{10}O_3$.**— “ “ 200°.
72·5	224		**Phenyl Cinnamate, $C_{15}H_{12}O_2$.**— “ “ 133°; Test 313.
73	480		**Ethyl Melissate, $C_{32}H_{64}O_2$.**— “ “ 90°.
73	85		**Hexaethyl Mellitate, $C_{24}H_{30}O_{12}$.**—(III, A, 1), “ 286° (clos'd tube)
74·5	242		**Methyl Benzilate, $C_{15}H_{14}O_3$.**— (III, A, 1), “ 150°.
75	182		**Ethyl 2, 5-Dioxybenzoate, $C_9H_{10}O_4$.**—(III, A, 2), m. p. 199°.
73–8	290		**Phenyl p-Phenoxybenzoate, $C_{19}H_{14}O_3$.**—(III, A, 2), “ 159·5°.
76		305d.	**Tetraethyl s-Ethanetetracarbonate, $C_{14}H_{22}O_8$.**—(III, A, 1), m. p. 169°.
77	186	290	**Methyl β-Naphthoate, $C_{12}H_{10}O_2$.**—(III, A, 2), m. p. 184°.
77·5	246		**Ethyl Piperate, $C_{14}H_{14}O_4$.**— “ “ 216°.
78		301–2	**Diphenyl Carbonate, $C_{13}H_{10}O_3$.**
79	78	285	**Trimethyl Citrate, $C_9H_{14}O_7$.**—(III, A, 1), m. p. 153°; Test 314.
79·5			**Ethyl Benzosalicylate, $C_{16}H_{14}O_4$.**
85	89	282	**Dimethyl Racemate, $C_6H_{10}O_6$.**—(III, A, 1), m. p. 205°; Test 314.
85	178		**Methyl m-Coumarate, $C_{10}H_{10}O_3$.**—(III, A, 2), “ 191°.
96	95		**Dimethyl 4-Oxyisophthalate, $C_{10}H_{10}O_5$.**—(III, A, 2), m. p. 305°.
102	72	192 (th. i.)	“ **Fumarate, $C_6H_8O_4$.**— “ sbl. 200°.
102	105		“ **4-Oxyphthalate, $C_{10}H_{10}O_5$.**— (III, A, 1), m. p. 181°.
109	290		**Phenyl Phenylethersalicylate, $C_{19}H_{14}O_3$.**— (III, A, 2), “ 113°.
109	258		† **Peucedanin, $C_{14}H_{11}O_3.OCH_3$.**—Tasteless, odorless, ndl. from Peucedanum officinale.—I. aq.; e. s. h. alc. or eth.—† Mix a warm saturated alc. sol. w. an equal vol. conc. HCl and boil half a minute. Cool. Wash the white cryst. ppt. w. c. alc. Recryst. fr. h. alc. The product of these operations, oreoselon, melts at 173° (uncor.).
111	198	270–80d.	**Methyl α-Anthracenecarbonate, $C_{16}H_{12}O_2$.**—(III, A, 2), m. p. 206°.
118	135	330	**Diphenyl Succinate, $C_{16}H_{14}O_4$.**—(III, A, 1), m. p. 185°; Test 320.
130d.	121		“ **Oxalate, $C_{14}H_{10}O_4$.**— “ “ 99°; Test 317.
131	152		**Methyl p-Oxybenzoate, $C_8H_8O_3$.**—(III, A, 2), m. p. 210°.
138	65·5		**Tetramethyl s-Ethanetetracarbonate, $C_{10}H_{14}O_8$.**—(III, A, 1), m. p. 169°.
140	97		**Dimethyl Terephthalate, $C_{10}H_{10}O_4$.**—(III, A, 2), sbl. a. 300°; Test 318–3.
158d.	183		**Diethyl Mucate, $C_{10}H_{18}O_8$.**— “ m. p. 213°.
146	164	abt. 330°	“ **α-Truxillate, $C_{22}H_{24}O_4$.**— “ “ 274°.
187	71		**Hexamethyl Mellitate, $C_{18}H_{18}O_{12}$.**— (III, A, 1), “ 286° (closed tube).
192d.	238		**Methyl Gallate + $3H_2O$, $C_8H_{14}O_8$.**— (III, A, 2), “ 222°–40°.
260–70			**Ethyl p-Toluylcarbonate, $C_{11}H_{12}O_3$.**— “ “ 95°–7°.

GENUS V, ESTERS.

DIVISION B,—LIQUID ESTERS WHOSE NEUTRAL SAPONIFICATION PRODUCTS, ETHYL, PROPYL, ISOPROPYL, ALLYL, AMYL AND ISOAMYL, BUTYL AND ISOBUTYL, HEXYL, HEPTYL, OCTYL AND BENZYL ALCOHOLS, ACETONE, AND PHENOL, ARE READILY VOLATILE WITH STEAM.

Boiling-point (C.°).	Sapon. Equiv.	**ESTERS.**—Liquid Esters whose Neutral Saponification Products are Readily Volatile with Steam.
		Generic Position and Properties of the Acidic Saponification Products.
32·3	60	† **Methyl Formate**, $C_2H_4O_2$.—G. 0·998$^0/_4$.—Acid (III, B, 1), b. p. 100·8°; Test 315. (Belongs with Acids, Gen. III, B, 1.)
54·4	74	**Ethyl Formate**, $C_3H_6O_2$.—G. 0·938$^0/_4$.—Acid (III, B, 1), b. p. 100·8°; Test 315.
57·5	74	† **Methyl Acetate**, $C_3H_6O_2$.—G. 0·958$^0/_4$.—Acid (III, B, 1), b. p. 118°; Test 311.
68–71	88	**Isopropyl Formate**, $C_4H_8O_2$.—G. 0·883(0).—Acid (III, B, 1), b. p. 100·8°; Test 315.
77	88	**Ethyl Acetate**, $C_4H_8O_2$.—G. 0·924$^0/_4$.—Acid (III, B, 1), b. p. 118°; Test 311.
79·9	88	**Methyl Propionate**, $C_4H_8O_2$.—G. 0·937$^0/_4$.—Acid (III, B, 1), b. p. 140·7°; Test 311.
80·3	86	**Methyl Acrylate**, $C_4H_6O_2$.—G. 0·973(0).—Acid (III, B, 1), b. p. 140°.
81	88	**Propyl Formate**, $C_4H_8O_2$.—G. 0·918$^0/_4$.—Acid (III, B, 1), b. p. 100·8°; Test 315.
82·5	86	**Allyl Formate**, $C_4H_6O_2$.—G. 0·932(17·5).—Acid (III, B, 1), b. p. 100·8°; Test 315.
90–3	102	**Isopropyl Acetate**, $C_5H_{10}O_2$.—G. 0·917(0).—Acid (III, B, 1), b. p. 118°; Test 311.
90·6c.		**Dimethyl Carbonate**, $C_3H_6O_3$.—G. 1·065(17).—Acid carbonic.
92·3	102	**Methyl Isobutyrate**, $C_5H_{10}O_2$.—G. 0·912$^0/_4$.—Acid (III, B, 1), b. p. 155°; Test 311.
98·3	102	**Ethyl Propionate**, $C_5H_{10}O_2$.—G. 0·912(0).—Acid (III, B, 1), b. p. 140·7°; Test 311.
98·5	102	**Isobutyl Formate**, $C_5H_{10}O_2$.—G. 0·905$^0/_4$.—Acid (III, B, 1), b p. 100·8°; Test 315.
98·5c.	100	**Ethyl Acrylate**, $C_5H_8O_2$.—G. 0·939(0).—Acid (III, B, 1), b. p. 140°.
101	116	**Methyl Trimethylacetate**, $C_6H_{12}O_2$.—Acid (III, A, 1), m. p. 35·5°.
102	102	**Propyl Acetate**, $C_5H_{10}O_2$.—G. 0·909$^0/_4$.—Acid (III, B, 1), b. p. 118°; Test 311.
102·3	102	**Methyl Butyrate**, $C_5H_{10}O_2$.—G. 0·919$^0/_4$.—Acid (III, B, 1), b. p. 162·5°; Test 311.
103·5	100	**Allyl Acetate**, $C_5H_8O_2$.—G. 0·938(0).—Acid (III, B, 1), b. p. 118°; Test 311.
106·9	102	**Butyl Formate**, $C_5H_{10}O_2$.—G. 0·911(0).—Acid (III, B, 1), b. p. 100·8°; Test 315.
109·2c.		**Methyl Ethyl Carbonate**, $C_4H_8O_3$.—G. 1·002(27).—Acid carbonic.
110·1	116	† **Ethyl Isobutyrate**, $C_6H_{12}O_2$.—G. 0·890$^0/_4$.—Acid (III, B, 1), b. p. 155°; Test 311.

Boiling-point (C.°).	Sapon. Equiv.	ESTERS.—Liquid Esters whose Neutral Saponification Products are Readily Volatile with Steam.
		Generic Position and Properties of the Acidic Saponification Products.
116·3	116	† **Isobutyl Acetate,** $C_6H_{12}O_2$.—G. $0\cdot892^{0}/_{4}$.—Acid (III, B, 1), b. p. 118°; Test 311.
116·7	116	**Methyl Isovalerianate,** $C_6H_{12}O_2$.—G. $0\cdot901^{0}/_{4}$.—Acid (III, B, 1), b. p. 176°.
115–20	114	**Ethyl Methacrylate,** $C_6H_{10}O_2$.—Acid (III, B, 1), b. p. 162°.
118·5 (th. i.)	130	“ **Trimethylacetate,** $C_7H_{14}O_2$.—G. 0·875(0).—Acid (III, A, 1), m. p. 35·5°.
119	98	**Ethyl Propiolate,** $C_5H_6O_2$.—Acid (III, B, 1), b. p. 144°.
119·9	116	“ **Butyrate,** $C_6H_{12}O_2$.—G. $0\cdot900^{0}/_{4}$.—Acid (III, B, 1), b. p. 162·5°; Test 311.
120·7	100	**Methyl α-Crotonate,** $C_5H_8O_2$.—G. 0·981(4).—Acid (III, A, 1), m. p. 72°.
123·3	116	† **Isoamyl Formate,** $C_6H_{12}O_2$.—G. $0\cdot894^{0}/_{4}$.—Acid (III, B, 1), b. p. 100·8°; Test 315.
124·5	98	**Propargyl Acetate,** $C_5H_6O_2$.—G. $1\cdot005^{20}/_{4}$.—Acid (III, B, 1), b. p. 118°; Test 311.
125	116	**Butyl Acetate,** $C_6H_{12}O_2$.—G. 0·902(0).—Acid (III, B, 1), b. p. 118°; Test 311.
126		**Diethyl Carbonate,** $C_5H_{10}O_3$.—G. $0\cdot976^{20}/_{4}$.—Acid carbonic.
127·3	116	**Methyl Valerianate,** $C_6H_{12}O_2$.—G. 0·910(0).—Acid (III, B, 1), b. p. 186°.
127c.	104	**Methyl Methoxyacetate,** $C_4H_8O_3$.—G. 1·089(0).—Acid (III, B, 1), b. p. 203°.
128·5		**Ethyl Isoacetoacetate,** $C_6H_{10}O_3$.—CO_2 and acetone; Test 711.
130·4	116	**Amyl Formate,** $C_6H_{12}O_2$.—G. 0·902(0).—Acid (III, B, 1), b p. 100·8°; Test 315.
131 (th. i.)	118	**Ethyl Methoxyacetate,** $C_5H_{10}O_3$.—G. 1·074(0).—Acid (III, B, 1), b. p. 203°.
133·5	128	**Allyl Isobutyrate,** $C_7H_{12}O_2$.—Acid (III, B, 1), b. p. 155°; Test 311.
134 (th. i.)	130	**Ethyl Methylethylacetate,** $C_7H_{14}O_2$.—G. $0\cdot870^{22}/_{17\cdot5}$.—Acid (III, B, 1), b. p. 177°.
134·3	130	† **Ethyl Isovalerianate,** $C_7H_{14}O_2$.—G. $0\cdot885^{0}/_{4}$.—Acid (III, B, 1), b. p. 176°.
134–7	102	**Methyl Pyruvate,** $C_4H_6O_3$.—G. 1·154(0).—Acid (III, B, 1), b. p. 165°.
136	114	**Ethyl Isocrotonate,** $C_6H_{10}O_2$.—G. 0·927(19).—Acid (III, B, 1), b. p. 169°.
139	130	† **Isoamyl Acetate,** $C_7H_{14}O_2$.—G. 0·884(0).—Acid (III, B, 1), b. p. 118°; Test 311.
141·5	128	**Ethyl Angelate,** $C_7H_{12}O_2$.—G. 0·935(0).—Acid (III, A, 2), m. p. 45°.
142	128	**Allyl Butyrate,** $C_7H_{12}O_2$.—Acid (III, B, 1), b. p. 162·5°; Test 311.
142–3	114	**Ethyl α-Crotonate,** $C_6H_{10}O_2$.—G. $0\cdot921^{20}/_{4}$.—Acid (III, A, 1), m. p. 72°.
143	128	“ **Allylacetate,** $C_7H_{12}O_2$.—Acid (III, B, 2), b. p. 188°.
144·5	130	“ **Valerianate,** $C_7H_{14}O_2$.—G. 0·894(0).—Acid (III, B, 1), b. p. 186°.
148	130	**Amyl Acetate,** $C_7H_{14}O_2$.—G. 0·896(0).—Acid (III, B, 1), b. p. 118°; Test 311.
148	118	**Methyl Ethoxyacetate,** $C_5H_{10}O_3$.—G. 1·015(0).—Acid (III, B, 1), b. p. 206°.
149·6	130	“ **Caproate,** $C_7H_{14}O_2$.—G. 0·904(0).—Acid (III, B, 2), b. p. 205·7°.
150 (th. i.)	118	**Ethyl Oxyisobutyrate,** $C_6H_{12}O_3$.—Acid (III, A, 1), m. p. 79°.
150		**Methyl Isobutylacetate,** $C_7H_{14}O_2$.—G. 0·898(18).—Acid (III, B, 1), b. p. 207·7° c.
151	144	**Ethyl Diethylacetate,** $C_8H_{16}O_2$.—G. 0·883(0).—Acid (III, B, 1), b. p. 190°.
151·2 (th. i.)	90	**Methyl Glycollate,** $C_3H_6O_3$.—G. 1·187(0).—Acid (III, A, 1), m p. 78°
152	132	**Ethyl Ethoxyacetate,** $C_6H_{12}O_3$.—G. 1·000(0).—Acid (III, B, 1), b. p. 206°.
153 (th. i.)	144	“ **Methylpropylacetate,** $C_8H_{16}O_2$.—G. 0·882(0).—Acid (III, B, 1), b. p. 193°.
153·6	130	**Hexyl Formate,** $C_7H_{14}O_2$.—G. 0·898(0).—Acid (III, B, 1), b. p. 100·8°: Test 315.
154–5	142	**Allyl Isovalerianate,** $C_8H_{14}O_2$.—Acid (III, B, 1), b. p. 176°.
155 (th. i.)	146	**Ethyl α-Ethoxypropionate,** $C_7H_{14}O_3$.—G. 0·950(0).—Acid (III, B, 1), b. p. 195°–8°.

(ORDER I, SUBORDER I.)

Boiling-point (C.°).	Sapon. Equiv.	**ESTERS.**—Liquid Esters whose Neutral Saponification Products are Readily Volatile with Steam. Generic Position and Properties of the Acidic Saponification Products.
156c.	128	**Ethyl Tiglate, $C_7H_{12}O_2$.**—G. 0·926(21).—Acid (III, A, 1), m. p. 64·5°.
156·9	144	**Isobutyl Butyrate, $C_8H_{16}O_2$.**—G. 0·888$^0/_4$.—Acid (III, B, 1), b. p. 162·5°; Test 311.
158–9		**Ethyl Orthocarbonate, $C_9H_{20}O_4$.**—G. 0·925.
160c.	104	" **Glycollate, $C_4H_8O_3$.**—G. 1·108(0).—Acid (III, A, 1), m. p. 78°
160·2	144	**Isoamyl Propionate, $C_8H_{16}O_2$.**—G. 0·888$^0/_4$.—Acid (III, B, 1), b. p. 140·7°; Test 311.
161	130	**Ethyl Isobutylacetate, $C_8H_{16}O_2$.**—G. 0·887(0).—Acid (III, B, 2), b. p. 207·7°.
159–62	128	" **Tetramethylenecarbonate, $C_7H_{12}O_2$.**—Acid (III, B, 2), b. p. 195°.
165	146	**Methyl Oxydiethylacetate, $C_7H_{14}O_3$.**—G. 0·990(16·5).—Acid (III, A, 1), b. p. 80°.
165	142	**Ethyl α-Ethylcrotonate, $C_8H_{14}O_2$.**—G. 0·920(13).—Acid (III, A, 2), m. p. 41·5°.
165	144	**Butyl Butyrate, $C_8H_{16}O_2$.**—G. 0·888(0).—Acid (III, B, 1), b. p. 162·5°; Test 311.
165	132	**Ethyl α-Oxybutyrate, $C_6H_{12}O_3$.**—G. 1·004(0).—Acid (III, A, 1), m. p. 43°.
166·6	144	" **Caproate, $C_8H_{16}O_2$.**—G. 0·889(0).—Acid (III, B, 2), b. p 205·7°.
168·2c.		**Dipropyl Carbonate, $C_7H_{14}O_3$.**—G. 0·949(17)—Acid, carbonic.
168·5c.	160	**Ethyl α-Ethoxybutyrate, $C_8H_{16}O_3$.**—G. 0·903(0).
168·8	158	**Isoamyl Isobutyrate, $C_9H_{18}O_2$.**—G. 0·876$^0/_4$.—Acid (III, B, 1), b. p. 155°; Test 311.
169·2	144	**n-Hexyl Acetate $C_8H_{16}O_2$.**—G. 0·890(0).—Acid (III, B, 1), b. p. 118°; Test 311.
170·5c.	118	**Propyl Glycollate, $C_5H_{10}O_3$.**—G. 1·064(0).—Acid (III, A, 1), m. p. 78°.
173	144	**Methyl Oenanthylate, $C_8H_{16}O_2$.**—G. 0·887(0) —Acid (III, B, 2), b. p. 223°.
173·7c.	132	" **Ethyl Oxalate, $C_5H_8O_4$.**—G. 1·156(0).—Acid (III, A, 1), m. p. 99°; Test 317.
175	160	**Ethyl Oxydiethylacetate, $C_8H_{16}O_3$.**—G. 0·961(18·7).—Acid (III, B, 2), b. p. 80°.
175	146	**Ethyl α-Oxyisovalerianate, $C_7H_{14}O_3$.**—Acid (III, A, 1), m. p. 83°–6°.
176–7	144	**Heptyl Formate, $C_8H_{16}O_2$.**—G. 0·894(0).—Acid (III, B, 1), b. p. 100·8°; Test 315.
177	158	**Ethyl Isoamylacetate, $C_9H_{18}O_2$.**—Acid (III, B, 2), b. p. 209°.
177·5	156	**Isobutyl Angelate, $C_9H_{16}O_2$.**—Acid (III, A, 2), m. p. 45°.
178	80	**Dimethyl Dimethylmalonate, $C_7H_{12}O_4$.**—G. 1·071(15).—Acid (III, A, 2), m. p. 192°.
178	160	**Ethyl Acetoxyl-α-propionate, $C_7H_{12}O_4$.**—G. 1·046(17).—Acid (III, A, 1), m. p. 166°.
178·4c.	130	**Ethyl β-Methoxyisocrotonate, $C_7H_{12}O_3$.**—G. 1·039(15).—Acid (III, A, 2), m. p. 128·5°.
178·6	158	† **Isoamyl Butyrate, $C_9H_{18}O_2$.**—G. 0·882$^0/_4$.—Acid (III, B, 1), b. p. 162·5°; Test 311.
179	73	**Methyl Isosuccinate, $C_6H_{10}O_4$.**—G. 1·107(15).—Acid (III, A, 1), m. p. 135°.
181·5c.	66	" **Malonate, $C_5H_8O_4$.**—G. 1·160(15).—Acid (III, A, 1), m. p. 132°.
183	172	**Ethyl Dipropylacetate, $C_{10}H_{20}O_2$.**—Acid (III, B, 2), b. p. 219·5°.
184		" **Dimethylacetoacetate, $C_8H_{14}O_3$.**—G. 0·991(16).—CO_2 and isopropyl acetone.
186·1c.	73	† **Diethyl Oxalate, $C_6H_{10}O_4$.**—G. 1·082(18·2).—For reactions of ester cf. page 74. (Belongs in Genus III, B.)
190		**Diisobutyl Carbonate, $C_9H_{18}O_3$.**—G. 0·919(15).—Acid, carbonic.
190	146	**Ethyl α-Oxyvalerianate, $C_7H_{14}O_3$.**—Acid (III, A, 1), m. p. 31°.

Boiling-point (C.°).	Sapon Equiv.	ESTERS.—Liquid Esters whose Neutral Saponification Products are Readily Volatile with Steam.
		Generic Position and Properties of the Acidic Saponification Products.
190	158	**Heptyl Acetate, $C_9H_{18}O_2$.**—G. 0·874(16).—Acid (III, B, 1), b. p. 118°; Test 311.
193	158	**Methyl Caprylate, $C_9H_{18}O_2$.**—G. 0·894(0).—Acid (III, B, 2), b. p. 237·5°.
194	172	**† Isoamyl Isovalerianate, $C_{10}H_{20}O_2$.**—G. 0·87(0).—Acid (III, B, 1), b. p. 176°.
195	168	**Ethyl Diallylacetate, $C_{10}H_{16}O_2$.**—Acid (III, B, 2), b. p. 227° c.
195·2 (th. i.)	73	**Methyl Succinate, $C_6H_{10}O_4$.**—G. 1·126(15).—Acid (III, A, 1), m. p. 185°; Test 320.
195·5	140	**Ethyl Sorbate, $C_8H_{12}O_2$.**—Acid (III, A, 2), m. p. 134·5°.
196 (sl. d.)	63	**Dimethyl Acetylenedicarbonate, $C_6H_6O_4$.**—Acid (III, A, 1), m. p. 178°–9°.
196	136	**Phenyl Acetate, $C_8H_8O_2$.**—G. 1·093°/4.—Acid (III, B, 1), b. p. 118°; Test 311.
196		**Ethyl Ethyleneacetoacetate, $C_8H_{12}O_3$.**—G. 1·048(15).—CO_2 and acetopropyl alc.
196·5	94	**Diethyl Dimethylmalonate, $C_9H_{16}O_4$.**—G. 1·002(15).—Acid (III, A, 1), m. p. 192°.
198	87	**Diethyl Isosuccinate, $C_8H_{14}O_4$.**—G. 1·021(15).—Acid (III, A, 1), m. p. 135°.
198c.	80	**† " Malonate, $C_7H_{12}O_4$.**—G. 1·077(0).—Acid (III, A, 1), m. p. 132°.
198	158	**Octyl Formate, $C_9H_{18}O_2$.**—G. 0·893.—Acid (III, B, 1), b. p. 100·8°; Test 315.
199c.	136	**† Methyl Benzoate, $C_8H_8O_2$.**—G. 1·103(0).—Acid (III, A, 2), m. p. 121°; Test 312.
199		**Ethyl *α*-Propionylpropionate, $C_8H_{14}O_3$.**—G. 0·995(0).—CO_2 and diethyl ketone.
200·5 (th. i.)		**Ethyl Methylethylacetoacetate, $C_9H_{16}O_3$.**—G. $0{\cdot}947^{22}/_{17\cdot5}$.—$CO_2$ and sec. butyl acetone.
203·7	172	**n-Amyl Valerianate, $C_{10}H_{20}O_2$.**—G. 0·881(0).—Acid (III, B, 1), b. p. 186°.
200–5		**Diethylacetylacetone, Me.CO.C.Et$_2$.CO.Me.**—Acid (III, B, 1), b. p. 118° and diethylacetone.
204·5	170	**Isoamyl Tiglate, $C_{10}H_{18}O_2$.**—Acid (III, A, 2), m. p. 64·5°.
205c.	144	**Ethyl Lævulinate, $C_7H_{12}O_3$.**—G. 1·033(0).—Acid (III, B, 1), b. p. 239°.
205 (th. i.)	72	**Dimethyl Maleate, $C_6H_8O_4$.**—G. 1·153(14).—Acid (III, A, 1), m. p. 130°.
205·1	172	**Hexyl Butyrate, $C_{10}H_{20}O_2$.**—G. 0·883(0).—Acid (III, B, 1), b. p. 162·5°; Test 311.
206c.	79	**Dimethyl Mesaconate, $C_7H_{10}O_4$.**—G. 1·136(4).—Acid (III, A, 1), m. p. 202°.
206	150	**Benzyl Acetate, $C_9H_{10}O_2$.**—G. 1·057(16·5).—Acid (III, B, 1), b. p. 118°; Test 311.
207	94	**Diethyl Ethylmalonate, $C_9H_{16}C_4$.**—G. $1{\cdot}008^{18}/_{15}$.—Acid (III, A. 1), m. p. 111·5°.
207·5	101	**Diethyl Methylethylmalonate, $C_{10}H_{18}O_4$.**—G. 0·994(15).—Acid (III, A, 1), m. p. 118°.
207·5	172	**Ethyl Caprylate, $C_{10}H_{20}O_2$.**—G. 0·887(0).—Acid (III, B, 2), b. p. 237·5°.
207·7c.		**Dibutyl Carbonate, $C_9H_{18}O_3$.**—G. 0·941(0).—Acid, carbonic.
208·2c.	80	**Methyl Ethyl Succinate, $C_7H_{12}O_4$.**—G. 1·093(0).—Acid (III, A, 1), m. p. 185°; Test 320.
208		**Ethyl *α*-Butyrylpropionate, $C_9H_{16}O_3$.**—G. 0·988(0).
210	172	**" Mesitonate, $C_9H_{16}O_3$.**—Acid (III, A, 1), m. p. 74°.
210	172	**n-Octyl Acetate, $C_{10}H_{20}O_2$.**—G. 0·885(0).—Acid (III, B, 1), b. p. 118°; Test 311.
210·5	79	**Dimethyl Citraconate, $C_7H_{10}O_4$.**—G. 1·121(15).—Acid (III, A, 1), m. p. 80°.
211c	150	**Phenyl Propionate, $C_9H_{10}O_2$.**—G. 1·054(15).—Acid (III, B, 1), b. p. 140·7°; Test 311.
210–2·5		**Methyl Itaconate, $C_7H_{10}O_4$.**—G. 1·140(14.7).—Acid (III, B, 1), b. p. 161°.
212c.	150	**† Ethyl Benzoate, $C_9H_{10}O_2$.**—Acid (III, A, 2), m. p. 121°; Test 312.

Boiling-point (C.°).	Sapon. Equiv.	ESTERS.—Liquid Esters whose Neutral Saponification Products are Readily Volatile with Steam. Generic Position and Properties of the Acidic Saponification Products.
213·5 (th. i.)	172	**Methyl Pelargonate, $C_{10}H_{20}O_2$.**—G. 0·892(0).—Acid (III, B, 2), b. p. 253°–4°.
213	93	**Diethyl Ethylenemalonate, $C_9H_{14}O_4$.**—G. 1·065(15).—Acid (III, A, 1), m. p. 140°.
213–4	101	**Diethyl Isopropylmalonate, $C_{10}H_{18}O_4$.**—G 0·997$^{20}/_{15}$.—Acid (III, A, 1), m. p. 87°.
213·5c.	82	**Dipropyl Oxalate, $C_8H_{14}O_4$.**—G. 1·038(0).—Acid (III, A. 1), m. p. 99°; Test 317.
214		**Ethyl Methylpropylacetoacetate, $C_{10}H_{18}O_3$.**—G. 0·959(15).—CO_2 and methyl propyl acetone.
214 (th. i.)	150	**p-Cresyl Acetate, $C_9H_{10}O_2$.**—G. 1·066$^{0}/_{4}$.—Acid (III, B, 1), b. p. 118°; Test 311.
214 (th. i.)	168	**Ethyl Pyrotritarate (Uvate), $C_9H_{12}O_3$.**—Acid (III, A, 2), m. p. 135°.
216	85	**Diallyl Oxalate, $C_8H_{10}O_4$.**—G. 1·055(15·5).—Acid (III, A, 1), m. p. 99°; Test 317.
216·5c.	87	† **Diethyl Succinate, $C_8H_{14}O_4$.**—G. 1·072(0).—Acid (III, A, 1), m. p. 185°; Test 320.
215–20	186	**Isoamyl Isobutylacetate, $C_{11}H_{22}O_2$.**—Acid (III, B, 2), b. p. 207·7° c.
217·5		**Ethyl Isobutylacetoacetate, $C_{10}H_{18}O_3$.**—G. 0·951(17·5).—Cf. Genus IV, B.
218		" **Diethylacetoacetate, $C_{10}H_{18}O_3$.**—G. 0·974(20).—CO_2 and diethyl acetone.
218·5c.	86	**Diethyl Fumarate, $C_8H_{12}O_4$.**—G. 1·063(10).—Acid (III, A, 2), sbl. 200°.
220	150	**Methyl Phenylacetate, $C_9H_{10}O_2$.**—G. 1·044(16).—Acid (III, A, 2), m. p. 76·5°.
221	101	**Diethyl Propylmalonate, $C_{10}H_{18}O_4$.**—G. 0·993(15).—Acid (III, A, 1), m. p. 96°.
221	176	**Methyl α-Phenylpropionate, $C_{10}H_{12}O_2$.**—Acid (III, B, 2), b. p. 264°.
221 (th. i.)	108	**Diethyl Methylisopropylmalonate, $C_{11}H_{20}O_4$.**—G. 0·990(15).—Acid (III, A, 1), m. p. 124°.
221	164	**Ethyl o-Toluate, $C_{10}H_{12}O_2$.**—Acid (III, A, 2), m. p. 102°.
221·5	101	**Diethyl(mal.)s-Dimethylsuccinate, $C_{10}H_{18}O_4$.**—G. 1·022(0).—Acid (III, A, 1), m. p. 129°.
220–3	108	**Diethyl Methylpropylmalonate, $C_{11}H_{20}O_4$.**—Acid (III, A, 1), m. p. 106°.
222·5c.	100	" **Allylmalonate, $C_{10}H_{16}O_4$.**—G. 1·014(15).—Acid (III, A, 1), m. p. 103°.
223	108	**Diethyl Diethylmalonate, $C_{11}H_{20}O_4$.**—G. 0·992(15).—Acid (III, A, 1), m. p. 121°.
223·5	186	**Methyl Caprate, $C_{11}H_{22}O_2$.**—Acid (III, A, 2), m. p. 31·3°
222–5	88	**Diethyl Tartronate, $C_7H_{12}O_5$.**—Acid (III, A, 1), m. p. 185°–7°.
223–6	101	" **Etnylsuccinate, $C_{10}H_{18}O_4$.**—G. 1·030(21).—Acid (III, A, 1), m. p. 98°.
225 (th. i.)	86	**Diethyl Maleate, $C_8H_{12}O_4$.**—G. 1·074(15).—Acid (III, A, 1), m. p. 130°.
225	108	" **Isobutylmalonate, $C_{11}H_{20}O_4$.**—G. 0·983(17).—Acid (III, A, 1), m. p. 107°.
225–6d.	100	**Diisopropyl Fumarate, $C_{10}H_{16}O_4$.**—Acid (III, A, 2), sbl. 200°.
226·5		**Ethyl Trimethyleneacetoacetate, $C_9H_{14}O_3$.**—G. 1·070(15).—M. p. +9°.—Acid (III, A, 2), m. p. 119°.
226–8	164	**Ethyl m-Toluate, $C_{10}H_{12}O_2$.**—Acid (III, A, 2), m. p. 110·5°.
225–30d.	148	" **αβ-Dioxybutyrate, $C_6H_{12}O_4$.**—Acid (III, A, 1), m. p. 74°–5°.
227·5 (th. i.)	186	" **Pelargonate, $C_{11}H_{22}O_2$.**—G. 0·866(17·5). Acid (III, B, 1), b. p. 253°.
227·5		" **Isoamylacetoacetate.**—Cf. Genus IV, A.
227·8c.	93	**Diethyl Itaconate, $C_9H_{14}O_4$.**—G. 1·050(15).—Acid (III, A, 1), m. p. 161°.

Boiling-point (C.°).	Sapon. Equiv.	ESTERS.—Liquid Esters whose Neutral Saponification Products are Readily Volatile with Steam.
		Generic Position and Properties of the Acidic Saponification Products.
228	178	**Methyl Ethylphenylacetate, $C_{11}H_{14}O_2$.**—Acid (III, A, 2), m. p. 42°.
228	164	**Ethyl p-Toluate, $C_{10}H_{12}O_2$.**—Acid (III, A, 2), m. p. 176°–7°.
228	166	**Methyl Methylethersalicylate, $C_9H_{10}O_3$.**—Acid (III, A, 2), m. p. 98·5°.
228·3c.	94	**Dipropyl Malonate, $C_9H_{16}O_4$.**—G. 1·027(0).—Acid (III, A, 1), m. p. 132°.
228·7c.		**Diisoamyl Carbonate, $C_{11}H_{22}O_5$.**—G. 0·912(15).—Acid, carbonic.
229 (th. i.)	93	**Diethyl Mesaconate, $C_9H_{14}O_4$.**—G. 1·060(4). Acid (III, A, 1), m. p. 202°.
229	101	**Diisobutyl Oxalate, $C_{10}H_{18}O_4$.**—G. 1·002(14).—Acid (III, A, 1), m. p. 99°; Test 317.
229c.	164	**Ethyl Phenylacetate, $C_{10}H_{12}O_2$.**—G. 1·086(16).—Acid (III, A, 2), m. p. 76·5°.
229·5c.	150	**Propyl Benzoate, $C_{10}H_{12}O_2$.**—G. 1·032(16).—Acid (III, A, 2), m. p. 121°; Test 312.
230	162	**Allyl Benzoate, $C_{10}H_{10}O_2$.**—Acid (III, A, 2), m. p. 121°; Test 312.
230	178	**Ethyl α-Phenylpropionate, $C_{11}H_{14}O_2$.**—Acid (III, B, 2), b. p. 264°.
231	93	**Diethyl Citraconate, $C_9H_{14}O_4$.**—G. 1·047(15).—Acid (III, A, 1), m. p. 80°.
231	188	**Ethyl α-Oxycaprylate, $C_{10}H_{20}O_3$.**—Acid (III, A, 2), m. p. 69·5°.
230–5	101	**Diethyl (fum.)s-Dimethylsuccinate, $C_{10}H_{18}O_4$.**—G. 1·013(0).—Acid (III, A, 2), m. p. 195°.
232	190	**Methyl α-Methylhydrocinnamate, $C_{11}H_{14}O_2$.**—Acid (III, A, 2), m. p. 37°.
233·5 (th. i.)	108	**Diethyl Butylmalonate, $C_{11}H_{20}O_4$.**—G. 0·988(15).—Acid (III, A, 1), m. p. 76°.
235	180	**Ethyl Methylethersalicylate, $C_{10}H_{12}O_3$.**—Acid (III, A, 2), m. p. 98·5°.
235–6		“ **Dipropylacetoacetate, $C_{12}H_{22}O_3$.**—G. $0·959^0/_4$.—CO_2 and dipropylacetone.
237	178	† **Isobutyl Benzoate, $C_{11}H_{14}O_2$.**—G. 1·002(15).—Acid (III, A, 2), m. p. 121°; Test 312.
237c.	94	**Diethyl Glutarate, $C_9H_{16}O_4$.**—G. 1·025(21).—Acid (III, A, 1), m. p. 97·5°.
236–8	93	“ **Glutaconate, $C_9H_{14}O_4$.**—Acid (III, A, 1), m. p. 132°.
237–8	178	**Ethyl m-Tolylacetate, $C_{11}H_{14}O_2$.**—G. 1·018(17·5).—Acid (III, A, 2), m. p. 61°.
236–40	108	**Diethyl Isopropylsuccinate, $C_{11}H_{20}O_4$.**—Acid (III, A, 1), m. p. 117°.
238·5	176	**Methyl Hydrocinnamate, $C_{10}H_{12}O_2$.**—G. 1·047(0).—Acid (III, A, 2), m. p. 48·7°.
240	178	**Ethyl p-Tolylacetate, $C_{11}H_{14}O_2$.**—Acid (III, A, 2), m. p. 91°.
240	168	“ **Cuminate, $C_{12}H_{16}O_2$.** –Acid (III, A, 2), m. p. 116·5°.
40 sl. d.		**Diethyl Diglycollate, $C_8H_{14}O_5$.**—Acid (III, A, 1), m. p. 148°.
240	120	“ **Diallylmalonate, $C_{13}H_{20}O_4$.** —G. $0·996^{14}/_{15}$.—Acid (III, A, 1), m. p. 133°.
239–41		**Ethyl Diallylacetoacetate, $C_{12}H_{18}O_3$.**—G. $0·948^{25}/_{17·5}$.—CO_2 and diallyl acetone.
241	178	**Ethyl 1 3-Dimethylbenzoate, $C_{11}H_{14}O_2$.**—Acid (III, A, 2), m. p. 166°.
241	115	**Diethyl Isoamylmalonate, $C_{12}H_{22}O_4$.**—Acid (III, A, 1), m. p. 93°.
243·4c.	101	**Dibutyl Oxalate, $C_{10}H_{18}O_4$.**—G. 1·010(0).—Acid (III, A, 1), m. p. 99°; Test 317
244	200	**Ethyl Caprate, $C_{12}H_{24}O_2$.**—G. 0·862.—Acid (III, A, 2), m. p. 31·3°.
245	180	**Methyl Ethylethersalicylate, $C_{10}H_{12}O_3$.**—Acid (III, A, 2), m. p. 19·4°.
245	101	**Diethyl Adipate, $C_{10}H_{18}O_4$.**—Acid (III, A, 2), m. p. 153° c.
247·1c.	101	**Diisopropyl Succinate, $C_{10}H_{18}O_4$.**—G. 1·019(0).—Acid (III, A, 1), m. p. 185°; Test 320.
247·3c.	178	**Butyl Benzoate, $C_{11}H_{14}O_2$.**—G. 1·000(20).—Acid (III, A, 2), m. p. 121°; Test 312.
247–9c.	178	**Ethyl Hydrocinnamate, $C_{11}H_{14}O_2$.**—G. 1·034(0).—Acid (III. A, 2), m. p 48·7°.

Boiling-point (C°)	Sapon. Equiv.	**ESTERS.**—Liquid Esters whose Neutral Saponification Products are Readily Volatile with Steam.
		Generic Position and Properties of the Acidic Saponification Products.
248	210	**Methyl Undecylenate, $C_{12}H_{22}O_2$.**—Acid (III, A, 2), m. p. 24·5°.
249·5	99	**Diallyl Succinate, $C_{10}H_{14}O_4$.**—Acid (III, A, 1), m. p. 185°; Test 320.
250·8c.	101	**Dipropyl Succinate, $C_{10}H_{18}O_4$.**—G. 1·016(4).—Acid (III, A, 1), m. p. 185°; Test 320.
249–52	107	**Diethyl Pentamethylenedicarbonate, $C_{11}H_{18}O_4$.**—Acid (III, A, 2), m. p. 159°–60°.
251	194	**Ethyl Ethylethersalicylate, $C_{11}H_{14}O_3$.**—G. 1·101.—Acid (III, A, 2), m. p. 19·4°.
250–3		**Ethyl Diisobutylacetoacetate, $C_{14}H_{26}O_3$.**—G. 0·947(10).—CO_2 and diisobutyl acetone.
251·5c.	108	**Dibutyl Malonate, $C_{11}H_{20}O_4$.**—G. 1·005(0).—Acid (III, A, 1), m. p. 132°.
255	85	**Diethyl i-Malate, $C_8H_{14}O_5$.**—G. 1·124$^{21}/_4$.—Acid (III, A, 1), m. p. 133°; Test 314.
256–7	178	**Ethyl Benzoylformate, $C_{10}H_{10}O_3$.**—G. 1·121(17·5).—Acid (III, A, 1), m. p. 65°–6°.
259	212	**Ethyl Undecylenate, $C_{13}H_{24}O_2$.**—G. 0·883(15).—Acid (III, A, 2), m. p. 24·5°.
261	192	**Isoamyl Benzoate, $C_{12}H_{16}O_2$.**—G. 1·004(0).—Acid (III, A, 2), m. p. 121°; Test 312.
263	194	**Ethyl m-Ethoxybenzoate, $C_{11}H_{14}O_8$.**—G. 1·088(0).—Acid (III, A, 2), m. p. 137°.
263	115	**Diisoamyl Oxalate, $C_{12}H_{22}O_4$.**—G. 0·968(11).—Acid (III, A, 1), m. p. 99°; Test 317.
265	120	**Dimethyl Camphorate, $C_{12}H_{20}O_4$.**—G. 1·075$^{20}/_4$.—Acid (III, A, 2), m. p. 180·7° c.
265c.	115	**Diisobutyl Succinate, $C_{12}H_{22}O_4$.**—G. 0·974(15),—Acid (III, A, 1), m. p. 185°; Test 320.
265–7	226	**Isoamyl Orthoformate, $C_{16}H_{34}O_3$.**—G. 0·864(23).—Acid (III, B, 1), b. p. 100·8°; Test 315.
269	228	**Ethyl Laurate, $C_{14}H_{28}O_2$.**—G. 0·867(19).—Acid (III, A, 2), m. p. 43·6°.
269·5c.	180	" **Anisate, $C_{10}H_{12}O_3$.**—Acid (III, A, 2), m. p. 184·2°.
270	208	**Isoamyl Salicylate, $C_{12}H_{16}O_3$.**—Cf. Genus IV, B; Test 319.
270·5	72	**Trimethyl Aconitate, $C_9H_{12}O_6$.**—Acid (III, A, 1), m. p. 191°.
271	176	† **Ethyl Cinnamate, $C_{11}H_{12}O_2$.**—G. 1·066(0).—Acid (III, A, 2), m. p. 133°; Test 313.
272	206	**n-Hexyl Benzoate, $C_{13}H_{18}O_2$.**—G. 0·999(17).—Acid (III, A, 2), m. p. 121°; Test 312.
275	117	**Diisopropyl Tartrate, $C_{10}H_{18}O_6$.**—G. 1·13(20).—Acid (III, A, 1), m. p. 168°; Test 314.
275	86	**Triethyl Aconitate, $C_{12}H_{18}O_6$.**—G. 1·074(14).—Acid (III, A, 1), m. p. 191°.
276d.	224	**Ethyl Camphocarbonate, $C_{13}H_{20}O_3$.**—G. 1·056$^{20}/_4$.—Acid (III, A, 2), m. p. 128°.
278·3d.	82	**Triethyl Ethenyltricarbonate, $C_{11}H_{18}O_6$.**—G. 1·095$^{20}/_4$.—Acid (III, A, 1), m. p. 159° d.
280	103	**Diethyl[+]Tartrate, $C_8H_{14}O_6$.**—G, 1·206(20).—Acid (III, A, 1), m. p. 168°; Test 314.
282	97	**Dimethyl Phthalate, $C_{10}H_{10}O_4$.**—Acid (III, A, 2), m. p. 184°; Test 318–1.
282–6	115	**Diethyl Suberate, $C_{12}H_{22}O_4$.**—G. 0·985(15).—Acid (III, A, 2), m. p. 140°.
284 (th. i.)	175	" **Carbopyrotritarate, $C_{12}H_{16}O_5$.**—Acid (III, A, 2), m. p. 230°–1°.
285	111	" **Isophthalate, $C_{12}H_{14}O_4$.**—Acid (III, A, 2), m. p. a. 300°; Test 318–2.
285·5	128	**Diethyl Camphorate, $C_{14}H_{24}O_4$.**—G. 1·029(16).—Acid (III, A, 2), m. p. 180° c.

(ORDER I, SUBORDER I.)

Boiling-point (C.°).	Sapon Equiv.	**ESTERS.**—Liquid Esters whose Neutral Saponification Products are Readily Volatile with Steam.
		Generic Position and Properties of the Acidic Saponification Products
290		**Methyl β-Benzoylpropionate, $C_{11}H_{12}O_3$.**—Acid (III, A, 2), m. p. 116°.
291–2	122	**Diethyl Azelate, $C_{13}H_{24}O_4$.**—G. 0·991$^0/_0$.—Acid (III, A, 2), m. p. 106°.
294	92	**Triethyl Citrate, $C_{12}H_{20}O_7$.**—G. 1·137$^{20}/_4$.—Acid (III, A, 1), m. p. 153°; Test 314
295c.	111	**† Diethyl Phthalate, $C_{12}H_{14}O_4$.**—G. 1·118$^{20}/_4$.—Acid (III, A, 2), m. p. 184°; Test 318–1.
295	256	**Ethyl Myristate, $C_{16}H_{32}O_2$.**—Acid (III, A, 2), m. p. 53·8°.
298·5	258	**Diisoamyl Succinate, $C_{14}H_{26}O_4$.**—G. 0·961(13).—Acid (III, A, 1), m. p. 185°; Test 320.
295–305	86·7	**Triethyl Tricarballylate, $C_{12}H_{20}O_6$.**—Acid (III, A, 1), m. p. 166°.
305	234	**Octyl Benzoate, $C_{15}H_{22}O_2$.**—Acid (III, A, 2), m. p. 121°; Test 312.
307–8	129	**† Diethyl Sebacate, $C_{14}H_{26}O_4$.**—G. 0·965(16).—Acid (III, A, 2), m. p. 133°.
308	212	**Methyl o-Phenylbenzoate, $C_{14}H_{12}O_2$.**—Acid (III, A, 2), m. p. 110°–1°.
308–9	200	**Ethyl β-Naphthoate, $C_{13}H_{12}O_2$.**—Acid (III, A, 2), m. p. 184° c.
309c.	200	**" α-Naphthoate, $C_{13}H_{12}O_2$.**—Acid (III, A, 2), m. p. 160°.
308·5–11	284	**" Diheptylacetate, $C_{18}H_{36}O_2$.**—Acid (III, A, 2), m. p. 26°–7°.
310 (th. i.)	166	**Methyl p-Oxyphenylacetate, $C_9H_{10}O_3$.**—G. 1·195$^0/_4$.—Acid (III, A, 1), m. p. 148°.
314	226	**Ethyl o-Phenylbenzoate, $C_{15}H_{14}O_2$.**—Acid (III, A, 2), m. p. 110°–1°.
323–4c.	212	**Benzyl Benzoate, $C_{14}H_{12}O_2$.**—G. 1·114(18·5°).—Acid (III, A, 2), m. p. 121°; Test 312.
a. 360	228	**Methyl Phenylethersalicylate, $C_{14}H_{12}O_3$.**—Acid (III, A, 2), m. p. 113°

CHAPTER VIII.

GENUS VI. ACID ANHYDRIDES AND LACTONES

OF

SUBORDER I, ORDER I.

(Colorless Compounds of Carbon, Hydrogen, and Oxygen.)

To this genus belong all species of the suborder, which, while not attacked rapidly enough by cold alkali to give Tests III or IV, yield a saponification equivalent of less than 500 in Test V, and form the sodium salt of an acid as their sole organic saponification product. No independent Generic Test VI exists, the claim of any species to membership in the genus being settled by the outcome of the examination of the reaction products obtained in Test V (p. 111).

The number of important species described under Genus VI is smaller than for any other genus in Order 1. It has already been mentioned elsewhere that many of the simpler and more important anhydrides, like acetic, benzoic, and succinic, and phthalid, are sufficiently reactive towards either cold decinormal or normal alkali to be entitled to positions with the acids or phenols. The number of species which might otherwise have established a valid claim for admission to the genus has been still further diminished by the difficulties that lay in the way of procuring pure preparations of representative types for direct examination, and the utter impossibility of drawing safe conclusions, *a priori*, as to the behavior of many of them towards alkali from the vague or conflicting statements that may be gleaned from a study of their literature. These unavoidable omissions, which can only be remedied by later investigations, consist almost exclusively of rare and unimportant compounds. The fact that Genus VI is a skeleton genus to a greater extent than most others, has, therefore, little practical significance, except to the investigator in a few special fields.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I].

GENUS VI, ACID ANHYDRIDES AND LACTONES

DIVISION A,—SOLID ACID ANHYDRIDES AND LACTONES WHICH DO NOT NEUTRALIZE COLD SODIUM HYDROXIDE SOLUTIONS READILY ENOUGH TO GIVE TESTS III OR IV, 2.

Melting-point (C.°).	**ACID ANHYDRIDES AND LACTONES.**—Colorless and Solid.
25	**Melilotic Anhyd., o-O.(.C_6H_4.C_2H_4.CO.).**—B. p. 272°.—Odor like vanilla grass or Tonka bean!—S. c. aq.; d. s. h. aq.; e. s. $CHCl_3$.—Boiled w. alkali gives melilotic ac., m. p. 82°–3°.—Br_2 substitutes in CS_2 sol. giving compound w. m. p. 106° (pr. fr. $CHCl_3$).
63–4	**3-Methoethylol(3′)-heptanon(6)-olid(1, 3′),$C_{10}H_{16}O_3$.**—B. p. 330°. — (An oxid. product of pinene, etc.).—Cryst. v. e. fr. h. aq.; s. aq.; v. s. $CHCl_3$; much less s. eth.—Sodium hydroxide and Br added to aq. sol. give CBr_4.—Neut. equiv. 184.
64	**Palmitic Anhyd., ($C_{16}H_{31}O)_2$.O.**
67	† **Coumarin, o-O(.C_6H_4.C_2H_2.CO.).**—Fragrant odor like vanilla grass or Tonka bean!—B. p. 290°–0·5°.—Alm. i. c. aq.; s. h. aq.; e. s. alc. or eth.—Does not give Test III or IV.—Test V gives coumaric ac.!—The solution in alkali has a peculiar greenish-yellow color!—Adds Br_2 in CS_2 sol. (Cryst. fr. alc., m. p. 105°.)
71–7	**Stearic Anhyd., ($C_{18}H_{35}O)_2$.O.**
73	† **Phthalid. o-O(.CH_2.C_6H_4.CO.).**—B. p. 290° (th. i.).—Ndl. fr. h. aq.; v. d. s. c. aq.; e. s. alc.—Alkaline $KMnO_4$ gives phthalic acid (Test 318–1) easily.—Test V gives o-Oxymethylbenzoic ac. (III, A, 2), m. p. 120°.—[Finely powdered dissolves after shaking 1–2 min. in Test IV–2, and so properly belongs in Genus IV.]!
86–7	**Glycolid, $C_4H_4O_4$.**—Lft. fr. alc., d. s. c. alc. or eth.; v. s. acetone.—Protracted boiling w. aq. gives glycollic ac.
102·5	**Meconine, $C_{10}H_{10}O_4$.** (from mother-liquors of opium alkaloids).—Sbl. in lustrous ndl.—(Cf. Genus III, A, 2.)
103·5	**Benzoylperoxide, $(PhCO)_2.O_2$.**—Rhomb. cryst., e. s. eth. or bz.—Explodes on heating!—Boiled w. KOH sol. gives benzoic ac. (Test 312) and oxygen.
128	**Lactid, $C_6H_8O_4$.**—Cryst. fr. h. alc., alm. i. c. aq.—Boiled w. aq. gives lactic ac.—(Cf. Genus III, A, 2.)
128–30	**Glycollic Anhyd.**—Powd. i. aq.—(Cf. Genus III, A, 2.)
134	**Benzoïn.**—Slightly attacked in Test V.—(Cf. Ketones, VII, A.)
160–61	**Saccharin, $C_6H_{10}O_5$.**—Pr. of bitter taste. 100 pt. aq. at 15° dissolve 13 pt.—Opt. act. [+]; salts however [−].—Ether extracts fr. strongly alk. sol. in Na_2CO_3.—Aq. sol. boiled w. $CaCO_3$ gives soluble uncryst. Ca saccharate.—Gives Test 801!
169–70	**Santonin, $C_{15}H_{18}O_3$.**—Cryst., s. in 5000 pt. c., or 250 pt. h. aq.; s. c. alc.; d. s. c. eth.; e. s. $CHCl_3$.—Opt. act.—Cryst. rapidly turn yellow in air!—Does not redden litmus.—Alcoholic KOH colors red!—Warming w. alkali gives santonic ac.
218c.	† **Cantharidin, $C_{10}H_{12}O_4$.**—Well-formed cryst., alm. i. c. or h. aq.; v. d. s. alc. or eth.—Alc. sol. placed on skin quickly produces painless blisters!—2 pt. heated at 100° for 15 min. w. 3 pt. phenylhydrazine hydrochloride, 4·5 pt. NaĀc, and 30 pt. aq. gives a hydrazonehydrate cryst. fr. alc. w. m. p. 194° c.—† Test V gives sodium cantharidate. The cantharidin may be recovered unchanged by boiling the cantharidate sol. for a few minutes after acidification w. dil. H_2SO_4; the cantharidic ac. in the heating loses water and gives i. cantharidin, which precipitates out.

Melting-point (C.°).	**ACID ANHYDRIDES AND LACTONES.**—Colorless and Solid.
220	**Polyglycolid,** $(C_2H_2O_2)_x$.—White powder, v. d. s. h. aq.—Reacts neutral, but by persistent boiling w. aq. or KOH gives glycollic ac.—Prepare aniline derivative, Bl., 30, 102.
220–1	**Camphoric Anhyd.**—B. p. 91°.—(Cf. Genus III, A, 2.)
223–4	**Umbelliferone,** $C_9H_6O_3$.—(Cf. Genus IV, A).—Odor when warm, fragrant, like coumarin.
334–5	**Biphthalyl,** $C_{16}H_8O_4$.—Sbl. in ndl.; i. aq.; alm. i. alc. or eth., s. h. glacial acetic ac. or conc. H_2SO_4.—The sol. in conc. H_2SO_4 shows blue fluorescence, but becomes transiently emerald-green if a trace of nitric acid is added.—Warmed w. KOH sol. gives diphthalylaldehydic ac.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I.]

GENUS VI, ACID ANHYDRIDES AND LACTONES.

DIVISION B,—LIQUID ACID ANHYDRIDES AND LACTONES WHICH DO NOT NEUTRALIZE COLD DECINORMAL SODIUM HYDROXIDE READILY ENOUGH TO TITRATE LIKE SPECIES OF GENUS III.

Boiling-point (C.°).	**ACID ANHYDRIDES AND LACTONES.**—Colorless and Liquid.
167 sl. d.	α-**Lævulinic Anhyd., $C_5H_6O_2$.**—M. p. 18°–18·5°.—E. volatile in air.—S. in 21 pt. aq. at 15°, but ppt. by K_2CO_3.—"5 hours' boiling w. aq. gives lævulinic ac."
204	β-**Methyl-γ-butyrolactone, O(.CH_2.CHMe.CH_2CO.).**—G. $1{\cdot}077^{0}/_{4}$.—S. in 1½–2 pt. aq.—$Ba\bar{A}_2$ ndl.; v. s. aq.—Pure ac. unknown.
206c.	γ-**Butyrolactone, O(.$(CH_2)_3$.CO.).**—G. $1{\cdot}129^{15}/_{0}$.—Misc. w. aq.; separated fr. conc. sol. by K_2CO_3.—Volat. w. st.—Reduces ammon. $AgNO_3$.—"Boiled 5 min. w. $N/_{200}$ NaOH is only ½ converted into salt of acid."—Oxid. by CrO_3 to succinic ac. (Test 320).
206	α-**Methyl-γ-valerolactone, O(.CHMe.$(CH_2)_3$.CO.).**—S. 20–25 pt. aq.; sat. sol. becomes turbid on warming, but clears at 80°.—Acid v. unstable.
207c.	γ-**Isocaprolactone, O(.CMe_2.C_2H_4.CO.).**—M. p. 7°–8°.—G. $1{\cdot}015^{16{\cdot}2}/_{4}$.—S. in 2 pt. c. aq.; sat. sol. becomes turbid on warming, but clears at 80°.—K_2CO_3 separates lactone fr. conc. aq. sol.—Free ac. cryst. but unstable, especially on warming.—Ag salt ppt. cryst. in flat ndl. fr. h. aq.
206–9	**Coumalin, O(.$(CH)_4$.CO.).**—G. $1{\cdot}200^{19{\cdot}5}/_{4}$.—Agreeable coumarine-like odor!—M. p. +5°.—Misc. w. aq. but separated fr. sol. by K_2CO_3.—Aq. sol. neutral, even after warming.—Neutralizes $N/_{10}$ NaOH very slowly, giving yellow sol.—Neutralized and then boiled w. x's alkali gives crotonic aldehyde (odor).
207–8c.	† γ-**Valerolactone, O(.$(CH_2)_4$.CO.).**—G. $1{\cdot}057^{18}/_{4}$.—Sapon. Eq. 100.—Misc. w. aq.—Ppt'd from the conc. neutral aq. sol. by K_2CO_3.—Half converted into salt of acid after 7 min. boiling w. equivalent quantity $N/_{200}$ NaOH; protracted boiling w. aq. gives only 6·6% acid.—Ac. very unstable. Its Ag salt ($AgC_5H_9O_3$), large triclin. ndl. fr. h. aq.
208–9	β-**Lævulinic Anhyd., $C_5H_6O_2$.**—G. 1·108(0°).—V. s. aq.—Hydrolyzed v. slowly and incompletely by h. aq.—Dec. by c. $Ba(OH)_2$ sol. to lævulinic ac. in 12 hours.
215	**Valerianic Anhyd., $(C_5H_9O)_2O$.**—G. $0{\cdot}929^{26{\cdot}7}/_{4}$.—"Slowly hydrolyzed by boiling aq."—Vapor produces coughing. When fresh has apple-like odor.—Sapon. equiv. 93.—Cf. Genus III, B, 2.
215	α-**Ethyl-γ-butyrolactone, O(.CH_2.CH_2.CHEt.CO.).**—G. 1·035(16°).—S. in 10–11 pt. c. aq., sol. becoming cloudy on heating; e. s. alc. or eth.—Separated fr. aq. sol. by K_2CO_3.—Boiling w. alkali gives salt of sirupy soluble ac.
219·5	α-**Ethylvalerolactone, O(.HCMe.CH_2.CHEt.CO.).**—G. 0·992(16°).—Rather d. s. aq.; aq. sol. sat. at 0° becomes turbid at 90°.—Ac. unknown.—Still liq. at −18°.
220	γ-**Caprolactone, O(.HCEt.CH_2.CH_2.CO.).**—S. in 5–6 pt. aq. at 0°; K_2CO_3 separates fr. sol.—Becomes turbid at 30°–50°, clearing again at 80°.—Still liq. at −18°.
235 (th. i.)	γ-**Œnantholactone, O(.HCPr.CH_2.CH_2.CO.).**—V. d. s. aq.—Ac. unknown.—Still liq. at −18°.
254–5	γ-**Ethyl-δ-Caprolactone, O(.HCMe.HCEt.CH_2.CH_2.CO.).**—G. $1{\cdot}080^{20}/_{4}$.—Still liquid at −20°.—Misc. alc. or eth.; s. 28 pt. aq.—Feeble aromatic odor.—Aq. sol. at first neutral, but a little acid forms after 24 hours in cold w. aq.—Ac. unstable liq.

(ORDER I, SUBORDER I.)

Boiling-point (C.°).	ACID ANHYDRIDES AND LACTONES.—Colorless and Liquid.
268–71	**Œnanthylic Anhyd.**, $(C_7H_{13}O)_2O$.—G. 0·932(21°).—Neutral reaction.—W. conc. NH_4OH solidifies at once to imide, which recryst. fr. h. aq. melts at 95°—Saponification gives acid, b. p. 223°, neut. equiv. 121.
272	**Melilotic Anhyd.**, o-$O(.C_6H_4.C_2H_4.CO.)$.—Odor like sweet grass or Tonka bean! —M. p. 25°.—Cf. V, A.
280–90	**Caprylic Anhyd.**, $(C_8H_{15}O)_2O$.—Odor very disagreeable.—Neutral.—Not attacked by boiling or distilling w. aq.; though a little acid forms upon long exposure to moisture.—Test V gives caprylic ac. (cf. III, B, 2), b. p. 237·5°.

CHAPTER IX.

GENUS VII. KETONES

OF

SUBORDER I, ORDER I.

(Colorless Compounds of Carbon, Hydrogen, and Oxygen.)

THIS genus includes all species of the Suborder containing the carbonyl radical that have not been described in the earlier genera. These species, with some exceptions, are recognized by their behavior towards phenylhydrazine or hydroxylamine in Test VII. The few that escape recognition by this test will at first appear to belong to Genus IX, in which they receive mention in connection with a reference to the position in Genus VII where they are described.

GENERIC TEST VII.

IF THE COMPOUND TO BE EXAMINED IS A SOLID HAVING A MELTING-POINT ABOVE 30°, EMPLOY PROCEDURE 1 OF THE TEST ONLY. IF IT IS A LIQUID, OR A SOLID WITH A MELTING-POINT NOT HIGHER THAN 30°, USE PROCEDURE 2 ONLY.

PROCEDURE 1.

(The Test with Hydroxylamine.)

Fit two dry six-inch test-tubes with perforated rubber stoppers, through each of which a meter length of glass gas delivery-tubing 7–8 mm. in internal diameter has been inserted. In the first tube place 0.04–0.06 grm. of the powdered substance, 0.5 cc. of a hydroxylamine hydrochloride solution,* and 2 cc. of the alcoholic sodium hydroxide solution described below. Charge the second tube, which is to be used for a blank experiment, in the same manner, except that 0.5 cc. of 25 per cent alcohol is to be substituted for the hydroxylamine solution. Support both tubes by clamps in vertical positions so that their lower extremities may be heated by immersion in the bath represented in Fig. 4 on page 152, which is at a temperature of 100°, or in a beaker nearly filled with water already boiling. Allow the solutions to boil up briskly for at least five minutes. Then cool; dilute each with 10 cc. of cold water, and *shake vigorously* to precipitate out any substances insoluble in dilute aqueous alkali. Filter through double wetted filters, repeating if necessary until clear filtrates are obtained. Add one drop of phenolphthaleïn to each filtrate, and then dilute hydrochloric acid, drop by drop, until the red color is just discharged. Again close the mouth of each tube and shake vigorously. Note whether the solutions remain clear, become turbid or opaque, or give precipitates.

If the solution from the tube to which hydroxylamine was added gives a precipitate, or becomes opaque after neutralization with acid and shaking, while the

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* **The Reagents for Test VII** (1).—*The hydroxylamine hydrochloride solution* is made by dissolving 7.25 grms. of the purest commercial salt in 9 cc. of water, and diluting to 35 cc. with strong alcohol.

The soda solution is made by dissolving 10 grms. of the purest sodium hydroxide in 20 cc. of hot distilled water, and then diluting to 140 cc. with strong or absolute alcohol. Small quantities of both solutions should be kept in stock in laboratories where tests are often made. The hydroxylamine solution may be preserved for some months, at least, without seriously deteriorating in strength. The soda solution will soon become strongly colored on keeping unless it is prepared with unusually pure alcohol.

solution in the blank experiment remains clear, or only becomes opalescent or slightly turbid, the compound under examination is to be sought in the tables of Genus VII. The precipitate in this case consists of an oxime which is soluble in alkali, but not in a neutral aqueous solution. A majority of the oximes which are precipitated in this test—though there are many exceptions to the rule—dissolve in an excess of cold dilute hydrochloric acid to clear solutions, from which they may be again precipitated by neutralization and shaking.

PROCEDURE 2.

(The Test with Phenylhydrazine.)

If the unknown compound is readily soluble in water, dissolve one drop in 2 cc. of cold water in a dry six-inch test-tube 18–20 mm. in diameter, and add four drops of a phenylhydrazine solution prepared by the method described below.* *If the compound is not soluble in water,* substitute for the latter 2 cc. of dilute alcohol (one volume of strong alcohol to two volumes of water). It is not necessary in this case that the substance should dissolve visibly. Suspending the test-tube by its lip between the thumb and forefinger, sway it from side to side with a slow pendulum motion (one or two swings a second) for at least a minute. Vigorous shaking might spoil the test by breaking up a difficultly soluble substance into minute droplets and forming an opaque emulsion.

If the solution remains clear, stopper the tube very loosely with a clean cork, and stand it upright in a beaker containing a layer of water 2–3 cm. deep. Have the water gently boiling at the moment when the tube is introduced, and continue to heat at 100° for five minutes. The water in the beaker should not boil actively during this period, for the steam arising then heats the side walls of the test-tube to such an extent that the loss of alcohol by evaporation may become too important a factor in the final result, and violent bumping of the mixture may cause emulsification of the original mixture. Whenever this test in hot solution has to be applied, a blank experiment must be made at the same time, using the same quantities of the substance and solvent, but omitting the phenylhydrazine.

If the solution still remains clear after five minutes' heating, remove it from the water-bath, and, after allowing it to stand twenty-five to thirty seconds, carefully observe its degree of transparency and its color. (The delay in making this observation is mainly to permit suspended drops of unchanged substance to settle out. The appearance of a precipitate or opacity *after* thirty seconds may be caused by the separation of the original substance from its supersaturated solution, and is without significance.) To test for opacity, hold the test-tube in front of, and in actual contact with, a piece of white paper on which a small cross has been drawn in lines 1 mm. in width in black ink. If the cross can not be seen through the solution when the position of the test-tube is slightly changed, the solution is to be considered "opaque."

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* [**The Phenylhydrazine Reagent for Test VII (2).**—Mix 0.3 cc. of glacial acetic acid with 7.0 cc. of cold water. To the mixture add 2 cc. of light-colored phenylhydrazine. The clear solution, if not exposed to direct sunlight, will remain in good condition for four or five days, but then becomes strongly colored and should be thrown away. If the phenylhydrazine does not give a clear solution in the specified mixture of acetic acid and water, it must be redistilled, and the end fractions of the distillate rejected. Phenylhydrazine often undergoes slight decomposition in storage, and the products—of which benzene is one—then interfere with the preparation of the reagent by causing a separation of layers.]

Any compound to which Test VII-2 has been applied is probably a ketone:

(a) If an "opaque" solution is obtained on treating it with phenylhydrazine in the cold by the method of the first paragraph.

(b) If an "opaque" solution is obtained during the five minutes' heating described in the second paragraph, or within thirty seconds after its removal from the bath, provided the solution in the corresponding blank experiment remains clear, or nearly so.

(c) If both solutions mentioned in (b) become "opaque" after heating, but the solution of the blank test remains unchanged in color, while the suspended matter in the solution containing phenylhydrazine assumes a much deeper yellow color.

Observations on Generic Test VII.

In using Procedure 2 of this test the analyst should never lose sight of the danger that exists of mistaking an alcohol or hydrocarbon containing traces of aldehydic impurities for a ketone; for aldehydes yield insoluble phenylhydrazones, and give opaque solutions under the test conditions, quite as easily and uniformly as the species of Genus VII.

A contamination with aldehyde that is barely sufficient to produce a very faint pink coloration with the fuchsine reagent in Test I, may cause a pronounced turbidity in the test with phenylhydrazine. Conclusions as to the ketonic character of a substance of doubtful homogeneity which reacts slightly with the fuchsine reagent, can not, therefore, be safely drawn from Test VII-2. It is necessary that such bodies shall first be purified with every possible care.

Of the two procedures 1 and 2, neither one can be trusted for the recognition of ketones belonging to the group for which its alternative is prescribed in the "generic test;" though it is true that most solid species do show a ketonic behavior in Procedure 2, and that very many liquid ketones, which it is directed shall be examined by Procedure 2, would also react as ketones when tested by Procedure 1.

Both reactions, in the form recommended, fail in certain special cases. Thus they are not given by aromatic ketones having two alkyl radicals substituting in the ortho position to the carbonyl group; or by the fatty ketones $(C_nH_{2n+1})_2CO$., in which "n" is 9 or a higher number, though still given by caprone $(C_5H_{11})_2CO$.* The liquid aliphatic ketones which are soluble in water are, in general, readily recognized by Procedure 2, but not by Procedure 1.

In explanation of the numerous rather arbitrary conditions imposed in these procedures, it should be said that the tests as they stand are the result of information obtained from a study of the behavior of about one hundred purified and typical species of Genera VII, VIII, and IX towards hydroxylamine and phenylhydrazine under a great variety of carefully controlled conditions. By lengthening the period of heating with the reagents, and by other devices, the number of ketones calling for mention in the tables of Genus IX might have been somewhat reduced, and a slight gain made in the direction of simplicity of classification; but this advantage would have been more than offset by the increased length or experimental difficulty of the operations necessitated.

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* The oximes of the higher fatty ketones are formed in the test with hydroxylamine, but they are not soluble enough in alkali to give a precipitate or opaque solution in the neutralization with acid.

GENUS VII, KETONES.

DIVISION A,—SOLID KETONES.

Melting-point (C.°).	Boiling-point (C.°).	KETONES.—Colorless and Solid.
20·5	202	† **Acetophenone, Me.CO.Ph.**—Odor aromatic!—Alm. i. aq.—(When melted, often refuses to solidify unless a crystal is added.)—Sol. in Test VII–2 becomes opaque and gives yellowish-white ppt. after 30 seconds in the cold. Color-reaction 701 is quite characteristic.—Identify by Test 712!
26–6·5	306	**Allotropic Benzophenone, $C_{13}H_{10}O$(?).**—Eth. sol. on evaporation leaves an oil that solidifies to benzophenone (m. p. 48°–9°) upon contact w. a crystal of the latter substance.
27	215	**Methyl Benzyl Ketone, Me.CO.CH_2.Ph.**—Combines easily w. $NaHSO_3$.—Mixed w. phenylhydrazine, reacts at once w. evolution of heat and separation of aq., giving a hydrazone, lft. fr. lgr., m. p. 83°.
27	273–5	**p-Propionylanisol, Et.CO.C_6H_4.OMe.**—$KMnO_4$ oxid. to anisic ac.—M. p. of oxime, 67°.
28	198·5	† **Phoron, $C_9H_{14}O$.**—Slightly yellow cryst.—Adds Br_4 instantly in the cold in CS_2 sol.; the addition product cryst. fr. alc. w. m. p. 88°–9°.—Sol. in Test VII–2 becomes opaque and yellow after 3 min. heating.
28	263	**Methyl Undecyl Ketone, Me.CO.$C_{11}H_{23}$.**—G. 0·829 (28°).
30		**p-Propionylphenetol, Et.CO.C_6H_4.OEt.**—Oxime, m. p. 97°.
30	264c.	**Dihexyl Ketone, $(C_6H_{13})_2$.CO.**—G. 0.825 (30°).—V. s. alc. or eth.
33·9	330·6c.	**Dibenzyl Ketone, $(C_7H_7)_2$.CO.**—Test 702 gives benzoic ac.—M. p. oxime, 119·5°.
33–4	205–6(100 mm.)	**Tetradecanone(2), Me.CO.$C_{12}H_{25}$.**—Test 702 gives lauric and acetic ac.
36	318c.	**Phenyl p-Xylyl Ketone, Ph.CO.C_6H_3.Me_2.**—V. s. alc. or eth.—Stable towards oxid. agents.—Warming w. conc. H_2SO_4 splits off benzoic ac. (Test 312.)
38	196	**Camphenylon, C_8H_{14}:CO.**—Strong camphor odor.—Forms oxime, ndl. fr. eth., m. p. 105°–6°.
39	294	**Methyl Tridecyl Ketone, Me.CO.$C_{13}H_{27}$.**—G. 0·818 (39°). Gives an oxime.
39	229d.	**Furfuralacetone, C_4H_3O.CH:CH.CO.Me.**—Sol. in acetylchloride is light red, becoming emerald-green on warming.
40	178	**Diheptyl Ketone, $(C_7H_{15})_2$.CO.**—Ndl. fr. alc.—Probably does not give a very satisfactory ketone reaction in Test VII–1.
40	244	**α-Hydrindone, C_9H_8O.**—Rhombic tbl. v. s. alc.—Oxid. by Test 905–3, gives phthalic ac. (Test 318–1).—M. p. of oxime 146°.
41–2	260–2 (th. i.)	**Benzalacetone, Me.CO.CH:CH.Ph.**—Thick tbl. e. s. alc. or eth.—S. in conc. H_2SO_4 w. orange color.—Dibromide melts at 124°–5°.—Oxime melts at 115°.—Forms $NaHSO_3$ comp. easily.
42		**Vinyl Phenyl Ketone, C_2H_3.CO.Ph.**—Ndl. v. s. alc. or eth.—$NaHSO_3$ comp. forms slowly.
42–3		**p-Tolyl Hexyl Ketone, C_7H_7.CO.C_6H_{13}.**—Oxime is an oil.

Melting-point (C.°).	Boiling-point (C.°).	**KETONES.**—Colorless and Solid.
43–3·5	230–1	**Hexadecanone(2), Me.CO.$C_{14}H_{29}$.**—Test 702 gives myristic and acetic acids.
46	310c.	**Diacetylmesitylene, $Me_3.C_6H.(CO.Me)_2$.**—Pr. fr. lgr.
48	319–20	**Methyl Quindecyl Ketone, Me.CO.$C_{15}H_{31}$.**
48–8·5	306c.	† **Benzophenone, Ph_2.CO.**—Rhombic pr., i. aq.; e. s. alc. or eth. —Sodium gives an intensely dark blue compound when gently heated w. the fused ketone! Identify by Test 714!
50–1	323	**Propyl Naphthyl Ketone, Pr.CO.$C_{10}H_7$.**—S. alc.—Oxime m. p. 89°.—M. p. picrate 68°–9°.
51–2	251–2(100 mm.)	**Octadecanone(2), $C_{16}H_{33}$.CO.Me.**—Gives oxime.
51–2	300–1	**β-Methyl Naphthyl Ketone, Me.CO.$C_{10}H_7$.**—Ndl. fr. lgr.—Oxime, m. p. 142°–3°.—Dibrom.-derivative, fr. CS_2, m. p. 101°.
abt. 56	266 (110 mm.)	**Methyl Heptadecyl Ketone, Me.CO.$C_{17}H_{35}$.**—Gives oxime.
57		**Benzyl Naphthyl Ketone, C_7H_7.CO.$C_{10}H_7$.**—Tbl. fr. alc., e. s. alc. or eth.
57–8	345–8	† **Benzylideneacetophenone, Ph.CH:CH.CO.Ph.**—Pale yellowish rhombic pr., s. alc., e. s. eth.—Gives isomeric solid oximes.—Heated w. HCl (sp. gr. 1·12) at 200° gives benzaldehyde and acetophenone.
58	a.350	† **Dinonyl Ketone, $(C_9H_{19})_2$.CO.** — Pearly lft. fr. alc.—[This, and the other symmetrical aliphatic ketones higher in the series, do not give Test VII–1 satisfactorily, because their oximes are not readily soluble in alkali.]
59		**m-Methylhydrindone, $C_{10}H_{10}O$.**—Long ndl. fr. lgr.
59	251 (15 mm.)	**Phenyl Pentadecyl Ketone, $C_{22}H_{36}O$.**—V. d. s. c. alc.; s. eth.
59–60	326 (th. i.)	† **p-Phenyl Tolyl Ketone, Ph.CO.C_7H_7.**—(M. p. of dimorphous hexagonal form is 55°.)—S. c. alc.; e. s. eth.—Oxid. by CrO_3 mixture to p-benzoyl-benzoic ac.—Gives isomeric solid oximes, m. p. 153°–4° and 115°–6°.—Heated w. soda-lime at 300° gives benzene (Test 913), and p-toluic ac.
60	262 (15 mm.)	**p-Tolyl Pentadecyl Ketone, $C_{23}H_{38}O$.**
60	320–2c.	**Desoxybenzoïn, Ph.CO.CH_2.Ph.**—Tbl. d. s. h. aq.; e. s. c. alc. or eth.—Easily attacked by HNO_3 or bz.—Oxime, ndl. fr. alc., m. p. 98°.
61	220–5d.	**β-Hydrindone, C_9H_8O.**—E. s. alc. or eth.—Oxime, ndl. fr. dil. alc., m. p. 155°.—M. p. of phenylhydrazone 120°.—Oxid. by $KMnO_4$ gives homophthalic ac.
63		**2, 5-Dimethyl-3, 4-diacetylfurfuran, $C_{10}H_{12}O_3$.**—Fine silky ndl. fr. h. aq., w. peculiar faint aromatic odor when warmed.—S. in conc. H_2SO_4 and ppt'd unchanged by aq.
63		**p-Methylhydrindone, $C_{10}H_{10}O$.**—Ndl. fr. lgr., e. s. alc. or eth.
67	278 (15 mm.)	**p-Tolyl Heptadecyl Ketone, C_7H_7.CO.$C_{17}H_{35}$.**—V. d. s. c. alc. —Oxid. by Test 905–3 gives p-toluic ac.
68	dec.	**Methyl Cinnamenylvinyl Ketone, $C_{12}H_{12}O$.**—Rhombic plates fr. eth.; e. s. alc. Color soon changes to light yellow.—Oxime, m. p. 153°.—Adds Br_2 easily in ethereal sol., giving dibromide of m. p. 173·5°.
69		**Laurone, $(C_{11}H_{23})_2$.CO.**—I. c. alc.—Probably does not give Test VII–1, oxime not being sol. in alkali.
72–3	a.360	**Benzylacetophenone, C_7H_7.CH_2.CO.Ph.**—V. s. alc. or eth.—Oxid. by Test 905–1 gives benzoic ac. (Test 312).—Br substitutes easily.—Oxime, m. p. 87°, v. s. alc.
73	255–60	**Methyl s-Duryl Ketone, $Me_4.C_6H$.CO.Me.**—Pearly lft.
75·5	385	**α-Phenyl Naphthyl Ketone, Ph.CO.$C_{10}H_7$.**—S. 41 pt. alc. at 12°.—Heating w. soda-lime at 350° gives naphthalene (Test 915) and benzoic ac.—Oxime, m. p. 140°–2°.

Melting-point (C.°).	Boiling-point (C.°).	KETONES.—Colorless and Solid.
76·3		† **Myristone, $(C_{13}H_{27})_2$.CO.**—Scales fr. abs. alc.—Oxime being v. d. s. in alkali does not give Test VII–1.
78		**6-Phenylindanone(7), $C_{15}H_{12}O$.**—B. p. 344° d.—E. s. alc. or eth.—Reduces ammon. $AgNO_3$ sol. on warming.—Oxime, m. p. 141°.—Oxid. by Test 905–3 gives benzoic and phthalic ac. (Tests 312 and 318–1).
81·5–2·5		**Lactarone, $(C_{14}H_{29})_2$.CO.**—Pearly lft. fr. alc.
82		**β-Phenyl Naphthyl Ketone, Ph.CO.$C_{10}H_7$.**—Ndl. s. 49 pt. c. alc.—Picrate fr. sat. sol. of picric ac. in bz., m. p. 112°–13°.—Heating w. soda-lime gives naphthalene (Test 915) and benzoic ac. (Test 312).
82·8		**Palmitone, $(C_{15}H_{31})_2$.CO.**—Lft. fr. alc.—Oxime being v. d. s. alk., probably does not give Test VII–1.—Gives no $NaHSO_3$ comp.
83		**Isodiphenylene Ketone, $C_{13}H_8O$.**—D. s. alc.—Stable toward oxid. agents.—Not changed by fusion w. KOH.
83·5–4		**Diphenylene Ketone, $(C_6H_4)_2$.CO.**—Large yellow tbl.—See Suborder II.
85		**Methyl Pentamethylphenyl Ketone, $C_{13}H_{18}O$.**—E. s. alc. or eth.—Oxid. by c. $KMnO_4$.
85·5–86		**Oxyacetophenone, Ph.CO.CH_2OH.**—V. s. alc. or eth.; s. h. aq.—Decomposed by heat alone, or by heating w. NaOH, giving benzaldehyde (Test 113).—Reduces Tollen's reagent giving benzaldehyde.—Gives Test 702.
87·8		† **Stearone, $(C_{17}H_{35})_2$.CO.**—Lft. d. s. h. alc. or eth.—Dibromderivative, m. p. 72°.—Because of insolubility of oxime in alkali does not give Test VII–1.
92		**s-(p)-Dimethylbenzophenone, $(C_6H_4.Me)_2$.CO.**—B. p. 335°–7°.—V. s. alc. or eth.—HNO_3 (sp. gr. 1·51) gives dinitro-comp., s. bz.; m. p. 144°.—Oxime, pr. fr. alc., m. p. 163°.—Boiled w. solid KOH gives p-toluic ac.
93–4		**9, 9-Dimethyldihydroanthrenone(10), $C_{16}H_{14}O$.**—Cryst. e. s. eth. or bz.—Oxid. by CrO_3 to acetic ac. and anthraquinone.
94		**Phenyl-p-Xylyl Ketone, Ph.CO.CH_2.C_6H_4.Me.**—4-sided pr.—Oxime, m. p. 109°.
95		**Benzoïnethylether, Ph.CH(OEt).CO.Ph.**—Pr. e. s. alc. or eth.
95		**o-Methylhydrindone, $C_{10}H_{10}O$.**—Ndl. fr. lgr.—Oxid. by Test 905–3 to methyl-phthalic ac.
99		**Benzoylveratol, $(MeO)_2$.C_6H_3.CO.Ph.**—Ndl. fr. alc.
99·5–100		**m-Phenylene Diphenyl Ketone, C_6H_4.(CO.Ph)$_2$.**—Dist. undec.—Oxime, m. p. 201°.—Fusion w. KOH gives only benzoic ac. (Test 312).
102–3		**Cinnamyleneacetophenone, $C_{17}H_{14}O$.**—Cf. Suborder II.
104·5		**Ledum Camphor, $C_{15}H_{26}O$** (fr. leaves of Ledum palustre, wild rosemary).—Sbl. v. e. in long ndl.—Sol. in conc. H_2SO_4 becomes violet w. a drop of HNO_3.—Gentle heating w. 50% H_2SO_4 gives a sesquiterpene, b. p. 255°.
106		**Cinnamylenebenzylideneacetone, $C_{19}H_{16}O$.**—Cf. Suborder II.
107–10		**β-Dibenzoylacetone, $C_{17}H_{14}O_3$.**—Ndl., d. s. eth., $CHCl_3$ and lgr.; s. in 100 pt. bz.—(Alcoholic sol. gives no color w. $FeCl_3$.)
109–10		**Anisoïn, $C_{16}H_{16}O_4$.**—Ndl. d. s. c. alc. or eth.—S. in conc. H_2SO_4 w. pale-green color changing to yellow and purple-red on warming!—Reduces Fehling's sol.
112–2·5		† **Dibenzylideneacetone, (Ph.CH:CH)$_2$.CO.**—See Suborder II.
115		**Methylhydrocotoïne, $(MeO)_3$.C_6H_2.CO.Ph.**—Br substitutes.—Fusion w. KOH gives benzoic ac., etc.
117		**Dibenzoylmesitylene, (Ph.CO)$_2$.C_6H.Me_3.**—B. p. abt. 300°.

Melting-point (C.°).	Boiling-point (C.°).	KETONES.—Colorless and Solid.
119–20		**Phenyldibenzoylmethane,** $(Ph.CO)_2.CH.Ph$.—B. p. 300°–5° (15 mm.).
120		**Piperonyloïne,** $C_{16}H_{12}O_6$.—Oxid. by dil. HNO_3 (Test 905–3) gives oxalic ac. (Test 317).
121		**m-Acetylbiphenyl,** $Me.CO.C_6H_4.Ph$.—B. p. 325°–7°.—E. s. alc. or acetone.—Oxid. by CrO_3 in Āc. to m-phenylbenzoic ac.
121c.		**Acenaphthenone,** $C_{12}H_8O$.—Ndl. v. s. alc.—Gives substitution product w. Br in CS_2 sol., m. p. 112°.—Boiled w. Zn dust and glacial Āc gives acenaphthylene.—Oxime, lft. fr. alc., m. p. 175°.
126		**1, 2, 4-Triphenylbutanedione(1, 4),** $Ph.CO.CH(Ph).CH_2.CO.Ph$.—Upon sol. in c. conc. H_2SO_4 and addition of aq. gives ppt. of triphenylfurfurane —Oxime, m. p. 151°.
129		**1, 2, 4-Triphenylbutenedione(1, 4),** $Ph.CO.C(Ph):CH.CO.Ph$.—Yellowish ndl., v. d. s. alc. or eth.—Dry, adds Br_2 cold; moist, Br substitutes.
abt. 133		† **Benzoïn,** $Ph.CH(OH).CO.Ph$.—B. p. 343°–4°.—6-sided pr. (often pale sulphur-yellow).—I. c. aq.; v. d. s. h. aq.; s. h. alc.—Gives Test VII–1.—Alc. sol. reduces Tollen's reagent (Test 101)!—Strongly heated above b. p. gives faint odor of benzaldehyde.—Boiled w. normal NaOH sol. in porcelain dish while air is blown through the solution the liquid soon assumes a RVT1 color.—Apply Test 713.
135		**αβ-Dinaphthyl Ketone,** $(C_{10}H_7)_2.CO$.—S. in 77 pt. alc. at 14°; e. s. eth.—Heated w. soda-lime at 350° gives naphthalene and α- and β-naphthoic ac.
144–5		**Diphenylbutanedione(1, 4),** $Ph.CO.CH_2.CH_2.CO.Ph$.—Ndl. d. s. alc. or eth.—Sol. in conc. H_2SO_4 is green, becoming red-brown w. blue-green fluorescence on warming.—Dioxime, m. p. 203°–4°.
159		**s(-p)-Ditoluylethane,** $C_7H_7.CO.CH_2.CH_2.CO.C_7H_7$.—Ndl., v. d. s. c. alc.; e. s. bz.—Boiling w. ammonium acetate and glacial Āc gives p-ditolylpyrrol.
159–60		**Terephthalophenone,** $C_6H_4.(CO.Ph)_2$.—Ndl. or lft., d. s. c. alc. or eth.—Oxime, m. p. 212°–13°; dioxime, fr. dil. alc., m. p. 235°.
162–3		**Triacetylbenzene,** $C_6H_3.(CO.Me)_3$.—Small ndl. d. s. aq., alc., or eth.—Oxid. by HNO_3 gives trimesic ac.
173–5		**Diacetyldibenzylethane,** $C_{20}H_{18}O_4$.—Ndl. fr. alc.—I. aq. or dil. alkalies.
176·4		† [+] **Camphor,** $C_{10}H_{16}O$. — ("Camphor.") — B. p. 205·3°. — Tough, white cryst., translucent, slightly unctuous mass, w. peculiar, penetrating, fragrant odor, and bitter, pungent taste! Small fragments thrown upon pure water, float and assume singular circulatory movements, which immediately cease upon the addition of a drop of oil.—Very volatile, subliming crystalline on sides of vessels in which it is contained at ordinary temperatures, and in the saponification test soon passing out of flask and depositing in condenser!—V. d. s. aq.; v. s. alc; e. s. eth.—Identify by Test 715! (The oxime forms so slowly that camphor does not give an appreciable ppt. in Test VII–1.)—"*Synthetic Camphor*" is opt. i.
198		† **α-Dibenzaltriacetophenone,** $C_{38}H_{32}O_3$.—Cryst. fr. bz.; v. d. s. alc.—Ppt. in Test VII–1 rather scanty.—Dist. splits to acetophenone (Test 712) and diphenylpropenone.—Warmed w. alc. NaOH gives (β) isomer, m. p. 256°.
208		**Phenyloxanthranol,** $C_{20}H_{14}O_2$.—Rhombic tbl., i. alkalies; e. s. alc.; s. conc. H_2SO_4 w. intense purple-red color.—Warmed w. glacial Āc and Zn dust gives phenylanthranol.
232		**"Octahedral" Oxylepidine,** $C_{18}H_{20}O_2$.—Cf. Suborder II.

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Boiling-point (C.°).	**KETONES.**—Colorless and Solid.
256		† (*β*)-**Dibenzaltriacetophenone,** $C_{38}H_{32}O_3$.—Thin lustrous pr. d. s. alc.—Does not give Test VII-2.—On dist. splits to acetophenone (Test 712) and diphenylpropenone.
269–70		**Duryldibenzoyl,** $Me_4.C_6.(CO.Ph)_2$.—Small pr. s. bz.; alm. i. h. alc.—Sbl.—Fusion w. KOH gives benzoic ac. and durene.
289		**Truxone,** $(C_9H_6O)_x$.—Sbl. in ndl.—Cryst. fr. HNO_3 (sp. gr. 1·38) in long lustrous ndl.

GENUS VII, KETONES.

DIVISION B,—LIQUID KETONES.

Boiling-point (C.°).	Specific Gravity.	**KETONES.**—Colorless and Liquid.
56·5c.	$0{\cdot}819^{0}/_{4}$	† **Acetone, Me.CO.Me.**—Misc. w. aq., alc., or eth.—Odor alcoholic-ethereal.—Identify by Test 711 !
80·6	0·805(19·8)	† **Methyl Ethyl Ketone, Me.CO.Et.**—Odor like acetone.—Oxid. by Test 702 gives acetic ac. only !
87·5–8	0·973(22)	† **Diacetyl, Me.CO.CO.Me.**—*Yellow* liquid w. peculiar sweetish-pungent odor. (Belongs to Div. B of Suborder II.)
95	$0{\cdot}822^{0}/_{0}$	**Methyl Isopropyl Ketone, Me.CO.Pr.—Oxid.** by Test 702 gives Āc and CO_2.
98–102		**2-Methylbutenon(1, 3), Me.CO.CMe:CH$_2$.**
102c.	0·812(15)	† **Methyl Propyl Ketone, Me.CO.Pr.**—Test 702 gives acetic and propionic acids.
102·7c.	$0{\cdot}834^{0}/_{4}$	† **Diethyl Ketone, Et.CO.Et.**—CrO_3 oxid. to acetic and propionic acids (cf. Test 702).—Gives $NaHSO_3$ comp. w. difficulty.
106 (th. i.)	0·800(16)	† **Pinacoline, Me.CO.C.Me$_3$.**—Alm. i. aq.—Peppermint-like odor.—No $NaHSO_3$ comp.—Test 702 oxid. to trimethylacetic ac.—Treated w. Cl cold gives $C_6H_{10}Cl_2O$, m. p. 51°; b. p. 178°.—Becomes opaque and yellow in 10 sec., cold, in Test VII–2.
114		**Acetyltrimethylene, Me.CO.C$_3$H$_5$.** — Polymerized by mineral acids.—$KMnO_4$ gives trimethylenecarbonic ac.
114·5	$0{\cdot}830^{0}/_{0}$	**Ethyl Isopropyl Ketone, Et.CO.Pr.**
116	$0{\cdot}803^{19}/_{0}$	**Methyl Isobutyl Ketone, Me.CO. Bu.**—Strong camphor-like odor.—Test 702 oxid. to isobutyric, isovalerianic, and acetic acids (disagreeable odor).—Gives a $NaHSO_3$ comp.
118c.	$0{\cdot}818^{14.5}/_{4}$	**Methylethylacetone, Me.CO.CH(Me)Et.**—Peppermint-like odor.—Test 702 gives acetic ac. (Test 311).
122	0·861(15)	**Ethylideneacetone, Me.CH:CH.CO.Me.**—S. aq.
122–4	0·818(17·5)'	**Ethyl Propyl Ketone, Et.CO.Pr.**—Test 702 oxid. to Āc, propionic and butyric acids.
123·7	$0{\cdot}806^{20}/_{4}$	**Diiosopropyl Ketone, (Me$_2$.CH)$_2$.CO.**—No comp. w. $NaHSO_3$.—CrO_3 gives acetic and isobutyric acids (Test 702).
126	0·810(21)	**2, 2-Dimethylpentanone(3), Et.CO.C.Me$_3$.** — Camphor odor. — Test 702 gives Āc and trimethylacetic ac.
127	0·830(0)	**Methyl Butyl Ketone, Me.CO. Bu.**
128	0·920(21·7)	**Acetylcarbinolethylether, Me.CO.CH$_2$.OEt.**—Misc. w. aq.—Reduces Tollen's $AgNO_3$ reagent —In HCl sol. gives acetone and ethyl alc. w. Na amalgam.
128–30	$0{\cdot}834^{27}/_{17.5}$	**Allylacetone, Me.CO.(CH$_2$)$_2$.CH:CH$_2$.**—Unpleasant odor.—Test 702 oxid. to acetic and oxalic ac. (Tests 311 and 317).
129·5–30c.	$0{\cdot}858^{20}/_{4}$	† **Mesityl Oxide, Me$_2$.C:CH.CO.Me.**—Peppermint odor.—I. aq.; v. s. alc.—Boiled w. v. dil. H_2SO_4 yields acetone (Test 711).—Gives no $NaHSO_3$ comp.—Shaken w. phenylhydrazine reacts w. evolution of heat (product oily). Solution opaque and yellow in 5 sec. in cold, in Test VII–2.
130c.	$0{\cdot}942^{21.5}/_{4}$	**Cyclopentanone, C$_4$H$_8$CO.**—Peppermint odor —Dil. HNO_3 gives glutaric and succinic ac.—Semicarbazon, m. p. 200°–5° d.
132	0·825(21)	**3, 3-Dimethylpentanone(2), Me.CO.C(Me$_2$)Et.**—Test 702 oxid. to dimethylethylacetic ac.

Boiling-point (C.°).	Specific Gravity.	**KETONES.**—Colorless and Liquid.
135	0·907(15)	**Methyl Tetramethylene Ketone, Me.CO.C_4H_7.**—Peppermint odor.—Gives a $NaHSO_3$ comp.
136	0·815$^{17}/_{0}$	**Ethyl Isobutyl Ketone, Et.CO. Bu.**—Test 702 oxid. to acetic and isovalerianic ac.
135–40	0·815(20)	**2, 3-Dimethylpentanone(4), Me.CO.CHMe.$CHMe_2$.**
137·5–9	0·817(22)	**3-Ethylpentanone(4), Me.CO.$CHEt_2$.**—Gives a bisulphite comp.
141–3	0·914$^{20}/_{0}$	**1-Methylcyclopentanone(3), Me.C_4H_7.CO.**—Opt. active [+].
144c.	0·818 (17·2)	**Methyl Isoamyl Ketone, Me.CO.C_5H_{11}.**—Test 702 oxid. to acetic, isovalerianic and isocaproic ac.
144	0·820$^{20}/_{20}$	**Dipropyl Ketone, Pr.CO.Pr.**—I. aq.—Test 702 oxid. to propionic and butyric acids.—Gives no $NaHSO_3$ comp.
147d.		**Acetylcarbinol (Acetol), Me.CO.CH_2OH.**—Misc. w aq., alc., or eth.—"Faint, sickly odor"!—Reduces Fehling's sol. cold.—Combines w. 2 mols. phenylhydrazine at 100° forming methylglyoxalosazone, m. p. 145°.—Phenylhydrazone oily.—"Soon acquires acid reaction." Position in tables in doubt.
149–50	0·914(0)	**2-Hexinone(5), Me.CO.CH_2.C : C.Me.**
151	0·829(21)	**3, 3-Dimethylhexanone(4), Et.CO.C.(Me_2)Et.**
151–2	0·837(0)	**Methyl Amyl Ketone, Me.CO.C_5H_{11}.**—Oxid. by Test 702 to acetic and valerianic acids.—Gives a $NaHSO_3$ comp.
155	0·831(0)	**Propyl Isobutyl Ketone, Pr.CO. Bu.**—Gives no $NaHSO_3$ comp.
155–6	0.900(15)	**Propionylcyclobutane, Et.CO.C_4H_7.**—Gives a $NaHSO_3$ comp.
155	0·947$^{20}/_{4}$	**Cyclohexanone, $(CH_2)_5$:CO.**—Odor like acetone.—E. s. aq.—Dil. HNO_3 oxid. to adipic ac.—Gives comp. w. $NaHSO_3$.
163·5–4·5	0·931(25)	**Diacetone Alc., Me.CO.CH_2.CMe_2.OH.**—Misc. w. aq. or alc.—Sol. in conc. H_2SO_4 gives mesityl oxide.
169	0·909(20)	[+] **1-Methylcyclohexanone(3), Me.C_6H_9O.**
170	0·850(0)	**Ethyl Amyl Ketone, Et.CO.C_5H_{11}.**—Gives no comp. w. $NaHSO_3$.
170–1	0·817(19)	**2-Methylheptanone(6), Me.CO.$(CH_2)_3$.$CHMe_2$.**
172·5	0·819$^{20}/_{4}$	**Methyl Hexyl Ketone, Me.CO.C_6H_{13}.**—Oxid. by HNO_3 gives œnanthic and acetic acids.—Gives comp. w. $NaHSO_3$.
173–4		**Dipropylacetone, Pr_2.CH.CO.Me.**
173–4	0·860(20)	**2-Methylheptene(2)-one(6), C_7H_{14}·CO.**—$KMnO_4$ oxid. to acetone and lævulinic ac.—Gives purple-red color to pine splinter moistened w. HCl.
174–5		**as.-Diallylacetone, $(C_3H_5)_2$.CH.CO.Me.**
176–7	1·000(15)	**Hydracetylacetone, Me.CH(OH).CH_2.CO.Me.**—S. aq., alc., eth., or $CHCl_3$.—Gives phenylhydrazone, m. p. 85°–7°.
179–81c.	0·969(0)	**Suberone, C_6H_{12}:CO.**—Peppermint odor.—Adds Br easily.
180	0·827(16)	**Methylbutyrone, C_8H_{16}O.**—Conc. HNO_3 oxid. to œnanthic ac.
181–2	0·833(20)	**2, 6-Dimethylheptanone(4), $(Me_2.CH.CH_2)_2$.CO.**—$NaHSO_3$ gives no comp.
190	0·825$^{20}/_{0}$	**Ethyl Hexyl Ketone, Et.CO.C_6H_{13}.**—Solid at −8°.
192–3	0·947(19)	† **[+]-Fenchone, $C_{10}H_{16}$O** (from oil of fennel.)—Odor pleasant and camphorous!—M. p. +5°–6°.—Heated w. P_2O_5 gives m-isocymene.—S. without decomposition in conc. H_2SO_4.—Gives an oxime, m. p. 164°–5° (r. h.).
194 (th. i.)	0·970$^{20·8}/_{4}$	† **Acetonylacetone, Me.CO.$(CH_2)_2$.CO.Me.**—E. s. aq., alc., or eth.—Gives pyrrol test (Test 703) w. splinter.—Combines w. x's phenylhydrazine on warming to osazone, cryst. fr dil alc., m. p. 120°.
196–8		**4-Methyloctonone(2), $C_{10}H_{20}$O.**
202 (th. i.)	1·032(15)	† **Acetophenone, Me.CO.Ph.**—Alm. i. aq.—M. p. 20.5°.—Gives Test VII–2 readily in the cold.—Identify by Test 712!

Boiling-point (C.°).	Specific Gravity.	KETONES.—Colorless and Liquid.
200–5	0·939(12)	**Camphorphoron, $Me_2C{:}C_6H_8O.Me$.** — Odor spicy. — Tribrom-comp., m. p. 52°.
203	0·913(20)	† **Thujone (Tanacetone), $C_{10}H_{16}O$** (fr. tansy-oil, Tanacetum vulgare).—Odor somewhat like tansy.—Opt. active [+].—($NaHSO_3$ comp. i. eth., forms *very* slowly.)—Dist. fr. P_2O_5 gives cymene —Boiling w. $FeCl_3$ gives carvacrol.—α-oxime, m. p. 54–5°.—5 cc. Br+5 grms. thujone and 30 cc. lgr. (cold) gives tribrom-deriv., d. s. alc., m. p. 121°–2°.
204–5		**Ditetramethylene Ketone, $(C_4H_7)_2.CO$.** — Peppermint odor. — $NaHSO_3$ comp. e. s.—Combines w. phenylhydrazine.
200–10	0·841(17)	**Isopropyl Hexyl Ketone, $Me_2.CH.CO.C_6H_{13}$.**—Gives no $NaHSO_3$ comp.
206c.	0·913(0)	**α-Menthone, $C_{10}H_{18}O$.**—Faint peppermint odor. Does not give Test 702.—Opt. active [+].—P_2O_5 gives a terpene, b. p. 170°–3° and a diterpene b. p. 320°–5°.
206–7	$0{\cdot}824^{20\cdot5}/_0$	**Propyl Hexyl Ketone, $Pr.CO.C_6H_{13}$.**—M. p. −9°.—Gives no $NaHSO_3$ comp.
206–8	0·900(20)	**[+]-Menthone, $C_{10}H_{18}O$.** — Similar to [−]-menthone. — Oxime syrupy.
207	0·896(20)	† **[−]-Menthone, $C_{10}H_{18}O$.** — Odor peppermint-like. — D. s. aq.; misc. alc. or eth.—Oxime by Test VII–1, m. p. 118°–19°.
208–9d	1·016(0)	**Acetylpropyl Alc., $Me.CO.(CH_2)_2.CH_2OH$.**—Slow dist. gives unstable anhydride, b. p. 72°–5°.—Misc. aq.; e. s. alc. or eth.—$NaHSO_3$ comp. e. s. aq. or alc.—May be oxid. by CrO_3 mixture to lævulinic ac.
211	0·825(20)	**Methyl Octyl Ketone, $Me.CO.C_8H_{17}$.**—M. p. +3·5°.—Odor orange-like.—Gives a $NaHSO_3$ comp.
210–15	$0{\cdot}948^{20}/_4$	**Eucarvol, $C_{10}H_{14}O$.**—Boiled w. conc. sol. of KOH in CH_3OH gives unstable blue color.
215	1·010(3)	**Methyl Benzyl Ketone, $Ph.CH_2.CO.Me$.**—Cf. Div. A, m. p. 27°.
217		**Isopropyl Phenyl Ketone, $Pr.CO.Ph$.**—Phenylhydrazone, m. p. 71°.—Oxime, m. p. 58°.
218	1·009(0)	**Propiophenone, $Ph.CO.Et$.**—M. p. +21°.—Gives no $NaHSO_3$ comp.—Oxime melts at 52°–53°.
220–2		**Propyl Phenyl Ketone, $Pr.CO.Ph$.**—No $NaHSO_3$ comp.—Test 702 gives benzoic and propionic acids (Tests 312 and 311).
221–2	0·932(20)	† **Pulegone, $C_{10}H_{16}O$.**—Odor of pennyroyal (Mentha pulegium).—Gives a $NaHSO_3$ comp. (forms very slowly); i. alc. or eth.—Opt. active [−].—Adds Br_2.—Oxime, m. p. 157°, silky ndl. d. s. alc.!
221–2	0·928(19)	**Dihydrocarvone, $C_{10}H_{16}O$.**—Opt. active [+ or −].—Gives $NaHSO_3$ comp. slowly.—Adds Br_2.—Oxime, m. p. 87°–9°.
222	1·013	**p-Methyl Tolyl Ketone, $Me.CO.C_6H_4.Me$.**—Oxid. by $KMnO_4$ gives terephthalic ac.—Dibrom-derivative, m. p. 100°.
224	0·829(17·5)	**Methyl Nonyl Ketone, $Me.CO.C_9H_{19}$.**—Chief constituent of oil of rue (Ruta graveolens). Freezes at +6°; m. p. +15°.—Test 702 gives acetic and pelargonic acids.
223–6	0·998(17·5)	**Ethyl Benzyl Ketone, $Et.CO.C_7H_7$.**—Gives no $NaHSO_3$ comp.—Test 702 gives benzoic and propionic acids (Tests 312 and 311).
224–5	0·996(19)	† **2-Methyl-1, 4-Xylyl Ketone, $Me.CO.C_6H_3.Me_2$.**—(Sol. in Test VII–2, becomes opaque and yellow after heating 1 min.)—No $NaHSO_3$ comp.—E. s. alc. or eth.—Oxime, m. p. 58°.
224–5	0·989(20)	**m-Methyl Tolyl Ketone, $Me.C_6H_4.CO.Me$.**—Gives isophthalic ac. on oxid. by alkaline $KMnO_4$.

Boiling-point (C.°).	Specific Gravity.	**KETONES.**—Colorless and Liquid.
225–6	0·993(17·5)	**Isobutyl Phenyl Ketone, Bu.CO.Ph.**—Test 702 gives benzoic and isobutyric acids.—Gives no $NaHSO_3$ comp.—Oxime, m. p. 74°.
226c	0·826(20)	† **Caprone, $(C_5H_{11})_2$.CO.**—M. p. 14·6°.—Gives no $NaHSO_3$ comp. —Sol becomes opaque and the undissolved drop deep yellow in Test VII–2 (This is the highest symmet. fatty ketone in its series known to give Test VII–2.)
226		**Diisoamyl Ketone, $(C_5H_{11})_2$.CO.**—Yellow oil.
230–2		**Diethylacetophenone, Ph.CO.CHEt$_2$.**
232–3		**p-Tolylacetone, Me.C_6H_4.CH_2.CO.Me.**—Gives no $NaHSO_3$ comp. —Oxime, m. p. 90°–1°.
235	0·989(0)	**Acetylmesitylene, Me.CO.C_6H_2.Me$_3$.**
235–6	$0·989^{23}/_{17}$	**Benzylacetone, Ph.CH_2.CH_2.CO.Me.**—Test 702 oxid. to benzoic and acetic acids.—Gives $NaHSO_3$ comp., rather d. s. aq.
235–6		**Isopropyl Tolyl Ketone, C_3H_7.CO.C_7H_7.**—Oxime, m. p. 92°.
237–8		**Ethyl p-Xylyl Ketone, Et.CO.C_6H_3.Me$_2$.**
237·5–8·5		**Butyl Phenyl Ketone, Bu.CO.Ph.**
237–9		**Ethyl p-Tolyl Ketone, Et.CO.C_6H_4.Me.**—Nitration w. fuming HNO_3 gives comp. having m. p. 50°–1°.—Oxime, m. p. 86–7°.
237–40		**Allylacetophenone, Ph.CO.CH_2.C_3H_5.**—Adds Br_2 easily.
238–9c.		**α-Methylbenzylacetone, Me.CO.CH(Me)(C_7H_7).**
238–9		**Ethyl m-Xylyl Ketone, Et.CO.C_6H_3.Me$_2$.**—Phenylhydrazone, m. p 126°.—Oxime, m. p. 72°.
239–40		**2-Isopropyl-1, 4-Xylyl Ketone, C_3H_7.CO.C_6H_3.Me$_2$.**—Odor like mushrooms.—Oxime, m. p. 76°.
240·5–1		**Benzoyltrimethylene, Ph.CO.C_3H_5.**—Br acts only at high temp. —Oxime, lft. fr. lgr., m. p. 90°–2°.
241·5–2·5		**Isoamyl Phenyl Ketone, C_5H_{11}.CO.Ph.**
244–5		**4-Isopropyl 1, 3-Xylyl Ketone, C_3H_7.CO.C_6H_3.Me$_2$.**—Oxime, m. p. 97°.
245·5–6·5c.		**β-Methylhydrindone, $C_{10}H_{10}O$.**—Peppermint odor.—$KMnO_4$ oxid. to phthalic ac.—Sol. in conc. H_2SO_4 fluoresces blue-violet.
246–7 (th. i.)	1·019(0)	**Methyl o-Xylyl Ketone, Me.CO.C_6H_3.Me$_2$.**—E. s. alc. or eth.— $KMnO_4$ oxid. to p-xylic ac.—Oxime, m. p. 85°.
246·5		**Methyl Pseudocumyl Ketone, Me.CO.C_6H_2.Me$_3$.**—M. p. 10°.— E. s. alc. and eth.
249		**2-Propyl 1, 4-Xylyl Ketone, Pr.CO.C_6H_3.Me$_2$.**—Aromatic oil.— Oxime, m. p. 47°.
251		**4-Propyl 1, 3-Xylyl Ketone, Pr.CO.C_6H_3.Me$_2$.**—E. s. alc. **or** eth.—Odor turpentine-like.
251–2		**Xylitone, $C_{12}H_{18}O$.**—Geranium odor.—I. aq.—Easily oxid.— $KMnO_4$ gives CO_2, acetic, and α-dimethylsuccinic acids.— Resinified by conc. acids.
253–5		**Methyl α-Duryl Ketone, Me.CO.C_6H.Me$_4$.**—E. s. alc. or eth.
254c	0·975(15)	**p-Acetylcumene, C_3H_7.C_6H_4.CO.Me.**—Nitrates to comp. having m. p. 49°.—Oxime, m. p. 70°–1°.
255–8		**4-Isopropyl 1, 2-Xylyl Ketone, Pr.CO.C_6H_3.Me$_2$.** — Turpentine odor.—Oxime, m. p. 68°
256–60		**Methyl o-Cymyl Ketone, Me.CO.$C_{10}H_{13}$.**—Aromatic oil.
259 (th. i.)	0·978(15)	**p-Acetylpropylbenzene, Me.CO.C_6H_4.Pr.**—Oxid. by alkaline $KMnO_4$ gives terephthalic and benzoic acids. (Tests 318–3 and 312.)
259	0·957(19)	**2-Isopropyl 1, 4-Isocymyl Ketone, Pr.CO.$C_{10}H_{13}$.**—Oxime is oily.
259	1·052(15)	**Benzoylcyclobutane, C_4H_7.CO.Ph.**—Oxime, d. s. lgr., m. p. 92°.
259		**Methyl v-Duryl Ketone, Me.CO.C_6H.Me$_4$.**—Phenylhydrazone, m. p. 129°.

(ORDER I, SUBORDER I.)

Boiling-point (C.°).	Specific Gravity.	KETONES.—Colorless and Liquid.
260–5c.		**Cumylacetone**, $Pr.C_6H_4.CH_2.CH_2.CO.Me$.—Oxime, m. p. 56°.
266–9		**Ethyl o-Cymyl Ketone**, $Et.CO.C_{10}H_{13}$.—Aromatic oil.
270·7		**Phenyl Hexyl Ketone**, $Ph.CO.C_6H_{13}$.—Lft. m. p. 17°.—Gives an oxime, m. p. 55°.
270–72	0·944(19)	**2-Isobutyl 1, 4-Isocymyl Ketone**, $Bu.CO.C_{10}H_{13}$.—Oxime is oily.
295–6	1·134(0)	**α-Methyl Naphthyl Ketone**, $Me.CO.C_{10}H_7$.—V. s. alc. or eth.—Oxime, m. p. 145°.—Picrate, fr. alc. sol., m. p. 116°.—Br substitutes readily.
300–4	0·826(17)	**Diheptylacetone**, $Me.CO.CH.(C_7H_{15})_2$.—Gives a $NaHSO_3$ comp.
305–7	1·108(0)	**α-Propanoylnaphthene**, $Et.CO.C_{10}H_7$.—V. s. alc. or eth.—Oxime, m. p. 57°–8°.—Picrate, yellow ndl., m. p. 77°–8°.
308–10	1·076(0)	**α-Isopropyl Naphthyl Ketone**, $Pr.CO.C_{10}H_7$.—Oxime, m. p. 140°.—Picrate, m. p. 66·7°.
a. 300		**p-Ethylbenzophenone**, $Ph.CO.C_6H_4.Et$.—Gives isomeric oximes.
312–14	1·062(0)	**β-Isopropyl Naphthyl Ketone**, $Pr.CO.C_{10}H_7$.—V. s. alc.—Oxime, m. p. 121°–2°.
314–16	1·088(17·5)	**m-Phenyl Tolyl Ketone**, $Ph.CO.C_6H_4.Me$.—V. s. alc. or eth.—Oxime, m. p. 100°–1°.
315–16		**o-Phenyl Tolyl Ketone**, $Ph.CO.C_6H_4.Me$.—Gives isomeric oximes.
322 (th. i.)		**α-Phenyl-m-Xylyl Ketone**, $Ph.CO.C_6H_3.Me_2$.—Gives isomeric oximes.
325–30		**Dioctylacetone**, $Me.CO.CH.(C_8H_{17})_2$.

NUMBERED SPECIFIC AND SEMI-SPECIFIC TESTS FOR THE KETONES.

[TESTS 701-800.]

701. Colorations with Sodium Nitroprusside.

Shake five drops of the ketone with 2 cc. of cold water. If the substance does not dissolve completely, filter through a wet filter. Add to the clear solution two drops of a 1% aqueous solution of sodium nitroprusside, and then two drops of sodium-hydroxide solution (1 : 10). Without any unnecessary delay, carefully note the color, and then quickly divide the solution into two equal portions, *a* and *b*, in small glass "weighing-tubes." To portion *b* add three drops of glacial acetic acid, and immediately note the color. Allow both solutions to stand for twenty minutes, and again carefully compare the color of each with the color standard.

Many of the aldehydes as well as ketones of Order I give colorations in this test; but its most important practical application is its use as a convenient specific reaction for acetone and acetophenone. It distinguishes these ketones readily from all related ketone species with which either is likely to be confused.

In the case of *acetone*, portion *a* at first is orange (O), but changes to a clear yellow (Y–YT1) within twenty minutes. Portion *b* after the acidification with acetic acid is a red (R–RT1) when viewed against a white background, with a very slight tendency to purple, that is most noticeable when the solution is viewed by a strong transmitted light. This *hue* will be found unchanged at the end of twenty minutes, though its intensity will have fallen about one tint, i.e. to (RT1–RT2). The persistency of this hue in acetic-acid solution is the most characteristic part of the test when used to distinguish acetone from its homologues.

In the case of *acetophenone*, the color of portion *a* is at first red with a very slight tendency to violet-red, just as in part *b* of the acetone test after acidification. This changes to yellow before the end of twenty minutes. Portion *b* upon acidification with acetic acid changes at once to a strong blue (B–VB), whose hue is not materially changed at the end of twenty minutes, although it will have faded nearly one tint to about (BT1–VBT1).

The most characteristic part of the acetophenone test is the strong blue coloration of portion *b*. Homologues of acetophenone, $CH_3.CO.R$, like methyltolyl- and methylxylyl ketone, do indeed give pale violet or bluish colorations, but they are much fainter than T3 of the color standard. Fatty-aromatic ketones, like ethyl-phenyl ketone, which contain no methyl radical in combination with —CO.R, appear not to give any blue coloration at all.

[Sodium-nitroprusside solution does not keep well, and should not be more than a few days old when used.]

702. Oxidations with Chromic Acid.

The aliphatic ketones and alcohols may all be easily oxidized by chromic acid to mixtures of fatty acids. These mixtures may then often be resolved into their constituents, and the latter identified by forming their silver salts. The method is not especially difficult if the acids are not too near one another in the homologous series.

The oxidation of an unsymmetrical ketone or secondary alcohol may occur in two ways; i.e. the splitting of the molecule may take place on either side of the carbonyl or hydroxyl group, as illustrated in the following reactions for the oxidation of ethyl-propyl ketone:

$$CH_3.CH_2.CO.CH_2.CH_2.CH_3 + 3O = 2CH_3.CH_2.CO_2H,$$

or

$$CH_3.CH_2.CO.CH_2.CH_2.CH_3 + 3O = CH_3.CO_2H + CH_3.(CH_2)_2.CO_2H.$$

Frequently, however, the tendency for one of the reactions to take place is so much greater than for the other, that only one acid will actually be formed in quantity large enough for isolation.

The chromic acid mixture for these oxidations is prepared by dissolving 10 grms. (2 molecules) of crystallized commercial chromic anhydride in a mixture of 60 cc. of water and 8 cc. (3 molecules) of concentrated sulphuric acid. Calculate how much of the mixture will be needed for any oxidation, by assuming that each cubic centimeter contains 0.05 grm. of "available oxygen," and that the reaction will take place according to the theoretical equation without secondary oxidations—which is not strictly true, since some of the substance will always remain unattacked. Perform the oxidation in a round-bottomed flask having a capacity of at least five times the volume of the solution. The flask should be fitted with a return-flow condenser. It is best to use as much as one or two grams of substance for each experiment. Support the flask on a piece of wire gauze, and boil briskly until the reduction of the chromic acid is complete. This will not require more than an hour if the substance is at all soluble in the mixture. Bumping may be prevented by dropping an ebullator tube (cf. p. 223) into the flask before bringing to a boil. The oxidation being ended, connect the flask with an inclined condenser; add a fresh ebullator tube, and distil rapidly until only a few cubic centimeters of liquid remain in the flask. Add 25 cc. more water, and distil again.

If only volatile fatty acids are to be sought, place the combined distillates in a flask; heat nearly to boiling, without attempting to remove any oily or solid matter that may be held in suspension; add an excess of moist silver oxide; and shake persistently to hasten the neutralization of the organic acids. Then dilute with hot water,—from 100 to 1000 cc., according to the solubility of the silver salts that it is expected will be formed,—bring to a boil, and filter hot. Repeat the extraction of the residue on the filter with a second but smaller quantity of boiling water. Filter. Unite this filtrate with the first, and separate the mixed silver salts by fractional crystallization. Since the solubility of the salts diminishes as their molecular weight increases, those of higher molecular weight will separate first, when a saturated solution is cooled or evaporated.*

The determination of silver in the salts is made by drying to constant weight at 100° in a porcelain crucible, igniting to destroy organic matter, and then weighing the residue of

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* In the case of the mixture of silver caproate and acetate, that is formed when 1 grm. of secondary octyl alcohol or methylhexyl ketone is oxidized, a single recrystallization from boiling water of the salt that separates from the original hot saturated solution on cooling, gives a silver caproate that contains the theoretical percentage of silver. The purification of the more soluble silver acetate in the mother liquors requires two or three additional crystallizations, in which the first crystals that separate are each time rejected. The separation of two salts whose acids lie nearer to each other in the homologous series is more difficult.

metallic silver. The following table gives the percentage of silver, and the approximate solubility of a few of the silver salts of the more important of the fatty volatile acids:

		Per Cent, Ag.	100 Parts of Water Dissolve	
Silver Acetate,	$Ag.C_2H_3O_2$	64.67	at 20° 1.04 pts.	at 80° 2.52 pts.
" Propionate,	$Ag.C_3H_5O_2$	59.67	" 0.84 "	" 2.03 "
" Butyrate,	$Ag.C_4H_7O_2$	55.38	" 0.48 "	" 1.14 "
" Isobutyrate,	"	"	" 0.96 "	" 1.90 "
" Valerianate,	$Ag.C_5H_9O_2$ . . .	51.67	" 0.30 "	" 70° 0.64 "
" Methyl ethylacetate,	"	"	" 1.18 "	" 80° 2.40 "
" Isovalerianate,	"	"	" 0.25 "	" 0.49 "
" Caproate,	$Ag.C_6H_{11}O_2$	48.43	" 0.11 "	" 0.34 "

703. Pyrrol-red Reaction for γ-Diketones.

Place one drop of the ketone if a liquid, or about 0.01 grm. if a solid, in a small test-tube, add 1 cc. of glacial acetic acid, three drops of concentrated ammonia, and a freshly cut splinter of soft pine wood, and boil gently for half a minute. Remove the splinter from the tube and moisten it at once with a drop of concentrated hydrochloric acid. If no pronounced color is produced in this way, return the splinter to the test-tube, add five drops of concentrated hydrochloric acid, and boil again for about one minute.

γ-Diketones of Genus VII, as well as certain species like diethyl diacetylsuccinate in other genera whose symbols contain the group —$CO.CH_2.CH_2.CO$— undergo condensation with ammonia in this test to pyrrol derivatives, which, in the presence of the mineral acid, produce an intense red stain upon the wood. With the simple γ-diketones like acetonylacetone the stain appears instantly and with the greatest brilliancy when the wood is moistened with hydrochloric acid in the first part of the test. The subsequent boiling with hydrochloric acid is, however, necessary to develop the color in the case of bodies like diethyl diacetylsuccinate.

711. Acetone. (Properties tabulated on p. 141.)

1. Apply the color reactions with sodium nitroprusside described in Test 701, bearing in mind that since nearly all soluble ketones and aldehydes give colorations of some kind when thus treated, the result will be significant only when the colors obtained correspond closely to the specified hues of the color standard.

This procedure is to be especially recommended for the preliminary examination of aqueous solutions and distillates supposed to contain at least several per cent of acetone. In examining such a solution, simply substitute 2 cc. of it for the same volume of the solution of definite concentration prescribed in the general directions. Very dilute solutions should first be somewhat concentrated by a rectification with the assistance of a small distilling-tower. If a solution contains only 1% of acetone, the color of "portion *a*" will at first be yellow-orange (YO), instead of orange; while "portion *b*," with acetic acid, will give a very pale tint of red, RT3, instead of R–RT1, which, after standing for twenty minutes, will fade to a tone of the same hue, but so pale as to be barely distinguishable.

2. Place in a dry six-inch test-tube two drops of the ketone and 0.4 cc. of cold water. Add 0.4 cc. of benzaldehyde, 2.0 cc. of strong alcohol, and 0.5 cc. of a ten per cent aqueous sodium-hydroxide solution. Mix by shaking. Boil very gently over a small flame for one minute, counting the time from the moment when the mixture first actually boils. If no precipitate appears, cool and shake vigorously. Filter off the crystals,* and wash

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* If the precipitate, instead of consisting of crystals, is an oil or pasty mass, the procedure given requires no modification. Such products usually become crystalline, either during the washing with alcohol, or upon the cooling of the solution prepared from the washed oil.

with 2 cc. of cold strong alcohol. Recrystallize from 2 cc. of boiling alcohol. Cool, and, if necessary, shake persistently until crystals appear. Filter. Wash with 1 cc. of cold alcohol. Press on filter-paper or porous tile. Then transfer to a watch-glass and dry half an hour or longer at 100°. In taking the melting-point raise the temperature at the rate of about one degree in twenty seconds.

The product formed in this test is dibenzylideneacetone $(C_6H_5.CH:CH)_2.CO$. It crystallizes in pale yellow lustrous plates which melt at 111.0°–112° (uncor.).

Observations on the application of Procedure 2 to aqueous solutions of acetone.—If a solution contains less than 75% of acetone, take 1 cc. instead of two drops as above directed, and add no water. The quantities of the other reagents and the method of procedure may be allowed to remain unchanged. The test has been used for solutions containing as little as 2% of acetone. But with solutions between 5% and 2%, cooling and shaking after heating frequently gives only an emulsion. The addition of 1 cc. of strong cold alcohol and shaking will, in such cases, produce a crystalline precipitate, which can then be treated in the usual manner.

If the quantity of crystals obtained from an acetone solution after the first filtration is small, wash with 1 cc. of alcohol (instead of 2.0 cc.), and recrystallize from 1 cc. of boiling alcohol (instead of 2 cc.). If no crystals then appear on cooling and shaking, add cold water (0.5 cc.–1.0 cc. is usually enough) until the solution becomes turbid. Shaking will then produce crystals. Wash these with 0.5 cc. of cold alcohol (instead of 1 cc.). Crystals thus obtained from dilute alcohol will be found to melt at 0.5°–1.5° lower than those from strong alcohol. It is, on the whole, advisable to concentrate very dilute acetone solutions by distillation rather than to test them by this method at very low concentrations.

For the detection of traces of acetone by this method, see Vorländer, Hobohm B. 29, 1840.

712. Acetophenone. (Properties tabulated on p. 136.)

1. Apply color reaction 701 with sodium nitroprusside. This is a very satisfactory and simple preliminary test. A single drop of the ketone will be enough for the preparation of the saturated aqueous solution required. If a negative result is not obtained in the experiment, proceed to part (2) of the test, which follows.

2. Place two drops of the ketone and four of phenylhydrazine in a dry test-tube. Heat until the mixture begins to boil. Cool. Add ten drops of glacial acetic acid, then 10 cc. of water, and shake. Collect on a filter and wash thoroughly with water. Dissolve in 12 cc. of boiling 50 per cent alcohol. Allow to cool. Filter off the abundant precipitate of thin flat crystals, and wash with 2 cc. of cold 50 per cent alcohol. Remove the mother-liquor by pressing on a porous tile, and recrystallize from 12 cc. of boiling 50 per cent alcohol. Allow to cool slowly. Filter. Wash with 3 cc. of 50 per cent alcohol. Remove the mother-liquor on a porous tile, and then dry ten to fifteen minutes at 50°–60° in the dark. Determine the melting-point at once.

Acetophenonephenylhydrazone is a rather unstable body, and is liable to undergo slight decomposition in drying. According to Reisenegger and Just, the pure compound melts at 105°. As obtained in this test it is perhaps not perfectly pure, as it shows signs of softening at 100°, and is completely melted at 103°.

713. Benzoïn. (Properties tabulated on p. 139.)

Place in a dry test-tube 0.05 grm. of the compound and 0.4 cc. of acetyl chloride. Add one drop of concentrated hydrochloric acid. Allow to stand two or three minutes, until the vigorous action that will occur ceases. Then heat very gently over a small flame until everything is dissolved, removing the tube from time to time to prevent overheating. Cool with running water for 5–10 seconds. Add 2.5 cc. of strong alcohol, and then 5 cc.

of cold water. Cool well, and shake until the precipitate has separated sufficiently to leave the mother-liquor nearly clear. Filter. Wash with 2 cc. of cold dilute alcohol (1 : 2). Heat to boiling with 9 cc. of dilute alcohol (1 : 2). Boil briskly for 10–15 seconds, and filter hot from any undissolved residue. Cool and shake as before. Filter. Wash with 2 cc. of cold dilute alcohol (1 : 2). Remove mother-liquor by pressing on a piece of porous tile. Dry in the air on a fresh piece of porous tile for 20–30 minutes.

The product in this test is *acetylbenzoïn*, crystallizing in small white needles and melting at 79.5–80.5 (uncor.).

714. Benzophenone. (Properties tabulated on p. 137.)

Convert 0.05 grm. into benzophenoneoxime, following the regular procedure of Generic Test VII–1, except that the period of heating should be extended to ten minutes. After the precipitation of the oxime with acid, collect in the point of a small filter, and wash thoroughly with 10–15 cc. of cold water applied in small successive portions. Dry for half an hour at 100° on a piece of porous tile, and determine the melting-point.

Benzophenoneoxime is obtained in this test as a flocculent white precipitate soluble in acids or caustic alkalies, and melting at 141°–142° (uncor.).

715. Camphor. (Properties tabulated on p. 139.)

Convert into camphor oxime by the method of Generic Test VII–1, using twice the specified quantities of substance, hydroxylamine-hydrochloride solution, and caustic-soda solution, and boiling for one hour instead of for five minutes. In all other details follow the general directions literally. After the precipitation of the oxime following the neutralization with acid, collect on a very small filter, and wash with at least 10 cc. of cold water applied in small portions, the filter being allowed to drain after each addition. Transfer the washed precipitate from the point of the filter to a piece of porous tile. Dry at about 50°, and determine the melting-point.

Camphor oxime as obtained by the foregoing method is a white, indistinctly crystalline powder melting at 118°–119° (uncor.).

CHAPTER X.

GENUS VIII. ALCOHOLS

OF

SUBORDER I, ORDER I.

(Colorless Compounds of Carbon, Hydrogen, and Oxygen.)

Genus VIII embraces all species of the suborder that contain the hydroxyl radical and have not been described in the foregoing genera. The few ketones that do not react readily with hydroxylamine or phenylhydrazine, but meet the requirements of Test VIII for alcohols, also receive mention in this section of the tables.

GENERIC TEST VIII.

IF THE COMPOUND UNDER EXAMINATION IS SOLUBLE IN LESS THAN FIFTY PARTS OF COLD WATER, SEE PROCEDURE 1 BELOW, THE APPLICATION OF PROCEDURES 2 AND 3 BEING UNNECESSARY. IF IT DOES NOT DISSOLVE IN FIFTY PARTS OF COLD WATER AND IS A LIQUID AT THE TEMPERATURE OF 75°, APPLY PROCEDURE 2 ONLY. IF IT IS NOT SOLUBLE IN FIFTY PARTS OF COLD WATER AND IS SOLID AT OR BELOW 75°, SEE PROCEDURE 3.

PROCEDURE 1.

(The Test by Solubility.)

If the solubility of the compound in cold water is not already known, determine it approximately by the method given on p. 38.

Any compound, either solid or liquid, that has failed to give the earlier generic tests, and which is completely dissolved by fifty parts of water at 20°, can not be a hydrocarbon, and should be looked for among the species of Genus VIII.

PROCEDURE 2.

(The Test with Sodium.)

If the compound is not soluble in fifty parts of cold water and is a liquid at temperatures below 75°, place about five drops in a narrow glass "weighing-tube" (internal diameter 5-6 mm., length 75 mm.) that has been carefully dried out just before use. Support the tube in a vertical position by thrusting it through a perforated cork held in a clamp. Place a piece of clean sodium, from which the crust has been removed, in a small porcelain dish containing a clear dry hydrocarbon oil. Grasping the sodium under the oil with crucible tongs or forceps, cut out a bright bit of the metal, about half as large as a grain of wheat (.01-.02 grm.), by the aid of a penknife. Seize the fragment with the forceps. Touch it quickly to a piece of dry filter-paper to remove most of the adhering oil; and then, without delay, drop it into the liquid in the weighing-tube. Allow to stand at the temperature of the laboratory for two minutes, and observe any disengagement of gas, or change in appearance of the metal.

At the end of this time, if the sodium has not disappeared, lower the clamp holding the tube so as to immerse the end of the latter in clear paraffin oil, the sulphuric acid mixture described on page 218, or any other anhydrous non-volatile liquid, previously heated to 75°, and contained in a beaker supported on a lamp-stand.* Continue the heating with the bath at 75° for about five minutes, carefully watching for the disengagement of gas, and for the disappearance of the sodium, or the formation of any incrustation or coloration on its surface. [The test at 75° will be omitted in the case of compounds that boil below this temperature.]

If a brisk effervescence, which continues well sustained until the sodium is either dissolved or the contents of the tube are changed to a thick paste, takes place in either part of this test, the compound is an alcohol. If the evolution of gas is rather slow, but is nevertheless well sustained after the first minute—especially if the bubbles approach the size of a small pin-head, or if the sodium shows signs of being more than superficially attacked—the compound is very likely to be found described with the alcohols.

If there is no effervescence, and the sodium remains unattacked during both parts of the test, the compound is not an alcohol. The same conclusion is usually to be drawn whenever there is a very scanty gas evolution which diminishes perceptibly after a minute or two—especially if the bubbles (which may be quite numerous) are nearly all microscopic in size. [For remarks on the interpretation of doubtful cases, read the "observations" on this test on page 154.]

PROCEDURE 3.

(The Test by Acetylation.)

As the test by acetylation is rather long, and is often not indispensable, it is well to precede its application by an examination of the descriptions of species having the proper melting-point both in Genus IX, Div. A, and in Genus VIII, Div. A, Sec. 3. If this does not lead to an identification, the employment of the acetylation test which follows will sometimes become desirable.

Weigh out accurately in a dry, thick-walled, six-inch test-tube, standing upright in the metal support usually furnished with analytical balances for such uses, 0.1000 to 0.1100 grm. of the unknown compound. A soft, sound, tight-fitting cork stopper

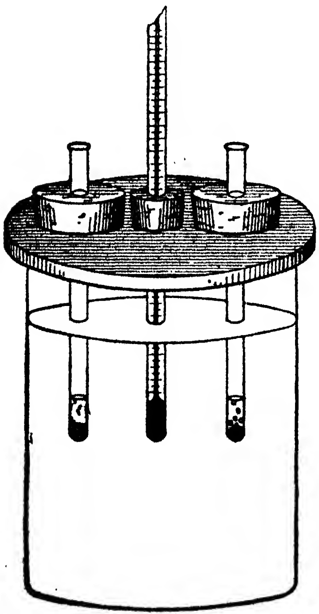

FIG. 4.

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* Fig. 4 represents a convenient form of bath for general use in heating small tubes to definite temperatures in Tests V-1, VII-1, and some of the numbered specific tests, as well as in the present procedure. The beaker has a height of 10 cm. and a diameter of 7.5 cm. The cover is best made from brass, or may be constructed from tinned iron or wood. Its three perforations are fitted with cork stoppers to bear the tubes and a thermometer. The diameters of the two larger perforations should be 23 to 25 mm. The cover, besides supporting the tubes, protects their upper portions from the radiated heat of the bath—which in some tests is a considerable advantage—and excludes dust when the bath is laid aside between experiments.

should be provided for the tube, and weighed with it. The substance having been weighed, drop in upon it—best from a safety pipette especially reserved for the purpose (cf. page 236)—0.40 cc. of good acetic anhydride, taking care not to allow the anhydride to wet the upper part of the tube, and ascertain the exact weight of the anhydride by weighing again. Next remove the cork, which must be inserted during the weighings, and hold the lower part of it, which will come within the test-tube, in clean hard paraffin that has been melted and heated to above 100° in a small porcelain evaporating-dish. The immersion in the hot paraffin should be continued for about half a minute, or long enough to bring about the expulsion of all the small air-bubbles that are seen to detach themselves from the cork as the hot paraffin penetrates and fills the minute cavities in its surface. By a quick movement shake off most of the excess of paraffin, and then quickly insert the cork in the test-tube; press it firmly into place; and hold it until the wax hardens.

Next thrust the tube through a circular hole cut by a brass cork-borer in a square piece of asbestos-board, and place the latter like a cover on a small beaker, so that the lower end of the test-tube shall be 1 cm. below the surface of the hot liquid bath within. The beaker is filled to within 2 cc. of its lip with paraffin- or cottonseed-oil, glycerine, concentrated sulphuric acid, melted paraffin, or some other stable liquid of high boiling-point, which has previously been brought to a nearly constant temperature of between 95° and 105° by heating with a very small flame. Or, if such an apparatus is at hand, heat the tube in the covered bath shown in Fig. 4 on page 152. Continue the heating at this temperature for fifteen minutes. Then remove the tube from the bath; cool; unstopper; and add 10 cc. of normal aqueous sodium-hydroxide solution from an accurately calibrated 10-cc. pipette. Reinsert the stopper firmly, and shake well, *cooling with running water from time to time if the mixture tends to become warm.* Again remove the stopper and wash it with distilled water, collecting the washings in a 75-cc. beaker. If the undissolved reaction product is solid or pasty, it may enclose unneutralized acetic anhydride. Hence the lumps must now be well crushed and churned up, while still in contact with an excess of alkali, by means of a glass rod with a flattened end. Then, rinse the mixture into the beaker containing the washings from the stopper, and titrate the free alkali with *decinormal* hydrochloric or sulphuric acid, using phenolphthaleïn as the indicator.

Finally, calculate from the data obtained how many milligrams of the acetic anhydride heated with the substance have combined with it to form a neutral acetate. *If the loss of anhydride due to this cause ("acetylation") exceeds* 6 *mgrms. when* 0.1000 to 0.1100 *grm. of substance was weighed out for the experiment, the compound is probably an alcohol, and should be sought in Genus VIII.* If the loss of anhydride is less than 6 mgrm., it is probably not an alcohol, but may be a species described in Genus IX. The calculation of the weight *in milligrams* of the anhydride consumed in acetylation will be facilitated by substituting the proper quantities in the following formula:

Wt. in milligrams of anhydride consumed $= a-[51.b(d-e)]$.

In this formula:

a=mgrm. pure anhydride* weighed out (i.e. apparent wt.×percentage purity).

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* A 100-cc. bottle of an anhydride whose percentage purity has been determined by careful titration should be specially reserved for these tests. The reagent will always contain traces

b = the exact normality of the approximately decinormal acid.
c = " " " " " " normal alkali.
d = cc. of above acid equivalent to 10 cc. of above alkali.*
e = cc. " " " required to neutralize alkali remaining uncombined (from 10 cc. portion) after shaking with products of acetylation experiment.

Observations on Generic Test VIII.

"*The Test by Solubility* (1)" requires no special comment.

In "*The Test with Sodium* (2)" the correct interpretation of the phenomena requires good judgment and some experience on the part of the observer. Very few commercial specimens of compounds of Genus IX are so free from traces of moisture as to give off no gas at all. The ability to make the right decision is most quickly gained by examining the behavior of a few representative compounds. Heat is employed in the second part of the test, partly to increase the number of species to which it is applicable, and partly to make the result more decisive when the alcohol is one that is attacked slowly in the cold. The temperature of 75° is one at which it is not known that any species of Genus IX is decomposed by sodium. At a much higher temperature, however, sodium attacks some of the hydrocarbons (e.g. melted anthracene) with considerable violence. Whenever the sodium test proves inconclusive, it may be supplemented by Procedure 3.

"*The Test by Acetylation* (3)," although requiring careful manipulation, will give no trouble if directions are closely followed. But if the cork stopper is not protected by paraffin, or if the test-tube is heated on a rapidly boiling water-bath so that the paraffin softens, or if a rubber stopper is used, the results will be worthless. The average accidental loss of acetic anhydride in a properly conducted experiment is a little less than 1 mgrm. Heating with the anhydride at 100° for fifteen minutes as recommended in the regular procedure is insufficient to completely acetylate many of the solid alcohols; but it appears that most monatomic alcohols whose acetates are insoluble in cold water will be found to combine with very nearly the theoretical quantity of anhydride if the heating is prolonged to thirty minutes.

Procedure 3 is not applicable to soluble polyatomic alcohols of Div. A Sec. 1, because they usually give soluble acetates which are rapidly saponified upon shaking with cold normal alkali. No more acetic anhydride is found to disappear in an acetylation experiment with ethylene glycol or erythrite, for instance than in a blank test.

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of acetic acid, but it will be allowable, for the present purpose to base the calculation of the percentage purity on the assumption that all alkali consumed in the titration is neutralized by anhydride only. On account of its peculiar action on phenolphthalein, in titrating acetic anhydride, always dissolve it first in an excess of alkali, and *then* add the indicator and titrate back with acid.

* $d = 10\frac{c}{b}$. Calculations will be simplified by recording the numerical value of d on the label of the alkali bottle.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I.

GENUS VIII, ALCOHOLS.

DIVISION A, SECTION 1,—SOLID ALCOHOLS SOLUBLE IN LESS THAN 50 PARTS OF COLD WATER.

[Containing all soluble solid species of the suborder not described in the preceding genera.]

Melting-point (C.°).	**SOLID ALCOHOLS.**—Colorless and soluble in less than 50 parts of cold water.
35–8	† **Pinacone, $Me_2.C(OH).C(OH).Me_2$.**—B. p. 172°–3°.—Clear cryst. w. faint peculiar odor.—S. c. aq.; e. s. h. aq. or c. alc.—Boiled w. dil. H_2SO_4 gives a very strong peppermint-like odor of pinacoline!—The hot aq. sol. on cooling deposits a hydrate, m. p. 56°.
46–7	**m-Tolylene Alc., $C_6H_4.(CH_2.OH)_2$.**—V. s. aq.; s. eth.—Oxidation gives isophthalic ac (Tests 905 and 318–2).
49·5	**(a)-Dimethylpinacone, Et.C(OH)(Me).C(OH)(Me).Et.**—Fairly s. aq.; e. s. alc. or eth.
51·5	**Diisopropyl Glycol, Pr.CH(OH).CH(OH)Pr.**—B. p. 222°–3°.—E. s. alc., or eth.—Combines w. $CaCl_2$.
52–3	**tert.-Butylcarbinol, $Me_3.C.CH_2.OH$.**—B. p. 112°–3°!—Odor camphorous.—"Somewhat" s. aq.—Test 702 gives trimethylacetic ac.—Very volatile.
52–3	**Methylphenylethylene Glycol, Me.CH(OH).CH(OH).Ph.**—E. s. aq., alc., or eth.—Tends to separate oily fr. solutions.
56	**Pinacone Hydrate, $C_6H_{14}O_2.6H_2O$.**—4-sided tbl.—Sbl. at ord. temperature.—Loses aq. over H_2SO_4, or on dist., giving pinacone.—E. s. h. aq.
64	**Phthalic Alc., o-$C_6H_4.(CH_2.OH)_2$.**—Tbl. fr. eth.—V. s. aq., alc., or eth.—Conc. H_2SO_4 resinifies.—Test 905 gives phthalic ac.
67–8	**Styrolene Alc., $Ph.CH(OH).CH_2.OH$.**—B. p. 273° (th. i.).—V. s. aq., alc., or eth.—Oxid. by Test 702 to benzoic ac. (Test 312).—65% H_2SO_4 gives hydrocarbon, $C_{16}H_{12}$.
87	**Isomannide, $C_6H_{10}O_4$.**—B. p. 274° d.—Hygroscopic cryst., v. s. aq ; s. alc.; i. eth.—Warmed w. 2 pt. PCl_5 gives chloride, m. p. 49°.
102	[−] **Arabite, $C_5H_7.(OH)_5$.**—Warty masses, v. s. aq. or h. 90% alc.—Does not reduce Fehling's sol.—Aq. sol. + borax weakly opt. act. [−].
112–13	**p-Tolylene Alc., $C_6H_4.(CH_2.OH)_2$.**—Ndl., v. s. aq., alc., or eth.—Oxid. by Test 702 gives terephthalic ac. (Test 318–3).
121	**Rhamnite, $Me.(CH.OH)_4.CH_2.OH$.**—Triclinic pr. fr. alc.—Opt. active.—V. s. aq. or alc.; alm. *i. eth.*
126	† **Erythrite, $C_4H_6.(OH)_4$.**—B. p. 330°.—Clear cryst.—Taste sweet.—V. s. aq.; d. s. alc.; i. eth.—Does not reduce Fehling's sol —The aq. sol. dissolves CaO in the cold. The sol. coagulates on boiling.—Schotten-Baumann reaction gives tetrabenzoate, mic. cryst. fr. Āc, m. p. 186·5°–7°.
150	**Pinolhydrate, $C_{10}H_{18}O_2$.**—B. p. 270°–1°.—S. in 30 pt. aq. at 15°; e. s. alc. or *eth.!* Br_2 dropped into cooled 5% $CHCl_3$ sol. gives cryst. dibromide, d. s. $CHCl_3$, m. p. 131°–2°.—Warmed w. dil. H_2SO_4 gives oily pinol, b. p. 183°–4°.
163–4	[−] **Mannite, $C_6H_8.(OH)_6$.**—Ndl., v. s. aq.; d. s. absolute alc.—Aq. sol. + borax is strongly [−].
166	† [+] **Mannite, $C_6H_8.(OH)_6$.**—Taste sweet.—Ndl., s. in 6·4 pt. aq. at 18°; v. d. s. abs. alc.; i. eth.—Aq. sol. + borax is strongly [+]; alone is opt. i.—Prevents ppt. of Fe_2O_3 fr. $FeCl_3$ by NaOH.—Oxid. by HNO_3 (cf. Test 205) gives no mucic ac. (dif. fr. dulcite).—Sbl. slowly when kept for some time at temperature somewhat above m. p.—1.8 pt. mannite dissolved in 3.6 pt. conc' HCl and shaken with 3.2 pt. benzaldehyde gives cryst. ppt. of mannitetribenzacetol, m. p. 207°; v. d. s. aq.; s. eth.!

Melting-point (C.°).	**SOLID ALCOHOLS.**—Colorless and soluble in less than 50 parts of cold water.
168	**i.-Mannite, $C_6H_8.(OH)_6$.**—Plates v. s. h. aq.; v. d. s. abs. alc.—Aq. sol. + borax is optically i.
173	**Rhamnohexite, Me.(CH.OH)$_5$.CH_2.OH.**—Pr., e. s. aq.; s. h. alc.—Opt. act. [+].
184–5	**1, 3, 5-Cyclohexantriol (Phloroglucite), $C_6H_9.(OH)_3$.**—Cryst. fr. aq. Faint but pure sweet taste. (Cryst. w. aq. which is easily expelled at 100°.)—E. s. aq. or alc.; i. eth.
188c.	[+ or −] **Perseïte, $C_7H_{16}O_7$.**—Ndl., s. 18 pt. aq. at 18°; d. s. c. alc.—Aq. sol. opt. i.—Does not reduce Fehling's solution.
188·5	**Dulcite $C_6H_8.(OH)_6$.**—Nearly tasteless.—Cryst. s. in about 25 pt. c. aq.; e. s. h. aq.; alm. i. alc. or eth.—Oxid. by HNO_3 (cf. Test 205) yields some mucic ac. !—Opt. i. even after addition of borax to sol.—Reactions similar to those of mannite.
203c.	**rac.-Perseïte, $C_7H_9.(OH)_7$.**—Cf. [+ or −] compound, m. p. 188° c.
225c.	**Inosite, $C_6H_6.(OH)_6$.**—Taste sweet.—Efflorescent cryst. w. $2H_2O$ fr. cold aq.; cryst. fr. aq. above 50° anhydrous.—S. in 5·7 pt. aq. at 24°; i. abs. alc. or eth.—Opt. i.—"A bit of inosite evaporated to dryness w. a little dil. HNO_3 on a crucible cover gives a reddish-colored mass when treated w. a little ammonia and $CaCl_2$ and again evaporated."
234 or 225 (?)	[+] **Quercite, $C_6H_7.(OH)_5$.**—Crvst. s. in 8–10 pt. c. aq.; d. s. alc.; i. eth. Boiled w. dil. H_2SO_4 and MnO_2 gives pungent quinone odor.—Oxid. by HNO_3 gives oxalic ac., but no mucic ac. (cf. Test 205).
253	**Pentaerythrite, C.$(CH_2.OH)_4$.**—Tetragonal cryst. s. 18 pt. aq. at 15°.—Opt. i.—Oxid. by dil. HNO_3 to glycollic and oxalic acids.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I]

GENUS VIII, ALCOHOLS.

DIVISION A, SECTION 2,—SOLID ALCOHOLS NOT SOLUBLE IN 50 PARTS OF COLD WATER.

Melting-point (C.°).	Boiling-point (C.°).	**SOLID ALCOHOLS.**—Not soluble in 50 parts of cold water.
24	143·5(15 mm.)	**Dodecyl Alc., $C_{12}H_{25}.OH$.**—Silvery lft. fr. dil. alc.
27–8		**s-Tetramethylpinacone, $Et_2.C(OH).C(OH).Et_2$.** — Alm. i. aq.; v. s. alc. or eth.
33	254	† **Cinnamyl Alc., $Ph.CH:CH.CH_2.OH$.** — Aromatic hyacinth-like odor —D. s. aq.; v. s. alc or eth. Dropping Br in cold $CHCl_3$ solution gives bromide, m. p. 74°; i. aq.; e. s. alc. or eth.
34	223 (th. i.)	**o-Tolylcarbinol, $Me.C_6H_4.CH_2.OH$.**—S. 100 pt. c. aq.; e. s. alc. or eth.
35	218	**Terpineol, $C_{10}H_{17}.OH$.**—Cf. Div. B, 2, b. p. 218°.—Lilac odor!
38	167(15 mm.)	**Tetradecyl Alc., $C_{14}H_{29}.OH$.**
41–2		**Dihexylcarbinol, $(C_6H_{13})_2.CH.OH$.**—V. s. $CHCl_3$ or bz.
42	210	† **[−]-Menthol, $C_{10}H_{19}.OH$.** — Cryst. w. strong peppermint odor!—D. s. aq.; e. s. alc, eth., or conc. HCl.—May be identified by conversion into its benzoate of m. p. 54·5°. (Cf. Beckmann, A, 262, 31.)
42	dist.	**Phenylbenzylcarbinol, $Ph.CH_2.CH(OH).Ph$.**—Boiling w. 20% H_2SO_4 gives stilbene.
45	258·8	**Anisic Alc., p-$MeO.C_6H_4.CH_2.OH$.**—Conc. H_2SO_4 gives a reddish resin.—Oxid. by dil. HNO_3 gives anisic ac.
50	344	† **Cetyl Alc., $C_{16}H_{34}O$.**—Cryst. in small lft. fr alc.—(**When** fused gives off H easily in Test VIII-2.)
51		**Piperonyl Alc., $CH_2O_2.C_6H_3.CH_2.OH$.**—Dec. on dist. w. formation of piperonal (heliotrope odor)!—Long cryst. not vol. w. st —D. s. c. aq.; v. s alc. or eth.
52–3		**p-Phenyltolylcarbinol, $Me.C_6H_4.CH(OH).Ph$.**—Silky ndl.
52–3		**tert.-Butylcarbinol.**—Cf. Sec. A. ("Somewhat s. aq.")
54–4·5	220d.	**α-Oxyhydrindene, $C_9H_9.OH$.**—Naphthalene-like odor.
59	210·5(15 mm.)	**Octadecyl Alc., $C_{18}H_{37}.OH$.**—Silvery lft. fr. alc.
59	217	**p-Tolylcarbinol, $Me.C_6H_4.CH_2.OH$.**—D. s. c. aq.; e. s. alc. or eth.
60	303c.	**α-Naphthylmethyl Alc., $C_{10}H_7.CH_2.OH$.**—Ndl., somewhat s. aq.; v. s. alc or eth.
67·5–8	297–8	**Benzhydrol, $Ph_2.CH.OH$.**—Silky ndl., s. in 2000 pt. c. aq.; v. s. alc or eth.—Easily oxid. in Test 702, giving benzophenone (Test 714).
68–9		**Carnaubyl Alc., $C_{24}H_{49}.OH$.**—CrO_3 gives carnaubic ac.—Fr. dil. alc. cryst w 73·3% aq.
69		**Ditolylcarbinol, $(C_7H_7)_2.CH.OH$.**—I. aq.; v. s. alc.
75	220(15 mm.)	**Cetene Glycol, $C_{16}H_{32}.(OH)_2$.**—I aq.—Cryst fr h. alc
75–6		**Dilauryl Alc., $(C_{11}H_{23})_2.CH.OH$.**—Tbl. fr eth.
79		**Ceryl Alc., $C_{27}H_{55}.OH$.**—S. alc —Heated w. soda-lime gives cerotic ac

Melting-point (C.°).	Boiling-point (C.°).	**SOLID ALCOHOLS.**—Not soluble in 50 parts of cold water.
80–0·5		**β-Naphthylmethyl Alc., $C_{10}H_7.CH_2.OH$.**—Lft. e. vol. w. st.—V. d. s. c. aq; e. s alc. or eth.
82		**Cerosine, $C_{24}H_{48}O$.**—Lft. i. c. alc.; d. s. h. eth.; alm. i. c. eth.
84–5		**Dipalmitylcarbinol, $(C_{15}H_{31})_2.CH.OH$.**—Silky cryst. fr. alc.
85		**Myricyl Alc., $C_{30}H_{61}.OH$** (fr. carnauba wax).—Small ndl· fr. eth.—W. soda-lime at 200° gives melissic ac.
90		**Methyl-p-tolylpinacone, $C_{18}H_{20}.(OH)_2$.**—Sbl.—Hexagonal tbl. fr. alc.; i. aq., v. s. alc. or eth.
101–4		**Coccerylic Alc., $C_{30}H_{62}O_2$.**—Cryst. powder fr. alc.—Oxid. by CrO_3 in Āc sol. gives pentadecylic ac.—(Fr. cochineal.)
119·5		**Isohydrobenzoïn, $C_{14}H_{12}.(OH)_2$.**—Cryst. fr. aq.; efflorescent.—S. in 526 pt. aq. at 15°, or 820 pt. at 100°; e. s. alc. or eth.—Oxid. by Test 702 gives benzoic ac.—Diacetate (fr. acetyl chloride), lft. fr. h. alc.; m. p. 117°–18°.
120		**Acetophenonepinacone, $(Ph.C(OH).Me)_2$.**—Ndl., i. aq.; e. s. alc. or eth.—In tube at 280° gives acetophenone and methylphenylcarbinol.—Acetic anhyd. gives a hydrocarbon, $C_{16}H_{14}$.
125		**Quebrachol, $C_{20}H_{33}.OH$.** — Lft. fr. alc.—Cryst. also w. x H_2O (easily lost).—I. c. aq. or alkalies; v. s. eth., bz., or acetone.—A sol. in $CHCl_3$ shaken w. equal vol. of H_2SO_4 (sp. gr. 1·76) becomes purple-red after 5 minutes.
132–3		**Phytosterine, $C_{26}H_{43}.OH$.** — (In peas, beans, etc.) — From $CHCl_3$ or eth. in ndl.; cryst. fr. dil. alc. w. $1H_2O$.—S. in 6·65 pt. eth. at 20°.—Color reactions w. H_2SO_4 same as for cholesterine. (Cf. m. p. 148·5°.)—Acetate, lft. fr. alc., m. p. 120°.
133–4		**Retenefluorene Alc., $C_{17}H_{17}.OH$.** — Silky ndl., fr. alc. — Alm. i. aq.; e. s. alc.—Oxid. gives retene ketone.—Acetate, m. p. 70°–1.
134–4·5		**Paracholesterine, $C_{26}M_{43}.OH$.**—(In Aethalium septicum.)—Cryst. w. aq. fr. dil. alc.; silky ndl. fr. eth. or $CHCl_3$; i. aq.—Gives same color reactions as cholesterine w. H_2SO_4 in $CHCl_3$ sol.
137–8		**Isocholesterine, $C_{26}H_{43}.OH$.**—(In suint.)—Gelatinous flocks fr. alc., d. s. c. alc.; e. s. h. alc. or eth.—Does not give the cholesterine reaction w. H_2SO_4 and $CHCl_3$, but gives a brown color.—When evaporated w. a few drops of conc. HNO_3 leaves yellow spot which becomes yellow-red w. ammonia.
138		**Hydrobenzoïn, Ph.CH(OH).CH(OH)Ph.**—B. p. a. 300°.—Adamantine lft. fr. dil. alc.; s. in 400 pt. c., or 80 pt. h. aq.; e. s. h. alc.—Oxid. by CrO_3 gives benzaldehyde.—E. acted upon by PCl_5 in cold.—Heated w. acetyl chloride or anhydride gives diacetate, pr. fr. eth., d. s. c. alc., m. p. 134°.
139		**Cholestol, $C_{22}H_{38}O$.** — Ndl. — Dist. — With $CHCl_3$ or acetic anhyd. and H_2SO_4 gives the same colors as cholesterine.
140		**Cupreol, $C_{20}H_{33}.OH$.**—(In cinchona barks.)—Cryst. w. aq. which is lost in desiccator.—I. aq.; e. s. eth.—$CHCl_3$ sol. shaken w. H_2SO_4 (sp. gr. 1·76) gives blood-red color.—Opt. active [–].
148·5c.		† **Cholesterine, $C_{26}H_{43}.OH.[+H_2O$, lost over $H_2SO_4]$.**—Dist. in vacuo above 360°—S. in 5 pt. h. alc.; e. s. eth. or CS_2.—Dissolve a few cgrms. in 2 cc. chloroform and shake w. 2 cc. H_2SO_4 (sp. gr 1·76). The $CHCl_3$ becomes blood-red, cherry-red, and finally a beautiful purple color w. strong green fluorescence in the acid layer. The $CHCl_3$ poured into a dish soon changes through blue and green to a dirty yellow!—This color reaction is also given by several other alcohols standing near cholesterine in this section.—Identify by Test 821!

Melting-point (C.°).	Boiling-point (C.°).	**SOLID ALCOHOLS.**—Not soluble in 50 parts of cold water.
149–50		**Paraphytosterine, $C_{24}H_{39}.OH$.**—D. s. c. alc.; e. s. eth. or $CHCl_3$.
150		**Diphenyltolylcarbinol, $Me.C_6H_4.C(OH).Ph_2$.**—Hexagonal tbl. fr. lgr.—E. s. alc. or eth.; less s. lgr.—Dist. undec.
153		**Fluorene Alc., $C_{13}H_9.OH$.**—S. alc., eth., or bz.—W. conc. H_2SO_4 turns blue!—Oxid. by Test 702 gives diphenylene ketone.
154		**Ergosterine, $C_{26}H_{39}.OH.+H_2O$** (from Ergot).—B. p. 185° (20 mm.).—Pearly lft. fr. alc.—S. in 500 pt. c. or 32 pt. h. 94% alc.; s. h. eth. or c. $CHCl_3$.—Sol. in conc. H_2SO_4 is orange-red, becoming red and then violet on addition of aq. The orange sol. when shaken w. $CHCl_3$ does not color the latter. (Dif. fr. cholesterine.)
162		† **Triphenylcarbinol, $Ph_3.C.OH$.**—B. p. a. 360° undec.—E. s. alc., eth., or bz.—Stable.
164–5		**Phenyltolylpinacone, $C_{28}H_{24}.(OH)_2$.**—E. s. bz.; d. s. alc.; s. eth.—E. oxid. by CrO_3 giving phenyltolyl ketone.—Decomposed by heating with acids.
166–7		**Chrysofluorene Alc., $C_{16}H_{10}.CH.OH$.**—E. s. alc. or eth.—S. conc. H_2SO_4 w. red-violet color.—Alc. sol. on addition of conc. H_2SO_4 becomes blue.
168d.		**Benzopinacone, $Ph_2.C(OH).C(OH)Ph_2$.**—S. in 39 pt. h. alc.—In melting splits into benzophenone (Test 714) and diphenylcarbinol.
170		**Hydranisoïn, $C_{16}H_{16}O_2.(OH)_2$.**—V. d. s. c. aq., c. alc., or eth.; e. s. h. alc.—Oxid. by CrO_3 mixture to anisic ald. and anisic ac.
175		**Illicyl Alc., $C_{22}H_{37}OH$.** (fr. bird lime).—B. p. a. 350°.—I. aq.; d. s. c. alc. or eth.—M. p. acetate 204°–6°.
182d.		**Anthrapinacone, $C_{28}H_{20}.(OH)_2$.**—Ndl. fr. bz.
183		**Homocholesterine, $C_{28}H_{48}O$.** (fr. Dalmatian insect powder).—V. s. eth. or $CHCl_3$; d. s. alc.—Gives the cholesterine color reactions.
192 sl. d.		**Camphene Glycol, $C_{10}H_{16}.(OH)_2$.**—Sbl. above 100°.—D. s. h. aq.; v. s. alc. or eth.; d. s. lgr.
203–4		† **[+]-Borneol (Borneo Camphor), $C_{10}H_{17}.OH$.**—B. p. 211°–12°.—Sbl. in lft.—Odor scarcely distinguishable fr. that of common camphor!—E. s. lgr.; v. d. s. aq.; e. s. alc. or eth.—Does not give an oxime. (Dif. fr. ordinary camphor.)
208·8		**[−]-Borneol, $C_{10}H_{17}.OH$.**—Closely resembles the [+] comp.—(Occurs in several natural oils.)
210·5		**i-Borneol, $C_{10}H_{17}.OH$.**—Closely resembles the [+] comp.
216		**Isoborneol, $C_{10}H_{17}.OH$.**—Closely resembles the [+] comp.—Opt. active [+].
258c.		**Betulin, $C_6H_6O_3$** (fr. birch bark).—Ndl. fr. alc.—Sbl. w. dec.—S. in 148 pt. cold, or 23 pt. h. alc.; s. h. eth.; d. s. c. eth.—Heated w. acetic anhyd. gives diacetate, pr. s. eth., m. p. 217°.—Emits odor like morocco leather when strongly heated.

GENUS VIII, ALCOHOLS.

DIVISION B, SECTION 1,—LIQUID ALCOHOLS (AND SOLUBLE ETHERS) WITH SPECIFIC GRAVITY LESS THAN 0·90 AT 20°/4°.

Boiling-point (C.°).	Specific Gravity.	**ALCOHOLS.**—Colorless and liquid, with Specific Gravity less than 0·90 at 20°/4°.
−24		**Methyl Eth., Me_2.O.**—Is absorbed in large quantity by c. conc. H_2SO_4; the sol. on dil. w. aq. evolves the gaseous ether unchanged.
+10·8	0·725(0)	**Methyl Ethyl Eth., Me.O.Et.**—Odor ethereal.
14	0·897(0)	**Ethylene Oxide, C_2H_4O.**—Misc. w. aq.—Aq. sol. reduces Tollen's reagent.—† Gives ppt. of MgO after long standing w. conc. $MgCl_2$ sol.—W. HCl gives chlorhydrine.—W. aq. and Na amalgam gives C_2H_5.OH.
35	$0{\cdot}719^{15}/_{4}$	† **Ethyl Eth., Et_2.O.**—Mobile liq. of ethereal odor; s. in 12 pt. aq. at 17·5°.
35	0·859(0)	**Propylene Oxide, Me.($CH.CH_2$).O.**—S. in 3 vol. aq.; misc. w. alc. or eth.—Heated w. aq. gives propylene glycol.—Heated w. conc. $MgCl_2$ sol. ppts. MgO.—Reduced by aq. and Na amalgam to isopropyl alc.
35·5	$0{\cdot}763^{14\cdot5}/_{17\cdot5}$	**Vinyl Ethyl Eth., C_2H_3O.Et.**—Gives Test 901.—Distil w. dil. H_2SO_4. The distillate gives reactions for acetaldehyde and ethyl alc. (Cf. Tests 111 and 814.)
38·9	0·747(0)	**Methyl Propyl Eth., Me.O.Pr.**
39		**Vinyl Eth., (CH_2:CH)$_2$.O.**—Gives Test 901.—Probably gives some acetaldehyde when dist. w. dil. H_2SO_4.
45·5	$0{\cdot}872^{15}/_{4}$	† **Methylal, CH_2.(OMe)$_2$.**—Described in Genus I.
46	0·77(11)	**Methyl Allyl Eth., Me.O.C_3H_5.**—Gives Test 901.—B. p. dibromide, 185°.
50		**1, 3-Propylene Oxide, ($CH_2.CH_2.CH_2$).O.**—B. p. a. 320°.—Misc. w. aq.—Boiled w. conc. aq. KOH gives polymeric oxides.
51–2	0·831(0)	**Isobutylene Oxide, Me_2.(C.CH_2).O.**—Combines w. aq. w. evol. of heat, giving isobutylene glycol.
54	0·745(0)	**Ethyl Isopropyl Eth., Et.O.C_3H_7.**—Dec. by 1% H_2SO_4 at 150° into its constituent alcohols.
56–7	0·834(0)	**s-Dimethylethylene Oxide, (Me.CH.CHMe):O.**—Unites quickly w. h. aq. to form corresponding glycol.
61–2	0·83(12)	**Methyl Propargyl Eth., Me.O.C_3H_3.**—Gives lemon-yellow gelatinous ppt. w. ammon. $AgNO_3$!
62–3	0·769(20)	**Ethyl Isopropenyl Eth., Et.O.CMe:CH_2.**—Dec. by 1% H_2SO_4 quickly and completely in the cold into acetone and ethyl alc. (Cf. Test 711–1.)
62–3		**Allylene Oxide, Me.(C:CH).O.**—S. aq. but separated fr. sol. by K_2CO_3.—Very stable.
63·6	0·755(0)	**Ethyl Propyl Eth., Et.O.Pr.**
66		**Ethyl Allyl Eth., Et.O.C_3H_5.**—Gives Test 901.—Dec. by heating w. 2% H_2SO_4 to ethyl and allyl alcohols (cf. Tests 814 and 811).
66	$0{\cdot}798^{15}/_{15}$	† **Methyl Alc., Me.OH.**—Misc. w. aq.—Odor alcoholic.—Identify by Test 819!
69c.	0·725(21)	**Isopropyl Eth., (C_3H_7)$_2$O.**

(ORDER I, SUBORDER I.)

Boiling-point (C.°).	Specific Gravity.	**ALCOHOLS.**—Colorless and liquid, with Specific Gravity less than 0·90 at 20°/4°.
78	0·875(0)	**1, 4-Oxypentane, Me.(CH.(CH$_2$)$_3$):O.**—S. in 10 pt. c. aq.; more s. c. than h.; v. s. alc. or eth.—Not attacked by aq. at 200°.—When heated w. a 60% HBr sol. gives $C_5H_{10}Br_2$.
78·4	$0.794^{15\cdot5}/_{15\cdot5}$	† **Ethyl Alc., Et.OH.**—Odor alcoholic.—Misc. w. aq.—Identify by Test 814!
80	$0{\cdot}833^{20}/_4$	**Ethyl Propargyl Eth., Et.O.C$_3$H$_3$.**—Penetrating odor.—D. s. aq.; misc. alc.—Unsat.—Gives yellow ppt. w. ammon. CuCl.—Heated w. 1% H_2SO_4 gives propargyl and ethyl alcohols.
81–2	0·880(0)	**Pentamethylene Oxide, (CH$_2$)$_5$.O.**—Less s. in h. than c. aq.; misc. alc. or eth.—Does not unite w. aq. at 200°.
82·8c.	$0{\cdot}789^{20}/_4$	† **Isopropyl Alc., Me.CH(OH).Me.**—Misc. w. aq.—Test 819–1 gives amber ring.—Test 801 applied in the *cold* to a 1% aq. sol. gives an immediate ppt. of iodoform.—Identify by Test 818!
82·9c.	$0{\cdot}780^{26}/_4$	† **Trimethylcarbinol, Me$_3$.C.OH.** — M. p. 25°. — V. s. aq. — Deliq. — Odor mild alcoholic. — The color produced in Test 819 resembles that given by methyl alc.!—Does not give iodoform in Test 801.
83–4	0·891(0)	**Glycol Dimethyl Eth., C$_2$H$_4$.(OMe)$_2$.**—HI gas gives glycol and methyl iodide.
90·7 (th. i.)	0·744(21)	† **Propyl Eth., Pr$_2$O.**—Gives Test 907.
94·3	0·805(18)	**Allyl Eth., (C$_3$H$_5$)$_2$.O.**—Gives Test 901.
96·6c.	0·871(0)	† **Allyl Alc., CH$_2$:CH.CH$_2$OH.**—Odor very penetrating and mustard-like!—Misc. aq.—Gives Test 901.—Test 819–1 gives a brown ring.—Identify by Test 811!
97·4c.	$0{\cdot}804^{20}/_4$	† **Propyl Alc., Pr.OH.**—Odor mild alcoholic.—Misc. aq.—Test 819–1 gives amber-colored ring.—Identify by Test 820!
99·8	0·827(0)	† **sec.-Butyl Alc., Me.CH(OH).CH$_2$.Me.**—Odor mild alcoholic.—E. s. aq.—1% aq. sol. gives some iodoform in the cold after a few seconds by Test 801.—Test 819–1 gives a pale lemon-yellow ring below a pale rose-red ring.
101·8	0·814(15)	† **Dimethylethylcarbinol, Me$_2$.C(OH).Et.**—Odor mild alcoholic.—Not v. s. aq.—Color given in Test 819–1 is similar to that from methyl alc.—Does not give iodoform in Test 801.
104·5–6	0·874(0)	**1, 5-Oxyhexane, Me.(CH.(CH$_2$)$_4$):O.**—Odor ethereal.—Rather d. s. aq.—Does not unite w. aq. at 230°.—Combines w. HCl to form its chlorhydrine.
106·5	0·817(0)	† **Isobutyl Alc., Me$_2$.CH.CH$_2$.OH.**—Odor alcoholic.—S. in 10·5 pt. aq.—Test 819–1 gives amber-colored ring.—Identify by Test 817!
112·5	0·833(0)	**Methylisopropylcarbinol, Me$_2$.CH.CH.(OH)Me.**—Oxid. by Test 702 w. cold, very dil. CrO$_3$ gives acetone, methylisopropyl ketone, and acetic acid.
114	$0{\cdot}840^{20}/_0$	**Vinylethylcarbinol, CH$_2$:CH.CH(OH).Et.** — Unsat. (Cf. Test 901.)
115–16	$0{\cdot}834^{20}/_0$	**Methylallylcarbinol, CH$_2$:CH.CH$_2$.CH(OH).Me.**—S. in 8 pt. aq.—Oxid. by KMnO$_4$ gives γ-pentenylglycerine.
116·5	0·832(0)	**Diethylcarbinol, Et$_2$.CH.OH.**
117	0·873(0)	**Crotyl Alc., Me.CH:CH.CH$_2$.OH.**—See Test 901.
117c.	$0{\cdot}810^{20}/_4$	† **Butyl Alc., C$_4$H$_9$.OH.**—Odor alcoholic.—S. in 12 pt. aq.—Identify by Test 813!
117·6	0·839(0)	**Dimethylisopropylcarbinol, Me$_2$.(C$_3$H$_7$)C.OH.** — Camphorous odor.
118·5	0·824(0)	**Methylpropylcarbinol, Me.CH(OH).Pr.**—S. in 6 vol. aq.—Is said to give iodoform in Test 801.

Boiling-point (C.°).	Specific Gravity.	**ALCOHOLS.**—Colorless and liquid, with Specific Gravity less than 0·90 at 20°/4°.
119·5	0·844(0)	**Dimethylallylcarbinol, $Me_2.C(OH).C_3H_5$.**—Oxid. by Test 702 gives acetone (Test 711), formic ac., etc.
120–1	0·835(0)	**Pinacoline Alc., $Me_3.C.CH(OH).Me$.**—M. p. 4°.—Silky ndl. w. camphorous odor.
123c.	0·824(20)	**Methyldiethylcarbinol, $Me.C(OH).Et_2$.**—Test 702 gives acetic ac. (Test 311).
123		**Dimethylpropylcarbinol, $Me_2.(Pr).C.OH$.**—Test 702 gives acetic and propionic acids.
123·5	0·863(0)	**Glycol Diethyl Eth., $C_2H_4.(OEt)_2$.**
128	0·838(0)	**Ethylisopropylcarbinol, Et.CH(OH).Pr.**
128·7	0·833$^{0}/_{4}$	**act. Amyl Alc., $Me(Et)CH.CH_2.OH$.**—Test 702 gives valerianic and acetic acids.
130		**Dimethylisobutylcarbinol, $Me_2.C(OH).C_4H_9$.** — V. d. s. aq. — Test 702 gives acetic and isobutyric acids (Test 311).
130	0·810$^{20}/_{4}$	† **Isoamyl Alc., $Me_2.CH.(CH_2)_2.OH$.**—Odor disagreeable, provoking coughing.—S. in 30·4 pt. aq. at 22°.—Burns w. smoky flame.—A few drops warmed w. x's of CrO_3 mixture gives at first the sweetish and fruity odor of valerianic aldehyde, soon followed by the unpleasant odor of isovalerianic ac.!—Warmed w. 1½ pt. conc. H_2SO_4 gives a red sol.
130–1	0·827(0)	**Methylisobutylcarbinol, Me.CH(OH).Bu.**
131		**2, 3, 3-Trimethylbutanol(2), $Me_3.C.CMe_2.OH$.**—Odor camphorous.—M. p. 17°.—Hygroscopic, giving a hydrate, m. p. 83°.
134	0·868(18)	**α-Ethylallyl Alc., $Et.C_3H_4.OH$.**—Unsat. (Cf. Test 901.)
135c.	0·834(0)	**Ethylpropylcarbinol, Et.CH(OH).Pr.**
136	0·833(0)	**Methylbutylcarbinol, Me.CH(OH).Bu.**—Oxid. by Test 702 gives acetic and butyric ac.
137		**Hexenyl Alc., $C_6H_{12}O$.**—Odor pungent and peppermint-like.—E. s. c. aq.
137·8 (th. i.)	0·828(0)	**Amyl Alc., $C_5H_{11}.OH$.**—I. aq.—Test 702 gives valerianic ac. (very unpleasant odor).
138–9	0·842$^{16}/_{17}$	**Methylcrotylcarbinol, $Me.CH(OH).C_4H_7$.**—D. s. aq.—Unsat. (Cf. Test 901.)
140	0·829$^{20}/_{4}$	**Diisopropylcarbinol, $(C_3H_7)_2.CH.OH$.**—Oxid. by Test 702 gives diisopropylketone, isobutyric ac., and acetone.
140·3c.	0·823$^{20}/_{0}$	**Methylethylpropylcarbinol, (Me)(Et)(Pr).C.OH.**—Test 702 gives acetic and propionic acids.
140–2	0·840(20)	**Triethylcarbinol, $Et_3.C.OH$.**—Test 702 gives acetic and propionic acids and diethyl ketone.
147	0·838(0)	**Methylpropylcarbincarbinol, $(Me)(Pr).CH.CH_2.OH$.**—Test 702 gives methylpropylacetic ac. and methyl propyl ketone.
147–8		**Ethylisobutylcarbinol Et(Bu).CH.OH.**—Test 702 gives acetic and isovalerianic acids, etc.
148–50	0·819(17·5)	**Methylisoamylcarbinol, $(Me)(C_5H_{11}).CH.OH$.**—Odor like fusel oil.—Oxid. by Test 702 gives methyl isoamyl ketone, isovalerianic ac., etc.
150		**Isohexyl Alc., $Me_2.CH.(CH_2)_3.OH$.**
151c.	0·876(0)	**Diallylcarbinol, $(C_3H_5)_2.CH.OH$.**—Alm. i. aq.—Test 702 gives CO_2 and some formic ac.
154 (th. i.)	0·830(15)	**act. Hexyl Alc., $Me.CH(Et)_2.(CH_2)_2.OH$ (?).—Test 702 gives act. caproic ac.**
154	0·820(20)	**Dipropylcarbinol, $Pr_2.CH.OH$.**—Test 702 gives **propionic and** butyric acids.

Boiling-point (C.°).	Specific Gravity.	**ALCOHOLS.**—Colorless and liquid, with Specific Gravity less than 0·90 at 20°/4°.
157c.	0·833(0)	**Hexyl Alc., $C_6H_{13}.OH$.**
157	$0{\cdot}871^{20}/_0$	**Diethylallylcarbinol, $Et_2(C_3H_5).C.OH$.**—Odor like camphor.—Test 702 gives diethyl ketone, etc.
158·4c.	0·864(0)	**Methyldiallylcarbinol, $Me(C_3H_5)_2.C.OH$.**—Test 702 gives acetic ac. (Test 311) and CO_2.
160	0·830(20)	**Diethylisopropylcarbinol, $Et_2(C_3H_7).C.OH$.**
160–1c.		**Cyclohexanol, $(CH_2)_5{:}CH.OH$.**—M. p. 16°–17°.—Odor like capryl alc.—S. in 28 vol. aq.—HNO_3 oxid. to adipic ac.—CrO_3 oxid. to cyclohexanone.
160·5c.	$0{\cdot}838^{20}/_0$	**Diethylpropylcarbinol, $Et_2(Pr).C.OH$.**—Test 702 gives propionic and butyric acids.
161·5c.	0·825(20)	**Methyldipropylcarbinol, $Me(Pr_2).C.OH$.**—Test 702 gives propionic and butyric acids.
164–5		**Methylamylcarbinol, $(Me)(C_5H_{11}).CH.OH$.**—Test 702 gives acetic and valerianic acids.
175	0·855(20)	**2-Methylheptene(2)-ol(6), $C_8H_{15}.OH$.**—Adds Br directly.—Heat several hours w. dil. H_2SO_4 to form the oxide, b. p. 127°–9°.
175–6	0·878(0)	**Ethyldiallylcarbinol, $(Et)(C_3H_5)_2.C.OH$.**—Oxid. by CrO_3 gives oxalic ac.
175·8 (th. i.)	0·834(0)	**† Heptyl Alc., $C_7H_{15}.OH$.**
179	$0{\cdot}819^{20}/_4$	**† Methylhexylcarbinol, $(Me)(C_6H_{13}).CH.OH$.—**Test 702 gives acetic and caproic acids. (Cf. foot-note on p. 147.)!
179·5	0·835(20)	**Ethyldipropylcarbinol, $(Et)(Pr_2).C.OH$.**—Test 702 gives acetic, propionic, and butyric acids.
190–5	0·870(20)	**[–] Linalol, $C_{10}H_{18}O$.**—(In origanum and other essential oils.)—Agreeable perfume odor!—Adds Br_4.—$KMnO_4$ oxid. to citral, lævulinic ac., and acetone
195·5 (th. i.)	0·838(0)	**Octyl Alc., $C_8H_{17}.OH$.**
194–8 sl. d.	0·868(20)	**Coriandrol, $C_{10}H_{17}.OH$.**—Fragrant odor!—Shaking w. 5% H_2SO_4 gives terpine hydrate.—E. oxid. by $KMnO_4$
210–11	0·839(0)	**Propylhexylcarbinol, $(Pr)(C_6H_{13}).CH.OH$.**
211c.	0·849(0)	**Diamyl Alc., $C_{10}H_{21}.OH$.**—Odor faint.
213·5 (th. i.)	$0{\cdot}842^{0}/_4$	**Nonyl Alc., $C_9H_{19}.OH$.**
214 sl. d.		**Anthemol, $C_{10}H_{16}O$.**—(Occurs in Roman camomile oil.)—Thick liq. w. camphorous odor.—Oxid. by CrO_3 gives CO_2 and aq.; by dil. HNO_3 p-toluic and terebhthalic acids. (Cf. Tests 905–3 and 318–3.)
215 (th. i.)		**Methylbenzylcarbinol, $(Me)(C_7H_7).CH.OH$.**
229–30	0·880(15)	**Geraniol, $Me_2.C{:}CH.(CH_2)_2.C(Me){:}CH.CH_2.OH$.**—B p. (15 mm.) 118–20°; still liq. at – 15°.—Odor like the geranium and rose.—I. aq.; misc. alc. or eth.—Opt. inactive.—Oxid. by $KMnO_4$ gives acetone and lævulinic ac.; by CrO_3 mixture, citral.—For identification as its diphenylurethane, cf. Journ. f. prakt. Chem. II, 56, 28.
231c.	0·830(20)	**Decyl Alc., $C_{10}H_{21}.OH$.**—Viscous, highly refractive oil.—M p. +7°.

COLORLESS COMPOUNDS CONTAINING C, H, AND O [SUBORDER I OF ORDER I]

GENUS VIII, ALCOHOLS.

DIVISION B, SECTION 2,—LIQUID ALCOHOLS WITH SPECIFIC GRAVITY GREATER THAN 0·90 AT 20°/4°.

Boiling-point (C.°).	Specific Gravity.	**ALCOHOLS.**—Colorless and liquid, with Specific Gravity greater than 0·90 at 20°/4°.
67	0·950(15)	**Hydrofurane** (cf. Genus IX, B, 3).
102	1·048(0)	**Dioxyethylene, $C_4H_8O_2$.**—M. p. +9°.
114–5	$0{\cdot}972^{20}/_{4}$	**Propargyl Alc., $CH \vdots C.CH_2.OH$.**—Odor agreeable.—S. aq —Unsat. (cf. Test 901). and gives an explosive greenish-yellow ppt w. ammon. CuCl in Test 906.—Heated w solid KOH gives acetylene, CO_2, and H.
135	0·926(13)	**Ethyleneglycol Monoethyl Eth., $HO.CH_2.CH_2.OEt$.**
138	1·113(18)	**Erythrite Anhyd., $C_4H_6O_2$.**—Misc. w. aq.—Reduces h. ammon. $AgNO_3$ sol.—Ppt's MgO fr. $MgCl_2$ sol.
160–1	$0{\cdot}915^{25}/_{25}$	**Trimethyleneglycol Ethyl Eth., $Et.O.(CH_2)_3.OH$.**—Odor pleasant.—V. s. aq.
161–2d.	1·165(0)	**Glycid, $C_2H_3O.CH_2.OH$.**—B. p. (15 mm.) 74°-5°.—Misc. w. aq., alc., or. eth.—Dist. under ordinary pressure gives acroleïn (Test 112).—Reduces Tollen's reagent in the cold (Test 101)!—Unites quickly w. aq., forming glycerine (Test 816).
168–70	1·136(20)	**Furfuralcohol, $C_4H_3O.CH_2.OH$.**—D. s. aq.!; e. s. alc. or eth.—Very unstable towards mineral acids; becomes green when treated w. conc. HCl!—Heated w. solid KOH gives succinic ac. (Test 320), CO_2, etc.
171–2	1·145(0)	**Glycerine Eth., $(C_3H_5)_2.O_3$.**—Misc. w. aq., alc., or eth.!—At 100° unites w. aq. to form glycerine (Test 816)!—After being warmed w. dil. HCl gives "iodoform reaction" and reduces Fehling's sol.—Br acts violently, giving dibromhydrine.
176–8	1·003(20)	**1, 2-Dihydroxy-2-methylpropane, $C_4H_{10}O_2$.**—Heated w. aq. at 180°–200° gives isobutyric ald.
183–4		**2, 3-Dihydroxybutane, $C_4H_8.(OH)_2$.**
184–5c.	0·960(15)	**Suberyl Alc., $(CH_2)_6:CH.OH$.**—Taste, burning, bitter.—PCl_5 gives suberyl chloride.
187·5	0 995(0)	**2, 3-Dihydroxypentane, $C_5H_{12}O_2$.**—Oxid. by Br aq. gives acetylpropionyl.
188–9	1·040(19·4)	**Propylene Glycol, $MeCH(OH).CH_2.OH$.**—Taste sweetish.—Misc. w. aq.; s. in 12–13 pt. eth.—Test 702 gives acetic ac. only.—Made into a paste w. $ZnCl_2$ and ignited as in Test 816 for glycerine gives propionic ald.
191	0·920(21)	**s-Diethylglycerine Eth., $C_7H_{16}O_3$.**
192	1·019(0)	**1, 2-Dihydroxybutane, $C_4H_8.(OH)_2$.**—E. s. aq.
197–7·5c.	1·125(0)	† **Ethylene Glycol, $CH_2(OH).CH_2(OH)$.**—Somewhat viscous liq.—Misc. w. aq.; v. s. alc.; d. s. eth.—Solidifies abt. −20° and then melts at −17.4°.—Ignited w. $KHSO_4$ as in acroleïn test for glycerine gives acetaldehyde. (Cf. Tests 816, 112, and 111.)
202–4	1·013	**Methylphenylcarbinol, (Me)(Ph).CH.OH.**
203–5	1·011	**Butanediol (1, 4), $C_4H_8.(OH)_2$.**—Viscous.

Boiling-point (C.°).	Specific Gravity.	**ALCOHOLS.**—Colorless and liquid, with Specific Gravity greater than 0·90 at 20°/4°.
204	1·126	**Butanediol(1, 3), $C_4H_8.(OH)_2$.**—V. s. aq.; i. eth.—Oxid. gives oxalic and acetic acids and crotonic ald.
204·7c.	1·043$^{20}/_4$	† **Benzyl Alc., $Ph.CH_2.OH$.**—Odor faintly aromatic.—S. in 25 pt. aq. at 17°.—Oxid. by Test 702 gives benzoic ac. (Test 312).—(Unless freshly prepared is likely to contain traces of benzaldehyde.)—Identify by Test 812!
206–7		**2, 3-Dihydroxyhexane, $C_6H_{12}.(OH)_2$.**
212	1·034(21)	**Benzylcarbinol, $C_7H_7.CH_2.OH$.**
214 (th. i.)	1·053(18)	† **Trimethylene Glycol, $CH_2(OH).CH_2.CH_2(OH)$.**—Viscous; misc. w. aq.—† Distilled w. $KHSO_4$ as in acroleïn test for glycerine (Tests 816 and 112) gives no color w. the fuchsine-aldehyde reagent. (Dif. fr. glycol and glycerine.)
217	1·036(0)	**m-Tolylcarbinol, $Me.C_6H_4.CH_2.OH$.**—Remains liq. at −20°.—S. in 20 pt. c. aq.
218	0·936(20)	† **Terpineol, $C_{10}H_{18}O$.**—Separates fr. eth. sol. in transparent cryst. w. m. p. 35°. (The commercial product is always liq.)—I. aq.; v. s. alc. or eth.—Adds Br_2, giving oily bromide. Gives a dihydrochloride, m. p. 50°.—The odor when sufficiently diluted resembles that of lilac flower!
221	1·000(0)	**1, 4-Dihydroxypentane, $C_5H_{10}.(OH)_2$.**—Viscous.—Misc. w. aq. or alc.!; i. lgr.
220–5		**s.-Dimethyl Dipropyl Glycol, $[(Me)(Pr)C.OH]_2$.**
235	1·008(18)	**Phenylpropyl Alc., $Ph.(CH_2)_3.OH$.**—Viscous, d. s. aq.; misc. w. alc. or eth.—May be oxid. by CrO_3 to hydrocinnamic ac.
225–30		**Ethyl Glyceryl Eth., $CH_2(OH).CH(OH).CH_2.O.Et$.**
240d.	1·101(25)	**Allyl Glyceryl Eth., $C_3H_5.O_3.C_3H_7$.**—S. in 2 or 3 vol. aq.!—Unsat. (Cf. Test 901.)
246·6c.	0·978(15)	**p-Cuminic Alc., $Me_2.CH.C_6H_4.CH_2.OH$.**—Misc. w. alc. or eth.—Oxid. by $KMnO_4$ to terephthalic and oxypropylbenzoic acids.—Persistent boiling w. Zn dust gives cymene.
247·5	1·120(23)	**Saligenin Methyl Eth., $o\text{-}MeO.C_6H_4.CH_2.OH$.**
250	1·132(0)	**Diethylene Glycol, $CH_2(OH).CH_2.O.CH_2.CH_2.OH$.**—S. aq. alc. or eth.
254	1·044$^{20}/_4$	**Cinnamyl Alc., $Ph.CH{:}CH.CH_2.OH$.**—Aromatic odor like hyacinths.—D. s. aq.; v. s. alc. or eth.—Gives Test 304 easily.
290	1·138	**Triethylene Glycol, $C_6H_{14}O_4$.**—Misc. w. aq.; d. s. eth.
290c.	1·260$^{20}/_4$	† **Glycerine, $CH_2(OH).CH(OH).CH_2.OH$.**—Viscous sweet-tasting syrup.—Misc. w. aq. or alc.; i. abs. eth.—Identify by Test 816!—(Commercial glycerine usually contains so much water that it may begin to boil 100° lower than the b. p. given. The temperature will rise nearly to the true b. p., however, if the distillation is continued.)—[N.B.—Several of the higher homologues of glycerine have been prepared. They are syrups, v. s. in water and almost insoluble in ether; but as they possess little interest, and can not be distilled without decomposition under the usual atmospheric pressure, their description is omitted.]
327	1·062(16·5)	**Dibenzylcarbinol, $(Ph.CH_2)_2.CH.OH$.**—E. s. alc. or eth.

NUMBERED SPECIFIC AND SEMI-SPECIFIC TESTS FOR THE ALCOHOLS.

[TESTS 801-900.]

801. The Iodoform Test.

The more or less ready formation of iodoform when certain aliphatic compounds are treated with iodine in dilute alkaline solution, furnishes a qualitative test that has found many applications in organic analysis. When the use of this reaction is directed in the tables for the purpose of distinguishing between some of the lower boiling liquid alcohols and ketones, proceed as follows:

Prepare a cold aqueous solution containing one drop of the pure compound in each cubic centimeter of water. If the test is to be made with a single centimeter of the solution, carry it out in a three-inch test-tube ("weighing-tube"). For each centimeter of solution used, add two drops of sodium-hydroxide solution (1 : 10); then, drop by drop, from a medicine-dropper, a concentrated iodine solution,* until a barely perceptible tint of yellow, that persists after standing for several seconds, remains. If too much iodine should be inadvertently used, cautiously add just enough more soda to destroy the excess of color. Let the mixture stand at the temperature of the laboratory for two minutes. Then shake and notice whether any iodoform has separated.

If no iodoform separates in the cold, immerse the bulb of a small thermometer in the solution; heat to 60°, and maintain this temperature for one minute. If the solution becomes entirely colorless during the heating, add just enough more iodine to restore the *trace* of yellow that was previously present. If no precipitate appears at once, set the tube aside for two minutes before making the final observation.

In the first part of the test, *in the cold, isopropyl alcohol and acetone give good precipitates of iodoform immediately;* secondary butyl alcohol rather slowly. Methyl, ethyl, propyl, isobutyl, tertiary butyl, isoamyl, and allyl alcohols give no precipitates under the same conditions.

After heating at 60°, *ethyl alcohol gives a good precipitate*, and allyl alcohol a very scanty one. The other compounds mentioned in the preceding paragraph which do not give iodoform in the cold, do not give any at 60° within the specified time limit.

The interpretation here given to the results of the test will not hold for solutions that vary greatly from the prescribed concentration. It is applicable, however, in testing the saponification distillates obtained by the procedure of Generic Test V-2, B. Under other conditions, which were first carefully studied by Lieben,† the delicacy of the reaction when used for the detection of smaller quantities of ethyl alcohol, etc., may be greatly increased. According to Lieben, most compounds containing the $CH_3.CO.C$ and $CH_3.CHOH.C$ groups may be made to yield iodoform by appropriate treatment with iodine and alkali; some, like levulinic acid, giving it very readily in the cold. Hence

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* *This iodine solution* should be kept in stock, and is prepared by rubbing 1 part iodine in a mortar with 5 parts of potassium iodide and 15 parts of cold water.

† Cf. Lieben, Liebig's Annalen, Spl. 7, 221.—The lower alcohols and acetone, if in very weak solutions, are easily concentrated by distilling through a tower. The first runnings will contain nearly all of the organic compound so that the second half of the distillate may be safely rejected. The process of "salting out" with potassium carbonate may be combined with distillation, as is illustrated in paragraph (i) of Generic Test V-2, B.

while the test is more used than any other as a preliminary reaction for the detection of ethyl alcohol and acetone in aqueous solutions, the result requires confirmation by additional evidence.

Iodoform is ordinarily recognized by its peculiar pervasive odor and pale-yellow color, though it is said that neither of these properties are characteristic of the chemically pure substance. Indeed, under the conditions of the test, the precipitate is at first often practically white, and the odor is not always well developed at the moment of formation. An iodoform odor, *unaccompanied by a precipitate,* should never be accepted as satisfactory evidence of the presence of any of the compounds giving the reaction. An iodoform precipitate, if washed with cold water, dissolved in a little warm and quite dilute alcohol, and then allowed to crystallize out *very slowly*, separates from the solvent in regular hexagonal plates of decidedly characteristic appearance, in which the opposite corners of the hexagon are connected by straight lines crossing its geometrical centre; or, sometimes, in regular six-rayed stars whose primary rays branch into a system of symmetrical subordinate rays after the manner seen in frost crystals.

811. Allyl Alcohol. (Properties tabulated on p. 161.)

Support a 25 cc. distilling-flask with a long side-tube in a vertical position by a clamp. Cool the bulb by surrounding it with cold water. Introduce two drops of the alcohol, and then three drops of a solution made by dissolving 1 grm. of chromic anhydride in a mixture of 6 cc. of water and 0.8 cc. of concentrated sulphuric acid. The liquids should be dropped from a medicine-dropper in such a manner that they will not come in contact with the side walls of the flask in falling. Cork quickly. Loosen the clamp, and incline the flask so that the lower end of the side tube shall dip into 2 cc. of water contained in a test-tube standing in a beaker partly filled with cold water. Boil the solution in the flask over a very small flame until it has evaporated nearly to dryness. Loosen the stopper before taking away the lamp.

Mix the aqueous solution in the test-tube with 5 cc. of the fuchsine-aldehyde reagent used in Test 112 (1). Allow to stand overnight and observe the color the next morning. Mix 2 cc. of the solution with 2 cc. of hydrochloric acid (sp. gr. 1.20), and again observe the color. Finally note the color of this acid mixture after it has been diluted with water to 100 cc.

In this test allyl alcohol is oxidized to acroleïn. The violet-red coloration which makes its appearance within a few seconds after adding the aldehyde reagent, and which within ten minutes renders the solution practically opaque, is *not* characteristic, very similar colors being obtained from many other alcohols when treated in the same manner. If, however, the color after standing overnight is a red-violet (RV), *of such intensity as to appear opaque except in thin layers*, and if this color upon addition of the hydrochloric acid changes to an impure dark yellow or dark yellow-green (about YS2 to YGS2, when viewed in very thin layers against a white background), and this color in turn, upon the dilution with water to 100 cc. gives a pure blue (BTI, occasionally approximating VBTI, the comparison being made in a six-inch test-tube against a white background), the compound, if it has the proper physical properties, must be allyl alcohol.

812. Benzyl Alcohol. (Properties tabulated on p. 165.)

Place in a 25–50 cc. distilling-flask two drops of the chromic-acid mixture used in Test 811 for allyl alcohol, 10 cc. of water, and four drops of the alcohol. Heat over a small flame, while shaking, for two or three minutes, until the solution appears distinctly greenish; the temperature meanwhile being kept a little below boiling, so that no vapor shall escape through the side tube. Next distil, collecting about 2 cc. of distillate in a test-tube containing 1 cc. of cold water. Do not use a condenser, but let the extremity of the side-tube of the flask almost touch the surface of the water in the test-tube. The test-tube should stand in a beaker half filled with cold water. When the distillation is finished, wash down the sides of the test-tube with 3 cc. of water and 6 cc. of strong alcohol. Add one drop of pure phenylhydrazine and boil for half a minute. From this point on, follow *literally* the directions given in part 1 of Test 113 for benzaldehyde.

The oxidation with chromic acid gives benzaldehyde; and the treatment with phenylhydrazine gives its phenylhydrazone, melting-point 156°. The hydrazone, being rather unstable in the light, will sometimes be found to melt one or two degrees below its true melting-point. (Benzyl alcohol oxidizes so readily, that specimens which have been exposed for some weeks to the air will be found to give aldehyde reactions.)

813. **Butyl Alcohol (Normal).*** (Properties tabulated on p. 161.

Convert six drops of the alcohol into n-butyl 3, 5-dinitrobenzoate by the procedure given in the first paragraph of Test 814–1.

To purify the ester, crush the reaction product when cold with a stirring-rod. Dissolve it in 10 cc. of ethyl alcohol (2 : 1). Filter hot if not clear. Cool well, shake persistently, and filter. Wash with 3 cc. of cold ethyl alcohol (2 : 1). Recrystallize from 8 cc. of the same alcohol and wash with 2 cc. Spread on a porous tile and allow to become air dry in a warm place. Determine the melting-point.

The ester obtained in this test is distinctly crystalline, has a pearly lustre, and melts at 64° (uncor.).

814. **Ethyl Alcohol.** (Properties tabulated on p. 161.)

The ready formation of iodoform at 50°–60°—but not in the cold—in Test 801 is the most convenient preliminary test for ethyl alcohol. The following very satisfactory confirmatory test is, of course, applicable only to a nearly pure alcohol containing not more than about 10 per cent of water. The same general procedure with slight modifications may be used in the identification of many of the homologues of ethyl alcohol.

1. Heat together gently in a three-inch test-tube held over a small flame, 0.15 grm. of 3, 5-dinitrobenzoic acid † and 0.20 grm. of phosphorus pentachloride. When signs of chemical action are seen, remove the heat for a few seconds. Then heat again, boiling the liquefied mixture *very gently* for one minute. Pour out on a very small watch-glass, and allow to solidify. As soon as solidification occurs, remove the liquid phosphorus oxychloride with which the crystalline mass is impregnated by rubbing the latter between two small pieces of porous tile. Place the powder in a dry five- or six-inch test-tube. Allow four drops of the alcohol to fall upon it, and then stopper the tube tightly without delay.—[When employing this procedure for the propyl and butyl alcohols, use six drops of the alcohol instead of four; for the alcohol must always be present in moderate excess.]—Immerse the lower part of the test-tube in water having a temperature of 75°–85°. Shake gently, and continue the heating for 10 minutes.

To purify the ester produced in the reaction, crush any hard lumps that may form when the mixture cools with a stirring-rod, and boil gently with 15 cc. of methyl alcohol (2 : 1) until all is dissolved, or for a minute or two.—[In testing for other alcohols than ethyl, all directions for the use of the solvent in this paragraph must be modified as elsewhere specified. Cf. tests for methyl, propyl, butyl, and isobutyl alcohols.]—Filter boiling hot if the solution is not clear. Cool. Shake, and filter. Wash with 3 cc. cold methyl alcohol (2 : 1). Recrystallize from 9 cc. of boiling methyl alcohol (2 : 1). Wash with

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* A preparation from Kahlbaum of Berlin.

† This new reagent is listed by C. A. F. Kahlbaum of Berlin at 8 marks per 100 grams, and may be obtained in New York from Eimer & Amend. It may also be readily prepared in the laboratory from benzoic acid.

2 cc. of the same solvent. Spread out the product on a piece of tile. Allow to become air dry, and determine the melting-point.

Ethyl 3, 5-*Dinitrobenzoate*, the product in this test, crystallizes in white needles melting at 92°–93° (uncor.).

815. Ethylene Glycol. (Properties tabulated on p. 164.)

Shake vigorously in a stoppered six-inch test-tube for five minutes, occasionally cooling with water, one drop of the alcohol, 0.4 cc. benzoyl chloride, and 5.0 cc. of a 10 pcn cent aqueous solution of sodium hydroxide. Add 10 cc. of cold water. Shake again for a few seconds, and then filter. Wash the precipitate with 20 cc. of cold water. Dissolve in 20 cc. of hot dilute alcohol (1 : 1), filtering hot if the solution is not clear. Cool and filter. Wash with 4 cc. of cold alcohol (1 : 1). Dry on a porous tile at the room temperature for an hour.

The *ethylene dibenzoate*, as obtained in this test, melts at 70.5°–71° (uncor.). The melting-point may be slightly raised by repeated crystallization.

816. Glycerine. (Properties tabulated on p. 165.)

Of the three tests for glycerine here described, color reaction 1 with pyrogallol has the advantage, as a preliminary test, of being rapid and directly applicable to rather dilute aqueous solutions, but results by procedures 2 and 3 are more conclusive.

In testing for glycerine in the presence of other organic compounds, such for example as in the aqueous solution resulting from the saponification of an ester by the method of Generic Test V–2, the glycerine should first be isolated in a nearly pure state by evaporating to dryness on a water-bath, and extracting the powdered saline residue with a mixture of equal volumes of nearly absolute alcohol and ether. Evaporation of the solvent will then give a syrup that will often be pure enough for identification by either one of the following methods. In the presence of sugars this purification will prove insufficient to permit the use of procedures 1 and 3; but method 2 may be safely used.

1. Dissolve one drop of the glycerine in 2 cc. of cold water. Add five drops of a one per cent aqueous solution of pyrogallol, and 2 cc. of concentrated sulphuric acid. Shake. Heat quickly to boiling and boil for 20–25 seconds. Cool immediately with running water. Dilute to 20 cc. with strong alcohol in a six-inch test-tube. Without delay compare the coloration produced with the color standard, holding the tube in front of a white background.

Glycerine in this test gives a characteristic purplish-red coloration to the alcohol that matches VRT1–T2 of the standard. The color fades away after standing for some minutes.

This procedure is directly applicable to quite dilute aqueous solutions if "2 cc. of the solution" is substituted for the "drop of glycerine, and 2 cc. of cold water" called for in the directions. The color from a one per cent solution will then be found to be as pure, and nearly as intense, as when a drop of pure glycerine is taken. The color given by solutions containing 0.1 per cent of glycerine is very pale indeed and fades rapidly, but it is still quite noticeable, and of the correct *hue*. Very weak solutions may require heating for thirty seconds or more. The presence of sugars, or of certain other polyatomic alcohols like erythrite, may obscure the reaction by giving rise to reddish- or yellowish-brown colorations.

2. Stir up into a stiff uniform paste on a watch-glass, by means of a thin wire, one drop of the syrupy compound and 0.5 grm. of powdered acid potassium sulphate. Drop the mass into a dry six-inch test-tube supported by a clamp in a slightly inclined position on a lamp-stand. Fit the tube with a clean perforated cork stopper carrying a glass gas-delivery tube, 20–25 cm. long, and bent downward so that one end is barely immersed beneath the surface of 2 cc. of distilled water contained in a second test-tube that stands

in a beaker partly filled with cold water. Ignite the sulphate mixture strongly with a gas-flame until frothing ceases and the mass is completely liquefied. Test the aqueous solution in the second test-tube for acroleïn by observing its odor, and by color reaction 112–1.

The vapors of acroleïn, the dehydration product of glycerine in this test, are remarkable for their painfully irritating action on the mucous membranes of the nose and eyes. Their effect must not be confounded with that due to sulphur dioxide, which is usually formed during the ignition, even in the absence of glycerine. Little difficulty will be found in making the distinction by any one who has ever performed the experiment with pure glycerine. The phenomena of the color reaction between acroleïn and the fuchsine-aldehyde reagent are fully discussed under the specific test for acroleïn, and are very characteristic.

Ethylene glycol gives acetic aldehyde, but like trimethylene glycol, erythrite, or mannite, does not give an acroleïn odor or interfering color reaction in the fuchsine test. This latter reaction is also not seriously interfered with by the small quantities of grape- or cane-sugar that remain with glycerine after the purification of a crude glycerine by the ether-alcohol extraction referred to in the introduction to this test. Sugars, if present in larger quantity, are likely to give confusing colorations, but never any acroleïn odor.

3. Place in a six-inch test-tube one drop of glycerine, 0.4 cc. benzoyl chloride, and 5.0 cc. of a 10 per cent aqueous solution of sodium hydroxide. Stopper, and shake vigorously, occasionally cooling under cold water, until a solid separates. This requires from five to eight minutes. Add 10 cc. of cold water, and shake again for ten to twenty seconds. Filter. Wash with 20 cc. cold water; then with 10 cc. of a cold mixture of 2 cc. glacial acetic acid and 8 cc. water. Crystallize from 15 cc. of boiling dilute alcohol (2 vols. alcohol : 1 volume aq.). Filter hot if all does not dissolve on boiling. Cool and shake till a precipitate gathers. Filter. Wash with 3 cc. of dilute alcohol (2 : 1). Dry on a porous tile in the air.

The product in this test is a white crystalline substance melting at 71°–72° (uncor.). It is presumably *glycerine tribenzoate*, for which several melting-points with the extreme values of 70° and 76° are to be found in the literature.

This procedure is applicable with only slight modification, to not too dilute solutions of glycerine in water. Thus, a fair yield of benzoate is obtained when one drop of glycerine dissolved in 1 cc. of water is substituted for one drop of pure glycerine as prescribed in the directions. It is of course inapplicable in the presence of polyatomic alcohols or other substances giving the Schotten-Baumann reaction.

817. Isobutyl Alcohol. (Properties tabulated on p. 161.)

Convert six drops of the alcohol into *isobutyl 3, 5-dinitrobenzoate* by the procedure given in Test 819–2 for preparing the methyl ester of the same acid.

The isobutyl ester is obtained in this test in white flocks melting at 83°–83.5° (uncor.).

818. Isopropyl Alcohol. (Properties tabulated on p. 161.)

Oxidize four drops of the alcohol with six drops of the chromic-acid mixture used in Test 811 for allyl alcohol. The procedure for the oxidation is identical with that given for allyl alcohol, except that the vapors are to be conducted into a six-inch test-tube containing 0.4 cc. of cold water, 0.4 cc. of benzaldehyde, and 2 cc. of strong alcohol. Shake and add 0.5 cc. of a ten per cent caustic-soda solution, and boil very gently over a small flame for one minute, counting from the time when actual boiling begins. Cool and shake. Filter off the crystalline precipitate and wash with 1 cc. of strong alcohol. Boil up with 1 cc. of strong alcohol. Cool, and shake vigorously, adding from one to four drops of water, if necessary, to start the separation of crystals. Filter, and wash with 0.5 cc. of cold alcohol. Press on a porous tile, and then dry fifteen minutes at a temperature not above 100°.

Isopropyl alcohol is oxidized in this test to acetone, which is then condensed with

the benzaldehyde to *dibenzylidene-acetone* (cf. Test 711–2), crystallizing in pale-yellow lustrous plates that melt at 111°–112° (uncor.).

819. Methyl Alcohol. (Properties tabulated on p. 160.)

1. (Color reaction.)—Dissolve one drop of the alcohol in 3 cc. of water in a six-inch test-tube. Wind a piece of rather light copper wire around a lead-pencil so that the closely coiled spiral shall form a cylinder 2 cm. in length, while 20 cm. of the wire is left unbent to serve as a handle. Oxidize the spiral superficially by holding it in the upper part of the flame of a Bunsen burner; and then, while still at a red heat, plunge it into the alcoholic solution. (This treatment oxidizes a portion of the methyl alcohol to formic aldehyde.) Withdraw the spiral immediately and cool the test-tube with running water. Repeat the oxidation of the solution twice more by the method given. Add one or two drops of 0.5 per cent aqueous solution of resorcin. Pour the mixture slowly into a second inclined test-tube containing 3–5 cc. of pure concentrated sulphuric acid. The procedure and the phenomena in the test from this point on, are the same as described in the latter part of Test 114–1 for formic aldehyde.

Many methyl ethers, and methyl esters that are sufficiently soluble in water to be tested by this method, and tertiary butyl alcohol, show the same behavior as methyl alcohol. Remember that the actual separation of bright-red solid flocks from the aqueous layer above the sulphuric acid, after standing, is essential to the proof that methyl alcohol is present.

Many compounds besides those mentioned give traces of formic aldehyde when oxidized by a hot copper wire, but not enough to give a separation of the characteristic flocks. Test 114–2 for formic aldehyde will often show the presence of these traces, and therefore must not be substituted for Test 114–1. Ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, and allyl alcohols, ethyl ether, and acetone, give strong yellow, amber, ocherous, or dirty greenish colorations; and, if present in relatively large quantities in mixtures containing methyl alcohol, will interfere with its detection by destroying the purity of color required in the flocks.

Weak aqueous solutions suspected to contain methyl alcohol may be oxidized directly with the copper wire and then tested with resorcin in the usual manner, solutions much weaker than the one recommended in the procedure giving entirely satisfactory results.

In examining organic mixtures for methyl alcohol the precautions mentioned in the following paragraphs should be observed.

(a) Use for the test only that part of any mixture that can be completely distilled between 50° and 100°, and which, after distillation, gives a clear, colorless solution when diluted with several volumes of water.

(b) Make a blank experiment, before oxidation with the copper spiral, by pouring 2 cc. of a clear aqueous distillate of the proper boiling-point, to which one drop of 0.5 per cent resorcin solution has been added, so as to form a layer upon concentrated sulphuric acid in a test-tube. If a precipitate or strongly colored ring makes its appearance, the solution is not suitable for testing without preliminary treatment.

(c) Do not test by this method any solution that is suspected to contain phenols or organic bases.

2. Convert four drops of the alcohol into its 3, 5-dinitrobenzoate by the procedure detailed in the first paragraph of Test 814–1 for ethyl alcohol.

Boil the reaction product with 12 cc. of dilute ethyl alcohol (3 : 1). Cool, shake, allow to stand for a minute or two, and filter. Wash with 2 cc. strong cold alcohol. Recrystallize from 12 cc. of boiling dilute alcohol (3 : 1). Cool, shake, and allow to stand for a minute or two, and filter. Wash the crystals with 2 cc. of cold strong alcohol. Dry at a temperature not above 100°, and determine the melting-point.

The crystalline *methyl dinitrobenzoate* obtained in this test melts at 107.5° (uncor.).

820. Propyl Alcohol. (Properties tabulated on p. 161.)

1. Oxidize four drops of the alcohol with six drops of the chromic-acid mixture used in Test 811 for allyl alcohol. The procedure for the oxidation is identical with that given for allyl alcohol, except that the aldehydic vapors are to be conducted into a three-inch test-tube containing a solution of 0.2 grm. β-naphthol in a mixture of 2.0 cc. glacial acetic acid and two drops of concentrated hydrochloric acid. Warm the mixture for at least half a minute over a small flame, and then boil gently for one minute. Cool and shake. If no precipitate appears, add one drop of water and shake again. Continue the addition of water in this way until a scanty permanent solid precipitate is produced, and the mixture begins to show signs of becoming milky. Allow the precipitate to settle. Filter and wash with 2 cc. of dilute alcohol (1 : 1). Boil the precipitate 30 seconds with 3 cc. of strong alcohol and 1 cc. of water. Cool, shake, and filter. Wash with 2 cc. of alcohol (1 : 1). Press on a tile and dry 15 minutes at 100°.

The condensation product formed in this test crystallizes in colorless plates, and melts at 153° (uncor.).

2. Convert into propyl 3, 5-dinitrobenozate, following exactly the directions given in Test 819–2 for methyl alcohol, except that the product must be dried at a temperature below 70°.

The melting-point of *propyl 3, 5-dinitrobenozate* is 73°–73.5° (uncor.).

821. Cholesterine. (Properties tabulated on p. 158.)

So many compounds closely resembling cholesterine have been described that tests (1) and (2) should both be applied.

1. Place 0.1 grm. of the compound and 0.5 cc. benzoyl chloride in a dry test-tube. Immerse the end of the test-tube in a paraffin bath and heat at about 160° for 5 minutes. Cool. Add 10 c.c. of strong alcohol and boil. Cool. Filter off the precipitate and wash it with 5 cc. of cold strong alcohol. Redissolve in 10 cc. of hot alcohol; cool; filter and wash as before. Then repeat these operations for a third time. Dry the product for 15 minutes at 100° and determine its melting-point in a wide capillary. After the compound has fused to a perfectly *clear liquid*, withdraw the tube quickly from the bath, hold it before a piece of black paper, and watch closely for color changes during solidification.

Cholesterine benzoate, formed in this test, crystallizes in pearly white leaflets which fuse to a turbid liquid at 145.5° (uncor.). At 178.5° (uncor.) the turbidity suddenly disappears. In cooling, a brilliant display of opalescent colors is exhibited, among which a brilliant blue, appearing at about the temperature of the higher melting-point, followed by a violet-blue just before complete solidification, are most prominent. The colors disappear very quickly.

2. Place 0.1 grm. of the substance, 0.1 grm. of *anhydrous* sodium acetate, and 1 cc. of acetic anhydride in a dry test-tube. Immerse the end of the test-tube in a paraffin-bath at 130°–135° and heat for fifteen minutes. Dissolve the reaction product in 5 cc. of hot dilute alcohol (4 : 1). Cool. Filter. Wash the precipitate with 2 cc. of the same dilute alcohol. Recrystallize from 10 cc. of the same alcohol. Recrystallize again from 3 cc. of boiling strong alcohol, and wash the precipitate with 1 cc. of cold strong alcohol. Dry on a porous tile, and then in an oven at 100° for fifteen minutes. Determine the melting-point of the substance, and observe any change in color during solidification, in the manner described for the benzoate in the preceding paragraph.

Cholesterine acetate, formed in this test, melts at 114° (uncor.). A play of opalescent color is observed during the few seconds that elapse between incipient and complete solidification.

CHAPTER XI.

GENUS IX. HYDROCARBONS AND OTHER COLORLESS COMPOUNDS OF CARBON, HYDROGEN, AND OXYGEN NOT INCLUDED IN EARLIER GENERA

OF

SUBORDER I, ORDER I.

GENUS IX COMPRISES ALL COLORLESS COMPOUNDS OF THE SUBORDER THAT FAIL TO GIVE GENERIC TESTS I–VIII INCLUSIVE. WITH THE EXCEPTION OF SOME ETHERS AND A FEW UNREACTIVE KETONES AND ESTERS, THESE SPECIES ARE ALL HYDROCARBONS. ALL ARE INSOLUBLE OR NEARLY INSOLUBLE IN WATER. THE GENUS HAS NO SPECIAL GENERIC TEST OF ITS OWN.

THE solid species of the genus constituting Division A are not subdivided into sections.

The liquid species, Division B, are, however, arranged in three sections: Section 1 contains the paraffins, C_nH_{2n+2}, and some saturated cyclic hydrocarbons; Section 2, unsaturated hydrocarbons from both the aliphatic and cyclic series, together with some alkyl oxides (ethers); and Section 3, the liquid aromatic hydrocarbons, terpenes, and a few fatty-aromatic ethers.

SECTIONAL TESTS.

To find the section of the tables to which any liquid species of the genus belongs, its specific gravity must first be known. Detailed directions for the determination of this constant with the necessary degree of accuracy, by a simple method requiring not more than 0.2 cc. of substance, will be found on page 228.

If the specific gravity at 20°/4° is found to be less than 0.850, the compound is to be sought in Section 1 or 2, Section 3 containing all liquid species having a higher gravity. In this case, in order to decide whether the body belongs to Section 1 or 2, apply Tests 901 902, and 903.

If a compound with specific gravity below 0.850 does not decolorize bromine solution *in the cold* in Test 901 and is not attacked or dissolved by the fuming sulphuric acid in Test 902, nor by the fuming nitric acid in Test 903, it is to be sought in Section 1.* If it shows the opposite behavior in any one of these tests, its place is among the unsaturated hydrocarbons and alkyl ethers of Section 2.

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* A few liquid paraffins like diisopropyl of tertiary structure (*i.e.*, containing a CH group joined to three carbon atoms) are said to be more reactive in these tests than their isomers, and may be misplaced in Section 1. (Cf. Engler-Höfer's "Das Erdöl," I, 231–5, for discussion.)

GENUS IX, HYDROCARBONS, ETC.

DIVISION A,—SOLID HYDROCARBONS.

Melting-point (C.°).	Boiling-point (C.°).	**HYDROCARBONS, ETC.**—Colorless and Solid.
4	274	**Cetene, $C_{16}H_{32}$.**—G. $0\cdot789^{15}/_4$.—Gives Test 901. Dibromide **an** oil
6·5	134 (15 mm.)	**Tetradecine(4), $C_{14}H_{26}$.**—G. $0\cdot800^{15}/_4$.—Gives Test 901.
10	270·5	**Pentadecane, $C_{15}H_{32}$.**—G. $0\cdot769^{20}/_4$.—Does *not* give Tests 901 to 903.
11	233	**Safrol, $C_{10}H_{10}O_2$.**—Odor like sassafras. Cf. Div. B, Sec. 3, of this genus.
11–12	236 (15 mm.)	**m-Methylhexadecylbenzene, $Me.C_6H_4.C_{16}H_{33}$.**—G. $0\cdot862^{11}/_4$.
13	250 (th. i.)	**1, 2, 4, 5-Tetraethylbenzene, $C_6H_2.Et_4$.**—Oxid. gives pyromellitic ac.
14	190–2 (13 mm.)	**Diphenylheptane, $Ph_2.CH.C_6H_{12}$.**—Nitrates easily.
15	155 (15 mm.)	**Hexadecine(1), $C_{16}H_{30}$.**—G. $0\cdot797$(20°).—Unsat. (Test 901). Gives floc. ppt. when shaken with $AgNO_3$ sol.
18	287·5	**Hexadecane, $C_{16}H_{34}$.**—G. $0\cdot775^{18}/_4$.—Does not give Tests 901 to 903.
18	179 (15 mm.)	**Octadecylene, $C_{18}H_{36}$.**—G. $0\cdot791^{18}/_4$.
20	160 (15 mm.)	**Hexadecine(2), $C_{16}H_{30}$.**—G. $0\cdot804^{20}/_4$. No ppt. w. alc. sol. of $AgNO_3$.
21·6	233c.	† **Anethol, $Me.C_2H_2.C_6H_4.O.Me$.**—Has odor and taste of anise oil, in which it occurs!—G. $0\cdot9855^{22}/_4$; N_D (18°) = 1·5615.—V. d. s. aq.; misc. alc. or eth.—Shaken w. a little conc. H_2SO_4 gives anisoïn, m. p. 140°–5°.—Heated w. solid KOH at 200°–30° gives p-oxybenzoic ac. and anol.
22–3	289	**Ditolylmethane, $(Me.C_6H_4)_2.CH_2$.**—Oxid. by CrO_3 to dimethylbenzophenone, etc.
22·5	303	**Heptadecane, $C_{17}H_{36}$.**—G. $0\cdot777^{22}/_4$.—Does not give Tests 901 to 903.
26	180 (15 mm.)	**Octadecine(1), $C_{18}H_{34}$.**—Gives cryst. ppt. w. alc. $AgNO_3$ sol. ($C_{18}H_{33}Ag.AgNO_3$).
26–7	261–2	† **Diphenylmethane, $Ph_2.CH_2$.**—G. $1\cdot001^{26}/_4$.—Agreeable orange-like odor.—Oxid. by CrO_3 gives benzophenone (cf. Tests 702 and 714).—See color reaction 904.
27	286	**Benzyl-p-tolyl-methane, $Ph.CH_2.CH_2.C_6H_4.Me$.**—E. s. alc.
27	230 (15 mm.)	**Cetylbenzene, $C_{16}H_{33}.Ph$.**—G. $0\cdot857^{27}/_4$.—D. s. c. alc.; e. s. eth. or bz.
27·5	240 (15 mm.)	**p-Methylhexadecylbenzene, $Me.C_6H_4.C_{16}H_{33}$.**—Test 905–3 gives p-toluic acid.
28	317	**Octadecane, $C_{18}H_{38}$.**—G. $0\cdot777^{28}/_4$.—Does not give Tests 901–3.
28	252–3	**Phenyl Eth., $Ph_2.O$.**—Odor like geranium!—Alm. i. aq.; e. s. alc.—Unchanged by CrO_3 in $\bar{A}c$, by ignition w. Zn dust, or by HI at 200°.—Dissolves in fuming HNO_3, giving dinitro-comp., m. p. 135°.
30	294	† **Apiol, $CH_2.O_2.C_6H(C_3H_5).(OMe)_2$.**—I. aq.; e. s. alc. or eth.—S. H_2SO_4 w. blood-red color.—Vol. w. st.
30	184 (15 mm.)	**Octadecine(2), $C_{18}H_{34}$.**—G. $0\cdot802^{30}/_4$.—Gives no ppt. w. alc. $AgNO_3$ sol.—Gives Test 901.

Melting-point (C.°).	Boiling-point (C.°).	HYDROCARBONS, ETC.—Colorless and Solid.
32	330c.	**Nonadecane, $C_{19}H_{40}$.**—G. $0{\cdot}777^{32}/_4$.—Does not give Tests 901-903.
32·5	241-2 (th. i.)	**β-Methylnaphthalene, $Me.C_{10}H_7$.**—Picrate dark-yellow ndl., m. p. 115°.
32·9	170d.	**Dicyclopentadiëne(1, 3), $C_{10}H_{12}$.**—G. $0{\cdot}977^{33}/_4$.—Lustrous stellate aggregates, e. s. alc. or eth.—On dist. partially decomposes to cyclopentadiene (IX, B, 2), b. p. 42·5°.
33·5	250 (15 mm.)	**1, 3 - Dimethyl - 4 - hexadecyl - benzene, $Me_2.C_6H_3.C_{16}H_{33}$.** — G. $0{\cdot}849^{33}/_4$.
35·5	350	**β-Benzylnaphthalene, $C_7H_7.C_{10}H_{17}$.**—G. 1·176(0°).—CrO_3 oxid. to benzoic ac. (Test 312).—Picrate yellow ndl. fr. alc. w. m. p. 93°.
36	249 (15 mm.)	**Octadecylbenzene, $C_{18}H_{37}.Ph$.**—Silvery lft.
36		**β-Naphthylacetylene, $C_{10}H_7.C{:}CH$.**—Ag salt, $AgC_{12}H_7$ (w. ammon. $AgNO_3$), colorless ppt.
36-7	300-3	**Benzoylmesitylene, $C_6H_2.(Me_3)(C_7H_7)$(1, 3, 5, 6).**—Lustrous ndl.—Tribrom-deriv. yellowish pr. fr. alc., m. p. 185°.
36·7	205 (15 mm.)	**Eicosane, $C_{20}H_{42}$.**—G. $0{\cdot}778^{36{\cdot}7}/_4$.—Does not give Tests 901-903.
37	274-5	**Ethyl β-Naphthyl Eth., $Et.O.C_{10}H_7$.**—Odor anise-like!—Cryst. mass.
38-9	286-7	**Phenyl Benzyl Eth., $Ph.O.C_7H_7$.**—Heated at 100° w. conc. HCl gives phenol and benzyl chloride.
39		**1, 4-Diphenylbutene(1), $Ph_2.C_4H_6$.**—S. alc. or eth.
40	258	**1, 3, 5-Trimethyl-6-hexadecyl-benzene, $Me_3.C_6H_2.C_{16}H_{33}$.**
40·4	215 (15 mm.)	**Heneicosane, $C_{21}H_{44}$.**—G. $0{\cdot}778^{40}/_4$.—Does not give Tests 901-903.
41-2	241	**Methylphenylfurfurane, $Me.C_4H_2O.Ph$.**—Ndl. fr. c. alc.; e. s. alc. or eth.; i. aq.—Vol. w. st.—On long standing changes to yellow oil.—E. oxid. by alkaline $KMnO_4$ to benzoic ac.—Br gives brown-colored i. lft., m. p. 208°-10°.
43		**Phloroglucin Triethyl Eth., $C_6H_3.(OEt)_3$.**—I. aq.; v. s. alc. or eth.—Vol. w. st.
44·4	224·5 (15 mm.)	**Docosane, $C_{22}H_{46}$.**—G. $0{\cdot}778^{44}/_4$.—Does not give Tests 901-903.
47	235	**Pyrogallol Trimethyl Eth., $C_6H_3.(OMe)_3$.**—E. s. alc. or eth.
47	157c.	**i-Camphene, $C_{10}H_{16}$.**—Feathery ndl., v. s. alc. or eth.—Properties like those of [+ or −] comp. of m. p. 51°-2°.
47·7	234 (15 mm.)	**Tricosane, $C_{23}H_{48}$.**—G. $0{\cdot}778^{47{\cdot}7}/_4$.—Does not give Tests 901-903.
48-50		**9, 9-Diethylanthracene-9, 10-dihydride, $C_{18}H_{20}$.**—Easily oxid. by cold sol. of CrO_3 in glacial $\bar{A}c$ to diethylanthrone, m p. 136°.
50	dist.	**p-Cresyl Eth., $(Me.C_6H_4)_2.O$.**—V. s. eth.; s. alc.
51·1	243 (15 mm.)	**Tetracosane, $C_{24}H_{50}$.**—G. $0{\cdot}779^{51}/_4$.—Does not give Tests 901-903.
51-2	159 (th. i.)	[+ or −] **Camphene, $C_{10}H_{16}$.**—(In many essential oils like citronella oil.)—Feathery cryst. fr. alc.; v. slowly attacked by conc. H_2SO_4.—Gives Test 901; is attacked in Test 905.—The hydrochloride ($C_{10}H_{16}.HCl$) is solid but unstable.
52	284	**Dibenzyl, $Ph.CH_2.CH_2.Ph$.**—G. 0·995.—Mod. s. c. alc.; e. s. eth.
52	255·5c.	**Phloroglucin Trimethyl Eth., $C_6H_3.(OMe)_3$(1, 3, 5).**—S in conc. HNO_3 w. deep-blue color! E. s. alc. or eth.
52		**s-Diphenylbutane, $Ph.(CH_2)_4.Ph$.**—E. s. alc. or eth.
53	230	**Pentamethylbenzene, $Me_5.C_6H$.**—W. conc. H_2SO_4 gives hexamethylbenzene, m. p. 164°.
55	300	**Cetyl Eth., $(C_{16}H_{33})_2.O$.**—Lft.
55-6		**Phenyl-ditolyl-methane, $Ph.CH.(C_7H_7)_2$.**—Ndl s alc ; v s. bz.
55-6		**Dimethyl Hydroquinonyl Eth., p-$C_6H_4.(OMe)_2$.**
57		**Isobutylanthracene, $C_{18}H_{18}$.**—Fluorescent ndl.—Reddish-brown picrate.

Melting-point (C.°).	Boiling-point (C.°).	HYDROCARBONS, ETC.—Colorless and Solid.
57–8		**Cerotene,** $C_{27}H_{54}$.—Gives Test 901.—Paraffin-like mass fr. Chinese wax.
58		† **Dinonyl Ketone,** $(C_9H_{19})_2.CO$.—Description w. Ketones. Cf. VII, A, p. 137.
59		**9-Isoamylanthracene,** $C_{19}H_{20}$.—Alc. sol. shows bluish fluorescence.—Picrate forms brown-red ndl. fr. alc., w. m. p. 115°.—Sol. in conc. H_2SO_4 is green, becoming red on warming.
59	350	**α-Benzylnaphthalene,** $PhCH_2.C_{10}H_7$.—S. in 30 pt. h. alc.; s. in 2 pt. eth.—Picrate forms yellow ndl., w. m. p. 100°–1°.
59·5	354	**Diphenyl-o-tolyl-methane,** $Ph_2.CH.C_6H_4.Me$.—D. s. c. alc.—May be characterized by conversion into rosaniline.
59·5	270 (15 mm.)	**Heptacosane,** $C_{27}H_{56}$.—G. $0·780^{59·5}/_4$.—Does not give Tests 901–903.
60	275–300	**Tolane,** $PhC⋮CPh$.—Lft. s. alc.—$CHCl_3$ sol. saturated w. Cl gives tetrachloride, m. p. 163°; s. in h. bz.—Gives Test 901.
60·5	310	**Benzylduryl,** $PhCH_2.C_6H.Me_4(Me_4 = 1, 2, 4, 5)$.—D. s. alc. or eth.
60–1		**Ethylanthracene,** $C_{14}H_9Et$.—Lft. s. alc.—Picrate melts at 120°.
62	a. 360	**m-Methyl-triphenylmethane,** $Ph_2.CH.C_6H_4.Me$.—Ndl. v. s. alc.—No picrate.—Shows blue phosphorescence on friction.
62	370–80	**Melene,** $C_{30}H_{60}$.—Cryst. s. h. alc.
63	290	**Anthracenehexahydride,** $C_{14}H_{16}$.—Lft. v s. alc.
63		**2, 5-Dimethyl-3, 4-Diacetylfurane,** $C_{10}H_{12}O_3$.—Cf. VII, A.
63–4	440	**Anthemene,** $C_{18}H_{36}$.—G. 0·942(15°).—V. d. s. c. alc.; s. eth.
64	129–30	**Hexadiene(1,4),** C_6H_{10}.—G. 0·739(0°).—Gives Test 901.
67		**Asarone,** $(MeO)_3.C_6H_2.C_2H_2.Me$.—(In root of Asarum Europæum.)—S. h. aq.; e. s. alc. or eth.
68·1	302 (15 mm.)	**Hentriacontane,** $C_{31}H_{64}$.—G. $0·78^{68}/_4$.—Does not give Tests 901–903.
69		**Laurone,** $(C_{11}H_{23})_2.CO$.—Description w. Ketones. Cf. VII, A, p. 137.
70	231–6	**tert.-Dibutylbenzene,** $C_6H_4.[C.Me_3]_2$.
70·5	254·6c.	† **Diphenyl,** Ph.Ph.—G. 1·165.—S. in 10 pt. c. alc.—p-Brom-derivative prepared by action of Br in cold CS_2 sol.; m. p. 310°.—Test 904 gives an intense and quite permanent blue (B) color!
70·5	310(th.i.15mm.)	**Dotriacontane,** $C_{32}H_{66}$.—Alm. i. c. alc.; s. h. eth.; v. s. h. glacial Āc.—Does not give Tests 901–903.
71	a. 360	**p-Diphenyl-tolyl-methane,** $Ph_2.CH.C_6H_4.Me$.—Pr. v. s. h. alc.
71		**2, 4-(β)-Dimethylanthracene,** $C_{14}H_8.Me_2$.—Ndl. fr. alc.—CrO_3 in Āc. sol oxid. to dimethylanthraquinone having m. p. 157°–8°.
72	274	**Methyl α-Naphthyl Eth. (Nerolin),** $Me.O.C_{10}H_7$.—Odor like oil of neroli (Orange blossoms.)—Lft fr. eth.; d. s alc.
74·7	331 (15 mm.)	**Pentatriacontane,** $C_{35}H_{72}$.—G $0·782^{74·7}/_4$.—Does not give Tests 901–903.
76·3		† **Myristone,** $(C_{13}H_{27})_2.CO$.—Description w. Ketones, VII, A, p. 138.
78		**β-Dibenzylbenzene,** $(C_7H_7)_2.C_6H_4$.—Flat ndl., s. alc.—Does not give a picrate.
abt. 79		**αβ-Dinaphthyl,** $(C_{10}H_7)_2$.—S. alc.—Picrate forms golden ndl., m. p. 155°–6°.
79	abt. 190	**Durene,** $C_6H_2.Me_4$, $(Me_4 = 1, 2, 4, 5)$.—V. s alc.—Odor like camphor.—Sbl
80	218·2	† **Naphthalene,** $C_{10}H_8$.—G. 1·152(15°).—Lft., s c. alc.—Characteristic odor.—Test 904 w. $AlCl_3$ gives a green-blue color!—Br substitutes very easily.—Oxid. w. $KMnO_4$ (Test 905–1) gives o-phthalic acid (yield small).—Identify by Test 915!

Melting-point (C.°).	Boiling-point (C.°).	**HYDROCARBONS, ETC.—Colorless and Solid.**
82·8		**Palmitone, $(C_{15}H_{31})_2.CO$.**—Description w. Ketones, VII, A, on p. 138.
83–4		**Isopropylstilbene, $C_3H_7.C_6H_4.C_2H_2.Ph$.**—Scales, v. s. h. alc.—Adds Br_2 (Test 901).
85	285(100 mm.)	**p-Benzyl-diphenyl, $C_7H_7.C_6H_4.Ph$.**—Lft. s. alc.—Heated w. H_2SO_4 evolves SO_2 and finally gives intense blue-red color.—Does not give a picrate.—Oxidation gives benzophenone (Test 714)
86		**α-Dibenzylbenzene, $(C_7H_7)_2.C_6H_4$.**—Flat ndl., v. s. h. alc.—No picrate.
86–7	287–8 (th. i.)	**Biphenylene Oxide, $C_{12}H_8O$.**—Small lft. fr. alc.; v. s. eth.; i. aq.—Picrate fr. alc. m. p. 94°.—Sol. in CS_2 gives with Br_4 a cryst. dibrom-deriv., m. p. 185°, d. s. alc.
87·8		† **Stearone, $(C_{17}H_{35})_2.CO$.**—Description w. Ketones, VII, A, p. 138.
88	270	**Perhydroanthracene, $C_{14}H_{24}$.**—Completely oxid. by CrO_3 (cf. Test 905-2).—Scarcely attacked by Br.
88		**Diphenyl-diacetylene, PhC⋮C.C⋮CPh.**—Long ndl., e. s alc.—Picrate light yellow rhombic cryst. fr. alc., m. p. 108°.—Adds Br (cf. Test 901).—Carbonized by h. conc. H_2SO_4.—Gives no ppt. w. ammon. $AgNO_3$ or CuCl.
88–9	a. 360	**Benzyl-pentaethyl-benzene, $C_7H_7.C_6.Et_5$.**—100 pt. alc. at 18° dissolve 0·9 pt.
89–90		**Ethylstilbene, p-Ph.$C_2H_2.C_6H_4$.Et.**—Lft. v. s. h. alc.—Unsat. (cf. Test 901)
91	343–5	**Diphenylfurfurane, $C_{16}H_{12}O$.**—E. s. alc. or eth.—S. conc. H_2SO_4 w. green color!
92	358–9	† **Triphenylmethane, $Ph_3.CH$.**—Lft. d. s. c., e. s. h. alc.; e. s. eth. or $CHCl_3$.—† Nitrate 0·1 grm. by dissolving in 2 cc. fuming HNO_3 without application of heat. Ppt. the yellowish trinitro-compound by diluting w. aq. Dissolve the ppt. in 10 cc. hot glacial acetic ac. and reduce by successive additions of small portions of Zn dust to the hot sol., until the strong red color that at first appears is nearly discharged. Decant, and add a few cgrm. PbO_2 to the solution. A very intense fuchsine-red color (pararosaniline) forms at once.—For color reaction w. $AlCl_3$ see Test 904.
92		**β-Dinaphthylmethane, $(C_{10}H_7)_2.CH_2$.**—M. p. of dibrom-derivative 164°.
92·5	a. 360	**Phenyl-di-p-xylyl-methane, Ph.CH.$(C_6H_3Me_2)_2$.**—E s. alc.—Sols. show bluish fluorescence.
92–3	265–75d.	**Acenaphthylene, $C_{12}H_8$.**—Golden yellow tbl. v. s. alc.—Picrate forms yellow ndl., v. d. s. c. alc.; m. p. 201°-2°.
94	323	**Dicamphenehydride, $C_{20}H_{34}$.**—Very stable.—Little attacked by CrO_3 mixture.
95	277·5	† **Acenaphthene, $C_{12}H_{10}$.**—Long ndl fr alc.—D. s. c. alc.; e. s. h. alc.—Identify by Test 911!
96·5–7		**Retenefluorene, $C_{17}H_{18}$.**—S. in alc. w. violet fluorescence.—Completely destroyed by CrO_3 in Āc sol.—HNO_3, G 1·43, gives a dinitro-compound, d s alc., m. p. 245°.
98·5	390	**Retene, $C_{18}H_{18}$.**—G $1·13^{16}/_{16}$.—Micaceous lft.—V. s h. alc.—Picrate forms orange ndl., m. p. 123°-4°.—Dibrom-compound, fr. Br+aq., tbl. fr. CS_2, m. p. 180°; alm. i. aq.
98·5		**Ethylene Diphenyl Eth., $C_2H_4.(OPh)_2$.**—D. s. c. aq.; e. s. h. aq. or eth.
100	340 (th. i.)	† **Phenanthrene, $C_{14}H_{10}$.**—Sbl easily.—Lft., s. in 10 pt. h. alc.—Identify by Test 916!
100·5	315c.	**Xanthene, $C_{13}H_{10}O$.**—Lft fr. alc.; alm. i. aq.; s. eth., s. conc. H_2SO_4 w. yellow color and green fluorescence.

(ORDER I, SUBORDER I.)

Melting-point (C.°).	Boiling-point (C.°).	**HYDROCARBONS, ETC.**—Colorless and Solid.
102		**Benzylfluorene, $C_7H_7.C_{13}H_9$.**
102–2·5	345c.	**β-Phenylnaphthalene, $Ph.C_{10}H_7$.**—Lft., c. s. h. alc.—Cryst. show blue fluorescence.—Vol. w. st.
105	a. 360	**β-Naphthyl Eth., $(C_{10}H_7)_2.O$.**—E. s. h. alc.; v. s. eth.—Picrate, orange lft. fr. warm eth., m. p. 122°.
105	290–300	**Sequoiene, $C_{13}H_{10}$.**—(In needles of Californian Sequoia gigantea.)—Odorless lft. w. faint bluish fluorescence.—Red picrate.
105–6	dist.	**Tetramethyl-m-stilbene, $Me_2.C_6H_3.C_2H_2.C_6H_3.Me_2$.**—S. h. alc.—Adds Br_2 (cf. Test 901).
108·5	313	**Anthracenedihydride, $C_{14}H_{12}$.**—Sbl. in ndl.—Warmed w. conc. H_2SO_4 gives SO_2 and anthracene (Test 912).
109	a. 360	**α-Dinaphthylmethane, $(C_{10}H_7)_2.CH_2$.**—S. in 15 pt. h., or 120 pt. c. alc.—Picrate (fr. h. $CHCl_3$ sol.) red-yellow ndl., m. p. 142°–3°.
109–10	217 (30 mm.)	**Fluoranthene, $C_{15}H_{10}$.**—Cryst. d. s. c. alc.—Equal parts of picric ac. and hydrocarbon in h. alc. give a stable picrate; long orange ndl., m. p. 182°–3°!
110	dist.	**α-Naphthyl Eth., $(C_{10}H_7)_2.O$.**—E. s. h. alc.; s. eth.—Picrate, m. p. 115°.—Sols. show pale bluish fluorescence.
111	315	**Benzhydrol Eth., Ph_4C_2O.**—Monoclinic cryst. fr. bz.; d. s. h. alc.—Boiled w. glacial Āc, Zn, and a little HCl gives tetraphenyl ethane.
112–13	295 (th. i.)	**Fluorene, $C_{13}H_{10}$.**—Lft. d. s. c. alc.—Unstable red-brown picrate fr. eth. sol., m. p. 79°–80°.—Diphenylene ketone is formed by oxid. w. CrO_3 mixture. The ketone may be dist. w. steam, slowly cryst. fr. alc., and mechanically separated from the unoxid. hydrocarbon (A, 166, 368).
113		**Dibenzyl-biphenyl, $C_{12}H_8.(C_7H_7)_2$.**—Lft., s. alc.
116	295	**γ-Methylenebiphenyl, $C_{13}H_{10}$.**—S. h. alc. w. pale-blue fluorescence.—Picrate forms blood-red ndl., m. p. 79°–81°.—CrO_3 mixture gives a quinone.
116–17		**Di-o-Oxyhydrobenzoïn-Diësoanhydride, $C_{14}H_{10}O_2$.**—Ndl. fr. alc.; e. s. alc. or eth.—Not attacked by h. dil. HCl or NaOH.
117–20	dist.	**Phenyl-p-tolylethylene, $Ph.CH:CH.(C_6H_4.Me)(1:4)$.**—Pearly lft., d. s. alc.—M. p. dibromide 186°–7°.
119		**Methyl-phenyl-anthracene, $Me.C_{14}H_8.Ph$.**—Yellowish cryst.—Dil. alc. sol. shows strong green-blue fluorescence.—CrO_3 oxid. to methyl-phenyl-oxanthranol.
120–0·5	dist.	**Phenylanthracenedihydride, $C_{20}H_{16}$.**—Hot alc. sol. shows blue fluorescence.—Brown-red picrate.—Oxid. by CrO_3 to phenyl-oxanthranol.
121	dist.	**p-Ditolyl, $C_7H_7.C_7H_7$.**—Glassy pr. fr. eth.
123·5		**Dimethyl-diphenyl-ethane, Me.CHPh.MeCH.Ph.**
124		**Distyrene, $(C_8H_8)_2$.**—Tbl.
124	306–7 (th. i.)	† **Stilbene, Ph.CH:CH.Ph.**—Tbl., d. s. alc.—Adds Br_2 hot.—Warmed w. CrO_3 mixture gives benzaldehyde (Test 113) and benzoic ac. (Test 312).
125		**Di-p-xylyl, $(C_6H_3.Me_2)_2$.**
126–7		**Hydrobenzoïn Anhyd., $C_{28}H_{24}O_2$.**—Cryst. fr. eth., i. aq.; e. s. h. alc.—Heated at 250°–70° gives benzaldehyde and stilbene.—Not vol. w. st.
128		**Diphenylene-tolyl-methane, $C_{12}H_8.CH.C_7H_7$.**—Silky ndl.—Gives no picrate.
128	292	**tert-Tributylbenzene, $C_6H_3.(CMe_3)_3$.**—Scales fr. alc.
128		**Methyl-ethyl-diphenyl-methane, (Me)(Et).C.Ph_2.**
129	298c.	**Hexaethylbenzene, C_6Et_6.**—May be cryst. fr. warm fuming H_2SO_4.

Melting-point (C.°).	Boiling-point (C.°).	**HYDROCARBONS, ETC.**—Colorless and Solid.
131	355 (12 mm.)	**Dibenzylmesitylene, $(C_7H_7)_2.C_6H.Me_3$.**—Cryst., v. d. s. alc.
132		**Metanethol, $(C_{10}H_{12}O)_x$.**—Sbl. at 115°–20°.—Not vol. w. st.—Ndl. fr. eth., d. s. c. alc.—Oxid. by CrO_3 gives acetic acid.
133·5–4·5		**Isoanthracene, $C_{14}H_{10}$.**—Pearly lft., d. s. c. alc.—CrO_3 in Āc sol. oxid. to a quinone w. m p. 211°–12°.
134·5		**p-Diethylstilbene, $(Et.C_6H_4)_2.C_2H_2$.**—Pearly lft., d. s. c. alc.—Oxid. gives terephthalic ac. (Tests 905 and 318–3.)
136		**1, 1-α-Dinaphthylethane, $(C_{10}H_7)_2.CH.CH_3$.**—Lft.—Solutions fluoresce violet.—S. c. alc.
141		**Naphthanthracene, $C_{18}H_{12}$.**—Sbl. in lft.—Shows intense yellowish-green fluorescence.—Forms a red picrate, ndl. fr. bz., m. p. 133°.
140–5		**Anisoïn, $(C_{10}H_{12}O)_x$.**—(Not identical with compound bearing same name in Genus VII.)—Small ndl. fr. eth.—Dec. on dist. to liq. metanethol.—Not attacked by dil. ac. or alk.
145	326	**Benzylduryl, $C_7H_7.C_6H.Me_4$.**—D. s. alc.
145·5	a. 360	**Biphenylene-phenyl-methane, $C_{13}H_9.Ph$.**—Ndl. d s. alc.—No picrate.—With Br in h. Āc sol. gives dibromide, m. p. 181°–2°.
148	250	**1, 4-Diphenylbutadiëne(1, 3), $C_{18}H_{14}$.**—Pearly tbl.—Tetrabromide melts at 230° d.
148–9	much a. 360	**Pyrene** (Phenylenenaphthalene), $C_{16}H_{10}$.—Tbl. s. h. alc.—Picrate, stable red ndl. fr. alc. sol. v. d. s. c. alc., m p. 222°.
148·5		Phenylene-diphenyl-methane, $C_6H_4.C.Ph_2$.—Oxid by CrO_3 mixture to benzophenone (Test 714) and benzoic ac (Test 312).
149		1, 1-Dinaphthylethylene, $(C_{10}H_7)_2.C_2H_3$.—Silky ndl. s h alc.
152–3	417	Phenylanthracene, $Ph.C_{14}H_9$.—Lft. s. h. alc.—Solutions show blue fluorescence.—Gives red cryst. picrate.
154	a. 360	**$\alpha\alpha$-Binaphthyl, $(C_{10}H_7)_2$.**—Tbl. s. alc.—Unstable red-brown picrate fr. bz., m. p. 145°, decomposes in air.
155–6		**Benzylphenanthrene, $C_{21}H_{16}$.**—V. d. s. alc.—Oxid. by CrO_3 in Āc sol. to phenanthrenequinone (Test 1013) and benzoic ac. (Test 312).
157	dist.	**Tetramethyl-p-stilbene, $(Me_2.C_6H_3)_2.C_2H_2$.**—Lft. d. s. h. alc
160		**1, 2-α-Dinaphthylethane, $(C_{10}H_7)_2.(CH_2)_2$.**—Greenish-yellow 6-sided tbl.; d. s. alc. w. green-blue fluorescence.
161		**Hexamethylstilbene, $(Me_3.C_6H_2)_2.C_2H_2$.**—S. alc.—Picrate garnet cryst. fr. bz., m. p. 123°.—Adds Br_2.
161		**α-Dinaphthostilbene, $(C_{10}H_7)_2.C_2H_2$.**—D. s. alc. or eth.; e. s. bz.—CrO_3 gives α-naphthoic ac.
161	dist.	**2, 6(β)-Dinaphthylene Oxide, $C_{20}H_{12}O$.**—Silvery lft., d. s. h. alc.; e. s. eth.; s. conc. H_2SO_4 w. red color (dif. fr. α), which changes to violet and dark blue on heating, and on dilution w. aq. gives an orange-red fluorescent sol.—Picrate vermilion ndl., m. p. 135°.
162	360	**Bi-phenylphenylene-methane, $(Ph.C_6H_4)_2.CH_2$.**—V. d. s. alc.—S. w. blue color in conc. H_2SO_4.—Gives no picrate.—CrO_3 oxid. to a ketone.
164	264	**Hexamethylbenzene, C_6Me_6.**—V. d. s. tbl. fr. alc.—Sbl. in lft.—Picrate, yellow rectangular tbl., m. p. 170° (dec. by alc.).
169–70	dist.	**s-Triphenylbenzene, $Ph_3.C_6H_3$.**—G. 1·206.—D. s. alc.—Oxid. by CrO_3 in Āc sol. to benzoic ac. (Test 312).—Br comp. fr. sol. in CS_2, m. p. 104°.
171		**Tri-p-tolylbenzene, $(C_7H_7)_3.C_6H_3$.**—Alm. i. c. alc.; cryst. fr. $CHCl_3$.
171–1·5		**s-Tetramethylanthracenehydride, $C_{18}H_{20}$.**—Alm. i. alc.; tbl. fr. bz.—Oxid. by CrO_3 in Āc sol. to dimethylanthraquinone, m. p. 236°.—Picrate red-brown ndl., m. p. 165°.

Melting-point (C.°).	Boiling-point (C.°).	**HYDROCARBONS, ETC.**—Colorless and Solid.
173–4	dist. 350–1	† **o-Benzophenone Oxide (Xanthone)**, $C_{13}H_8O_2$.—Long ndl. fr. alc., i. c. aq.; s. h. alc.; d. s. eth.; s. conc. H_2SO_4 w. yellow color and intense light-blue fluorescence!—(Does not react w. phenylhydrazine or hydroxylamine.)—Fusion w KOH gives salicylic acid and phenol!—CrO_3 mixture oxid. to CO_2.
173		**Phthalacene**, $C_{21}H_{16}$.—D. s. h. alc.—W. an equal weight of Br in Āc sol. gives brom-derivative w. m. p. 184°.
175		**Tetraphenylfurane (Lepidene)**, $Ph_4.C_4O$.—Scales, i. aq.; s. 170 pt. h. alc., 52 pt. c. eth., or 85 pt. c. bz.—Dibrom-derivative (by heating Āc sol. w. Br), lft., m. p. 190°.
176·4		† **Camphor**, $C_{10}H_{16}O$.—B. p. 205·3°.—Description w. Ketones, VII, A, p. 139, and Test 715.
179	304–5	**p_2-Dimethylstilbene**, $(Me.C_6H_4)_2.C_2H_2$.—Lft. d. s. h. alc.—Oxid. by CrO_3 (Test 905–2) gives terephthalic ac. (Test 318–3).
181–1·5		**9, 10-Dimethylanthracenehydride**, $C_{14}H_{10}.Me_2$.—Yellow ndl., s. alc.—Oxid. by CrO_3 in Āc to anthraquinone (Test 1011).
184		**α-Dinaphthylene Oxide**, $C_{20}H_{12}O$.—I. aq. or alkalies; d. s. alc.; e. s. eth.—Picrate, dark-red ndl., e. s. alc. or bz., m. p. 173°.
187		**ββ-Binaphthyl**, $(C_{10}H_7)_2$.—D. s. alc.—Picrate orange ndl., m. p. 184°–5° (B. 20, 662).
187–8	a. 360	**Dibiphenylene-ethylene**, $(C_{12}H_8)_2.C_2$. — Yellowish-red ndl. — Heated w. Zn dust gives fluorene.—The picrate forms unstable red-brown ndl. fr. alc.
188		**Tri-p-xylylmethane**, $CH.(C_6H_3Me_2)_3$.—Grains, s. alc.
189		**Benzal-β-dinaphthyl Oxide**, $C_7H_6.C_{20}H_{12}O$.—D. s. alc. or eth.; i. alkalies.
196		**Isochrysene**, $C_{18}H_{12}$.—Long ndl.—Gives no picrate.
199–200		**α-Methylanthracene**, $C_{14}H_9.Me$.—Gives unstable red picrate.—Oxid. by CrO_3 to 1-methylanthraquinone.
199–200		**β-Methylanthracene**, $C_{14}H_9.Me$.—Gives unstable red picrate.—Oxid. by CrO_3 in h. Āc to anthraquinonecarbonic ac.
203		**Isomethylanthracene**, $C_{14}H_9.Me$.—Oxid. by CrO_3 in Āc gives γ-anthraquinonecarbonic ac.
204–5		**α-Benzpinacoline**, $C_{26}H_{20}O$.—Stable at 350°.—Alm. i. c. alc.; e. s. bz. or CS_2.—Does not react w. KOH or phenylhydrazine.—CrO_3 oxid. gives benzophenone (cf. Tests 905–2 and 714).
205		**p-Diphenylbenzene**, $Ph_2.C_6H_4$.—B. p. 383°.—Lft., v. d. s. h. alc.—Gives no picrate.—Oxid. by CrO_3 to terephthalic ac. (Tests 905–2 and 318–3).
207		**Photoanethol**, $C_{10}H_{12}O$.—(Fr. anethol in sunlight.)—Odorless, tasteless, pearly lft.—Sbl.—D. s. alc.; v. d. s. eth.
209		**s-Tetraphenylethane**, $Ph_2.CH.CH.Ph_2$.—B. p. 379°–83° c.—Ndl. fr. $CHCl_3$.—G. 1·182.—D. s. h. alc.—Gives no picrate.—CrO_3 oxid. to benzophenone (Test 714).
216·5c.		† **Anthracene**, $C_{14}H_{10}$.—B. p. 351°.—Lft. or tbl., usually yellowish, but when perfectly pure, colorless w. beautiful violet fluorescence.—D. s. h. alc.—Gives a deep-red unstable picrate (fr. bz. sol.), e. s. bz., and melting at 138°.—Identify by Test 912!
215		**Tetratolylethylene**, $(C_7H_7)_4.C_2$.
221		† **Tetraphenylethylene**, $Ph_4.C_2$.—B p. 415°–25°.—V. d. s. alc.; e. s. bz.—CrO_3 in Āc sol. gives benzophenone (Test 714).—† Fails to give Test 901 for unsaturation, and is not acted upon by alkaline permanganate in Test 304.
222		**1, 3, 6-Trimethylanthracene**, $C_{14}H_7.Me_3$.—D. s. alc.
227		**1, 4, 6-Trimethylanthracene**, $C_{14}H_7.Me_3$.—D. s. alc.—CrO_3 in Āc sol. gives trimethylanthraquinone.
231–2		**Dimethylanthracene**, $C_{14}H_8.Me_2$.—CrO_3 in Āc oxid. to a quinone w. m. p. 161°–2°.
243		**1, 2, 4-Trimethylanthracene**, $Me_3.C_{14}H_7$.
244–5		**Tetraxylylethylene**, $(Me_2.C_6H_3)_4.C_2$.—Yellowish lft.

Melting-point (C.°).	**HYDROCARBONS, ETC.**—Colorless and Solid.
246	**2, 3-Dimethylanthracene, $Me_2.C_{14}H_8$.**—Lft. w. blue-green fluorescence.
250	**Chrysene, $C_{18}H_{12}$.**—Scales w. red-violet fluorescence.—V. d. s. h. alc.; V. d. s. eth. or CS_2.—The picrate fr. bz. sol. of components cryst. in long red ndl., m. p. 273°; it is not stable in alc. sol.—CrO_3 oxid. to chrysoquinone, which dissolves in conc. H_2SO_4 w. deep-blue color.
253	**1, 2-(β)-Dinaphthylethane, $(C_{10}H_7)_2.C_2H_4$.**—Pearly tbl., d. s. h. alc.—Solutions fluoresce blue-violet.
254–5	**Hydroxylepidene, $C_{28}H_{22}O_2$.**—S. 100 pt. h. glacial Āc; s. after long boiling in alc., then melting at 260°–1°; i. eth. or alkalies.—Said not to give a phenylhydrazone or oxime. (Position in classification open to question.)—W. conc. HCl at 130°–40° gives lepidene.
268	**Carbopetrocene, $C_{24}H_8$.**—Lft. or ndl. i. c. alc. or eth.; s. CS_2 or h. bz.—Gives orange-colored picrates.
abt. 280d.	**Tetramethylanthracene, $C_{18}H_{18}$.**
300	**Bianthranyl, $C_{28}H_{18}$.**—Lft. fr. toluene.—Convert into dinitro-compound, m. p. 337° d. (B. 20, 2433).
307–8	**Benzerythrene, $C_{24}H_{18}$(?).**—Lft. fr. bz.—Alm. i. alc.; v. d. s. c. bz.—Dissolves w. green color in conc. H_2SO_4.
315	**Tetraphenylethylene Dioxide, $C_{26}H_{16}O_2$.**—Sbl.—Ndl. fr. bz., i. alc.; s. conc. H_2SO_4 w. yellow color.—Adds Br_2.—Boiled w. dil. HNO_3 gives xanthone.—Sols. show bluish-green fluorescence.
364c.	**Picene, $C_{22}O_{14}$.**—B. p. 518°–20°.—Colorless lft. w. blue fluorescence.—D. s. h. bz. or $CHCl_3$; s. conc. H_2SO_4 w. green color.—Oxid. by CrO_3 in Āc sol. to a quinone. Sol. in $CHCl_3$ gives with Br a comp., m p. 294°.
a. 360	**Truxene, $C_{18}H_{12}$.**—Tbl. fr. h. xylene.—Alm. i. most solvents.—CrO_3 mixture gives a deep yellow i. quinone.

GENUS IX, HYDROCARBONS.

DIVISION B, SECTION 1,—LIQUID HYDROCARBONS WITH SPECIFIC GRAVITY LESS THAN 0·85 AT 20°/4° THAT DO NOT GIVE TESTS 901 TO 903 IN THE COLD.

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS.**—Colorless Liquids with Specific Gravity less than 0·85 at 20°/4° that do not give Tests 901 to 903.
-153		**Methane, CH_4.**
-86	$0\cdot446(0)$	**Ethane, C_2H_6.**
-38–9	$0\cdot535(0)$	**Propane, $Me.CH_2.Me$.**
abt. 0	$0\cdot603(0)$	**Trimethylmethane, $Me_3.CH$.**
$+1$	$0\cdot60(0)$	**Butane, C_4H_{10}.**—S. in 18 vol. c. alc.
9·5		**Tetramethylmethane, $Me_4.C$.**—M. p. $-20°$.
31	$0\cdot628^{13\cdot7}/_4$	**2-Methylbutane, $Me_2.CH.CH_2.Me$.**
37	$0\cdot634(15)$	**Pentane, C_5H_{12}.**
39–42		**Methylcyclobutane, $Me.C_4H_7$.**—Does not add HI cold.
49·7	$0\cdot649^{20}/_0$	**Trimethyl-ethyl-methane, $Me_3.C.Et$.**
50–1	$0\cdot751^{20\cdot5}/_4$	**Cyclopentane, C_5H_{10}.**—Br substitutes, but only at a high temperature.—Oxid. by HNO_3 gives glutaric ac., etc.
58	$0\cdot668(17\cdot5)$	**Diisopropyl, $Me_2.CH.CH.Me_2$.**
62	$0\cdot677(0)$	**2-Methylpentane, $Me.(CH_2)_2.CH.Me_2$.**
64	$0\cdot677^{20\cdot5}/_4$	**Methyldiethylmethane, $Me.(Et_2).CH$.**
69	$0\cdot658(20\cdot9)$	† **Hexane, C_6H_{14}.** † No evidence whatever of chem. action in Tests 901–903.
71–2	$0\cdot750^{21}/_4$	**Methylcyclopentane, $Me.C_5H_9$.**—Not easily attacked by warm $HNO_3+H_2SO_4$.—Fuming HNO_3 oxid. to formic, acetic, and glutaric acids.
80·8	$0\cdot790^{20}/_4$	**Cyclohexane (Hexanaphthene), C_6H_{12}.**—M. p. 4·7°.—"Not attacked by cold mixture of equal vol. conc. H_2SO_4 and fuming HNO_3." "Attacked by Br at 100°–110°"
86–7	$0\cdot711(0)$	**Dimethyldiethylmethane, $Me_2.C.Et_2$.**
90·3c.	$0\cdot682(17\cdot5)$	**2-Methylhexane, $Me_2.CH.(CH_2)_3.Me$.**
91	$0\cdot690(20)$	**3-Methylhexane, $Me.CH(Et).(CH_2)_2.Me$.**
94	$0\cdot754^{20}/_4$	**1, 3-Dimethylcyclopentane, $Me_2.C_5H_8$.**
95–8	$0\cdot689(27)$	**Triethylmethane, $Et_3.CH$.**
98·4	$0\cdot689(14\cdot9)$	**Heptane, C_7H_{16}.**
101–2	$0\cdot769(^{20}/_4)$	**Hexahydrotoluene (Heptanaphthene), $Me.C_6H_{11}$.**—"Not attacked by *c.* nitro-sulphuric" ac. W. Br and $AlBr_3$ gives pentabromtoluene, m. p. 282°.
108	$0\cdot711^{0}/_4$	**2, 5-Dimethylhexane, $Me_2.CH.CH_2.CH_2.CH.Me_2$.**
118–9	$0\cdot759(^{20}/_0)$	**Hexahydro-m-xylene (Octonaphthene), $Me_2.C_6H_{10}$.—Cf. p. 186, Section 2.**
118 (th. i.)	$0\cdot809(20)$	**Cycloheptane, C_7H_{14}.—Heated w. Br in sealed tube gives pentabromtoluene.**
120·5–21	$0\cdot769(^{20}/_4)$	**Hexahydro-p-xylene, $Me_2.C_6H_{10}$.—Cf. p. 186, Section 2.**

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS.**—Colorless Liquids with Specific Gravity less than 0·85 at 20°/4° that do not give Tests 901 to 903.
124		**Methylethylcyclopentane**, $Me.C_5H_8.Et$.
125·5c.	0·719$^{0}/_{4}$	† **Octane**, C_8H_{18}. † No evidence whatever of chem. action in Tests 901–903 !
129·5–31·5	0·725(24·7)	**β-Nonane**, C_9H_{20}.
135–6	0·767($^{20}/_{0}$)	**Hexahydropseudocumene (Nonaphthene)**, $Me_3.C_6H_9$(1, 3, 4).
135–8		**Mesitylenehexahydride**, $Me_3.C_6H_9$(1, 3, 5).
135–7	0·742(12·4)	**α-Nonane**, C_9H_{20}.
147–50	0·787(20)	**Hexahydrocumene**, $Pr.C_6H_{11}$.
149·7c.	0·718$^{20}/_{4}$	**Nonane**, C_9H_{20}.—M. p. −51°.
159·5	0·736$^{9·8}/_{4}$	† **2, 7-Dimethyloctane**, $Me_2.CH(CH_2)_4.CH.Me_2$.—S. in 12 pt. c. glacial Āc.
159–62	0·746(22)	**3, 6-Dimethyloctane**, $Et.CHMe.(CH_2)_2.CH(Me)Et$.—**Opt. active.**
160–62	0·783(18)	**Dekanaphthene**, $C_{10}H_{20}$. (Fr. petroleum.)
160–62	0·788$^{20}/_{0}$	**α-Terpenetetrahydride**, $C_{10}H_{20}$.—"Not attacked by conc. H_2SO_4. With fuming H_2SO_4 heat is evolved, but the hydrocarbon is apparently not changed."
164	0·793$^{19}/_{0}$	**β-Terpenetetrahydride**, $C_{10}H_{20}$.—"Br substitutes when hot.—Nitro-sulphuric ac. gives no cryst. nitro product."
abt. 170	0·80(15)	**Hexahydro-p-cymene ("Terpane," "Terpilenehydride")**, $C_{10}H_{20}$.—"Is not attacked by cold fuming HNO_3, fuming H_2SO_4, or Br."
173c.	0·730(20)	**Decane**, $C_{10}H_{22}$.—M. p. −30°–32°.
173–80	0·837($^{19}/_{0}$)	**Naphthalenedecahydride**, $C_{10}H_{18}$.
abt. 190	abt. 0·805(20)	**Undekanaphthene**, $C_{11}H_{22}$. (Fr. petroleum.)
194·5c.	0·741$^{20}/_{4}$	**Undecane**, $C_{11}H_{24}$.—M. p. −26·5°.
197	0·801(20)	**Dodekanaphthene**, $C_{12}H_{24}$. (Fr. petroleum.)
208–10	0·813(20)	**Tridekanaphthene**, $C_{13}H_{26}$. (Fr. petroleum.)
214·5c.	0·751$^{20}/_{4}$	**Dodecane**, $C_{12}H_{26}$.—M. p. −12°.
234	0·757$^{20}/_{4}$	**Tridecane**, $C_{13}H_{28}$.—M. p. −6·2°.
240–46	0·819(17)	**Tetradekanaphthene**, $C_{14}H_{28}$. (Fr. petroleum.)
246–8	0·829(17)	**Pentadekanaphthene**, $C_{15}H_{30}$. (Fr. petroleum.)
252·5c.	0·765$^{20}/_{4}$	**Tetradecane**, $C_{14}H_{30}$.—M. p. +5·5°.
268c.	0·792(14)	**7, 8-Dimethyltetradecane**, $C_{16}H_{34}$.—**Still liq. at −30°.**
270·5c.	0·769$^{20}/_{4}$	**Pentadecane**, $C_{15}H_{32}$.—M. p. 10°
287·5c.	0·775$^{18}/_{4}$	**Hexadecane**, $C_{16}H_{34}$.—M. p. 18°.
303	0·777$^{22}/_{4}$	**Heptadecane**, $C_{17}H_{36}$.—Does not give Test 901–3.
317c.	0·777$^{28}/_{4}$	**Octadecane**, $C_{18}H_{38}$. —M. p. 28°.—Does not give Test 901–3.

GENUS IX, HYDROCARBONS.

DIVISION B, SECTION 2,—LIQUID HYDROCARBONS AND LIQUID ALIPHATIC ETHERS WITH SPECIFIC GRAVITY LESS THAN 0·85 AT 20°/4° THAT ARE ATTACKED OR DISSOLVED EITHER IN TEST 901, 902, OR 903.

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS, ETC.** — Colorless Liquids with Specific Gravity less than 0·85 at 20°/4° that are attacked or dissolved either in Test 901, 902, or 903.
−102·7	0·610	**Ethylene, $CH_2:CH_2$.**—† Easily absorbed by liq. Br, giving $C_2H_4Br_2$, b. p. 130°, m. p. +9·5°.
−85	0·451(0)	**Acetylene, $CH \vdots CH$.**—V. d. s. aq.—† Apply Test 906 w. ammon. CuCl sol.! (Dull-red ppt.)—Absorbed in Br gives liq. tetrabromide, b. p. 124°–6° (15 mm.).
−50·2		**Propylene, $Me.CH:CH_2$.**—† The gas is freely absorbed by c. conc. H_2SO_4 or liq. Br.—Dist. of the H_2SO_4 sol. largely diluted w. aq. gives isopropyl alc. (cf. Test 818).—B. p. of dibromide 141·5° c.!
abt. −35		**Cyclopropane, $(CH_2)_3$.**—Absorbed slowly by conc. H_2SO_4 or Br. —B. p. of dibromide 165°; G. $1\cdot923^{17\cdot6}/_4$.
+1		**Butadiëne(1, 3), $CH_2:CH.CH:CH_2$.**
1·5	0·635(13·5)	**cis-Butene(2), $MeCH:MeCH$.**—B. p. of dibromide 158°.—Not absorbed by conc. $H_2SO_4 + \frac{1}{2}$ vol. aq.
2·5		**trans-Butene(2), $Me.CH:HC.Me$.**—M. p. of dibromide 161°.
4–5	0·691(20)	**Methylcyclopropane, $Me.C_3H_5$.**
14·5	0·65(−20)	**Caoutchene, C_4H_6.**—M. p. −10°.
18		**Ethylacetylene, $Et.C \vdots CH$.**—Gives Test 906 w. ammon. CuCl.—Bromide, $C_4H_6Br_4$, cryst. solid.
18–19		**Butadiëne(1, 2), $CH_2:C:CH.Me$.**—Odor like garlic.
21·2		**Isopropylethylene, $Me_2CH.CH:CH_2$.**—I. at 0° in 2 vols. conc. H_2SO_4 and 1 vol. aq.
21	$0\cdot660^{20}/_4$	**1, 1-Dimethylcyclopropane, $Me_2C.(CH_2)_2$.**—Easily attacked by Br, but "rather stable toward 1% $KMnO_4$."—Soluble at 0° in 2 vols. conc. H_2SO_4 and 1 vol. aq.
28		**Butine(2), $MeC \vdots CMe$.**—Strong odor.—B. p. of dibromide 147°–8°. —Shaking w. conc. HCl polymerizes to hexamethylbenzene.
28–9	0·685(0)	**Isopropylacetylene, $Me_2.CH.C \vdots CH$.**—Gives Test 906 w. ammon. CuCl.
31–2	0·670(0)	**uns.-Methylethylethylene, $MeCEt:CH_2$.**
35·8	$0\cdot691^{0}/_4$	**Isoprene, $CH_2:CH.CMe:CH_2$.**—Very unstable.—Treated w conc. HCl and distilled w steam leaves rubber-like mass!
36·5		**s-Methylethylethylene, $MeCH:CHEt$.**—HI gives methylpropylcarbinol, b. p. 145°
37·1	$0\cdot685^{0}/_4$	**Trimethylethylene, $Me_2C:CHMe$.**—Polymerized by conc. H_2SO_4 —S. in 2 vol. H_2SO_4 + 1 vol. aq.
38–9		**3, 3-Dimethylbutine(1), $Me_3C.C \vdots CH$.**
39–40		**Propylethylene, $PrCH:CH_2$.**
40·5–41·5	$0\cdot694^{20}/_4$	**2-Methylbutadiëne(2, 3), $Me_2.C:C:CH_2$.**

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS, ETC.** — Colorless Liquids with Specific Gravity less than 0·85 at 20°/4° that are attacked or dissolved either in Test 901, 902, or 903.
42		**Piperylene, CH_2:CH.CH_2.CH:CH_2.**—The tetrabromide cryst. fr. alc in pearly ndl., m. p. 114·5°.
42·5	0·805$^{19}/_4$	**Cyclopentadiëne(1, 3), C_5H_6.**—Conc. H_2SO_4 or HNO_3 attacks violently.—Reduces ammon. $AgNO_3$ sol.—Polymerizes easily to dicyclopentadiëne, m. p. 32·9°.
45		**Cyclopentene, C_5H_8.**
48–9		**Propylacetylene, PrC⋮CH.**—Gives Test 906 w. ammon. CuCl and $AgNO_3$.
50		**Valylene, C_5H_6.**—Odor of garlic.—Test 906 gives yellow ppt.—Br gives cryst. hexabromide.
55·5–6		**Valerylene, C_5H_8.**—Test 906 gives no ppt.—Heated w. dil. H_2SO_4 gives methyl propyl ketone.
59·5c.	0·690(20·7)	**Diallyl, (CH_2:CH.CH_2)$_2$.**—Odor pungent.—H_2SO_4 attacks w. violence.—Br gives cryst. tetrabromide, m. p. 63°.
60		**Pirylene, C_5H_6.**—Peculiar odor.—Test 906 gives no ppt.
65–7	0·687(19)	**Dimethylethylethylene, Me_2C:CHEt.**—Gives iodide w. HI, b. p. 142°.
68	0·670(0)	**s-Methylpropylethylene, Pr.CH:CH.Me.**—S. in 3 vol. c. H_2SO_4+ 1 vol. aq.; the sol. is ppt'd by aq.
68–70		**Butylethylene, Bu.CH:CH_2.**
69–71	0·785(20)	**1-Methylcyclopentene(2), Me.C_5H_7.**—Oxid. by $KMnO_4$ gives α-methylglutaric ac.
abt. 70		**Butylacetylene, BuC⋮CH.**—Gives Test 906.
70	0·858(18·2)	**Diallylene, C_3H_5.CH_2.C⋮CH (?).**—Test 906 gives yellow-green ppt.—Alc. $AgNO_3$ gives ppt. of Ag compound.
69·5–71	0·698(19)	**Methylethylpropylene, Me(Et)C:CH.Me.**
70–1	0·731(0)	**3-Methylpentadiëne(1, 2), Et.C.Me:C:CH_2.**
70·3	0·763(0)	**Methyl Butyl Eth., Me.O.Bu.**—See Test 907!
71–2	0·750$^{21}/_4$	**Methylcyclopentane, C_6H_{12}.**—Cf. IX, B, 1.
71–2·5	0·732(0)	**2-Methylpentine(3), Me_2.CH.C⋮C.Me.**—Adds HBr.
70–74		**Methyl Isocrotyl Eth., Me_2.C:CH.O.Me.**—Dec by 2-3 hrs. heating at 140° w. 1% H_2SO_4 giving methyl alcohol and isobutyl aldehyde.
72	0·776$^{20}/_0$	**1-Methylcyclopentene(1), Me.C_5H_7.**
72–4	0·714(12)	**Hexadiëne(1, 3), Et.CH:CH.CH:CH_2.**
72–4		**β-Ethyldivinyl, CH_2:CEt.CH.CH_2.**
73	0·712(0)	**Tetramethylethylene, Me_2.C:C.Me_2.**—S in 2 vols. conc. H_2SO_4+ 1 vol. aq.—Acetone is among products of oxidation by c. dil. CrO_3 sol. (cf. Tests 702 and 711).
75–80	0·719(21)	**2, 3-Dimethylpentene(2), Me_2.C:C(Me)Et.**
77–8	0·730(0)	**2-Methylpentadiëne(2, 3), Me_2.C:C:CH.Me.**—W. Br in CS_2 gives $C_6H_6Br_3$
78–80	0·751	**Ethyl Isobutyl Eth., Et.O.C_4H_9.**—See Test 907!
78–80		**2, 2, 3-Trimethylbutene(3), Me_3.C.CMe:CH_2.**—Odor of camphor and turpentine
78–83	0·825(0)	**Hexadiïne(1, 4), Me.C⋮C.CH_2.C⋮CH.** — Polymerizes readily.—Gives Test 906.
82–5		**1, 2-Dihydrobenzene, C_6H_8.**
83–4	0·714(0)	**2, 5-Dimethylpentene(2), Me_2.C:CH.CH.Me_2.**—Adds HI easily.
83–4	0·738(13)	**Methylpropylacetylene, MeC⋮CPr.**—CrO_3 mixture oxid to acetic and butyric ac. (cf. Test 702).—Br reacts violently.—Prolonged shaking w. 5 pt conc H_2SO_4+1 pt. aq. gives methyl butyl ketone.
85–6		**1, 4-Dihydrobenzene, C_6H_8.**

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86–7	0·819(0)	**Hexadiïne(1, 5), $CH\vdots C.CH_2.CH_2.C\vdots CH$.**—Ammon. CuCl in Test 906 gives greenish-yellow ppt.—Alc. $AgNO_3$ gives white ppt. —Adds Br_4 violently.
92	0·752(20)	**Ethyl Butyl Eth., Et.O.Bu.**—See Test 907!
92–4		**Ethyl Isocrotyl Eth., $Me_2.C:CH.O.Et$.**—Unsat.—Dec. by heating w. 1% H_2SO_4 giving isobutyric ald. and C_2H_5OH.
96–8	$0{\cdot}748^0/_0$	**3-Ethylpentadiëne(1, 2), $Et_2.C:C:CH_2$.**
97–8	$0{\cdot}725^{15}/_4$	**3-Ethylpentene(2), $Et_2C:CHMe$.**
98		**Heptene(2), $Me.(CH_2)_3.CH:CHMe$.**—CrO_3 mixture oxid. to valerianic and acetic acids. (Cf. Test 702.)—In the cold adds fuming HCl.
98–9	0·703(19·5)	**Heptene(1), $Me.(CH_2)_4.CH:CH_2$.**—Does not unite w. cold fuming HCl.
102	0·751(0)	**Œnanthylidene, $Me.(CH_2)_4.C\vdots CH$.**—Ammon. CuCl (Test 906) gives yellow ppt.; ammon. $AgNO_3$ also gives ppt.—Gives a liq. dibromide.
102·5c.	0·715(25)	**Diisobutylene, $Me_2.C:CH.CMe_3$.**—CrO_3 mixture, cold, oxid. to acetone, etc. (cf. Test 702).—Adds HCl or HI at 100°.
103–4	0·803(20)	**Heptine, C_7H_{12}.**—Odor peculiar.—Absorbs O.—HNO_3 attacks violently.—H_2SO_4 polymerizes to diheptine, b. p. 247°.—Adds Br.—Does not give Test 906.—(Fr. dist. of rosin.)
105	$0{\cdot}814^0/_4$	**Toluenetetrahydride, $Me.C_6H_8$.**—Nitrated by nitrosulphuric ac.
105–6	0·760(0)	**Ethylpropylacetylene, $PrC\vdots CEt$.**—H_2SO_4 gives butyrone.
105–8		**Dihydrotoluene, $Me.C_6H_7$.**
108·5	0·796(15)	**1, 1, 2-Trimethylcyclopentene, C_8H_{14}.**—Faint odor like camphor and turpentine.
111–3	0·763(0)	**Methylbutylacetylene, $Me.C\vdots C.C_4H_9$.**—Alc. $AgNO_3$ gives no ppt.
111–4		**Ethyl Valeryl Eth., $Me.C(Et):CH.O.Et$.**—Heated w. 1% H_2SO_4 at 130°–40° gives methylethylacetaldehyde and C_2H_5OH.
112	0·764(18)	**Ethyl Isoamyl Eth., $Et.O.C_5H_{11}$.**—See Test 907!
113–4		**2, 5-Dimethylhexadiëne(1, 5), $CH_2:C(Me).CH_2.CH_2.C(Me):CH_2$.**
114–5	0·841(0)	**Cycloheptene, C_7H_{12}.**
115		**Heptone, C_7H_{10}.**—Gives oily hexabromide, $C_7H_{10}Br_6$.
115·5		**s-Dimethyldiethylethylene, $Me_2C:CEt_2$.**
116–8		**Hexenyl Eth., $(C_6H_{11})_2.O$.**—Oil w. very pungent odor; **i. aq.**
116–8	0·741(22)	**2-Methylheptadiëne (4, 6), C_8H_{14}.**
117·1	0·777(0)	**Propyl Butyl Eth., Pr.O.Bu.**—See Test 907!
116–20		**s-Diisopropylethylene, $Pr.CH:CH.Pr$.**
117–9		**Octadiëne(2, 6), C_8H_{14}.**
118–9	$0{\cdot}759(^{20}/_0)$	**Hexahydro-m-xylene, $Me_2.C_6H_{10}$.**—Hot nitrosulphuric ac. gives trinitro-m-xylene, m. p 172°–4°
120.5–21	$0{\cdot}769^{20}/_4$	**Hexahydro-p-xylene, $C_6H_{10}(CH_3)_2$.**—E. s. on warming in mix. of HNO_3 and H_2SO_4
120		**Allyl Isoamyl Eth., $C_3H_5.O.C_5H_{11}$.**
120–1	0·756(21)	**sec.-Butyl Eth., $(Me(Et).CH)_2O$.**
122–2·5	0·762(15)	**Isobutyl Eth., $Bu_2.O$.**—See Test 907!
122–3	0·760(14)	**4-Ethylhexadiëne(1, 4), $CH_2:CH.CH_2.CEt:CHMe$.**—Absorbs O fr. air slowly.—CrO_3 mixture oxid. to $\bar{A}c$ and propionic ac. (Tests 905–2 and 311)
123·5	0·799(0)	**Glycol Diethyl Eth., $C_2H_4.(OEt)_2$.**—See Test 907!
124·6	0·722(17)	**Octene(1), $C_6H_{13}.CH:CH_2$.**
131–2	0·770(0)	**Octine(1), $C_6H_{13}.C\vdots CH$.**

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132–4	0·773(18)	**2, 5-Dimethylhexadiëne(2, 4), $Me_2C:CH.CH:CMe_2$.**—M. p. + 6°.—Very unstable, absorbing O rapidly fr. the air.—Polymerizes on keeping.—Gives liquid tetrabromide.
132–4	0·828(20)	**m-Dihydroxylene, $Me_2.C_6H_6$.**—Conc. HNO_3 gives nitro-m-xylene.
133–4		**Octine(2), $Me.(CH_2)_4.C:C.Me$.**—The tetrabromide is oily.
133–5		**Octone, C_8H_{12}.**—Absorbs O fr. air.—Br or HCl gives a resin.
134–5		**o-Dihydroxylene, $Me_2.C_6H_6$.**—Odor like camphor.—Quickly oxid. in air to a resin.—Adds HCl in eth. sol.
134·5–5·5		**p-Dihydroxylene, $Me_2.C_6H_6$.**—Odor like turpentine.—HBr gives cryst. addition product.
134–7		**Ethyl Hexyl Eth., $Et.O.C_6H_{13}$.**—See Test 907!
abt. 135	0·803(20)	**Campholene, C_9H_{16}.**—Odor like turpentine.—Absorbs Br_2 in dil $CHCl_3$ sol.
138	0·798(22)	**Trimethylcyclohexene, C_9H_{16}.**
139·5c.	$0{\cdot}743^{20}/_0$	**Nonylene, C_9H_{18}.**—(Several isomers boiling between 140° and 150°.)
141	0·769(20)	**Butyl Eth., Bu_2O.**—See Test 907!
140–1	$0{\cdot}835^{25}/_{25}$	**Trimethyleneglycol Diethyl Eth., $(CH_2)_3.(OEt)_2$.**—Fruity odor.—I. aq.
141·5		**2-Methyloctene(1), $Me.C(C_6H_{13}):CH_2$.**—Odor aromatic.
142–3	0·757(20)	**2, 6-Dimethylheptadiëne(2, 6), C_9H_{16}.**
145	0·831(15)	**Octylene Oxide, $C_{18}H_{16}O$.**
145–50		**Decone, $C_{10}H_{16}$.**—Odor like turpentine.—Absorbs O rapidly.
147·5–9·5		**Propylhexamethylene, $Pr.C_6H_{11}$.**
149·8	0·795(0)	**Methyl Heptyl Eth., $Me.O.C_7H_{15}$.**—See Test 907!
150		**Decenylene and Rutylene, $C_{10}H_{18}$.**
150–2		**1, 2-Methylethylcyclohexane, $Me.C_6H_{10}.Et$.**
153		**1, 2-Dimethylcycloheptane, $Me_2.C_7H_{12}$.**
154–6	0·772(20)	**Diamylene, $C_{10}H_{20}$.**
155–7		**Nonone (Carpene), C_9H_{14}.**—Oxid. to a resin in the air.
156	0·86(20)	**Pinene (Terebenthene), $C_{10}H_{16}$.**—Cf. (IX, B, 3).
158	$0{\cdot}766^{21}/_0$	**4-Propyl-3, 6-heptadiëne, $C_{10}H_{18}$.**—Unstable oily tetrabromide.
166	0·795(0)	**Ethyl Heptyl Eth., $Et.O.C_7H_{15}$.**—Cf. Test 907!
167·4c.	$0{\cdot}806^{20}/_4$	**Menthene, $C_{10}H_{18}$.**—Opt act—Easily oxid. by shaking with c 1% permanganate sol.—(Descriptions conflicting.)
167–70		**3, 6-Dimethyloctadiëne(3, 5), $C_{10}H_{18}$.**
171–2	0·856(10)	**Phellandrene, $C_{10}H_{16}$.**—Cf (IX, B. 3).
173	0·801(0)	**Methyl Octyl Eth., $Me.O.C_8H_{17}$.**—Cf Test 907!
173c.	0 781(15)	**† Isoamyl Eth., $(C_5H_{11})_2.O$.**—Cf Test 907!
175 (th. i)	0 853(25)	**Cymene, $C_{10}H_{14}$.**
176–7	0·851(16)	**Sylvestrene, $C_{10}H_{16}$.**—(In Swedish turpentine oil.)
176·5	$0{\cdot}853^{'''}/_4$	[+ or −] **Limonene, (Hesperidene, Citrene, Carvene), $C_{10}H_{16}$.**—([+] variety in lemon oil, etc)—Cf IX, B, 3.
173–80	$0{\cdot}837^{19}/_0$	**Naphthalenedecahydride, $C_{10}H_{18}$.**—Hot fuming HNO_3 attacks violently.
177·8	0·774(0)	**Triisobutylene, $Me_2.C:C.(CMe_3)_2$.**—Oxid. slowly in air; Br acts w. violence.
180		**Diallyl Eth., $(C_6H_{11})_2.O$.**
179–82		**Terpinene, $C_{10}H_{16}$.**—Cf. IX, B, 3
181–2	0·844(20)	**i-Limonene, $C_{10}H_{16}$.**—Odor like oil of lemons —Cf. IX, B, 3.
183–5c.		**Terpinolene, $C_{10}H_{16}$.**—Cf IX, B, 3.

Boiling-point (C.°).	**Specific Gravity.**	**HYDROCARBONS, ETC.** — Colorless Liquids with Specific Gravity less than 0·85 at 20°/4° that are attacked or dissolved either in Test 901, 902, or 903.
189·2	0·801(0)	**Ethyl Octyl Eth., Et.O.C_8H_{17}.**—Cf. Test 907!
abt. 195	abt. 0·8	**Undecylene, $C_{11}H_{22}$.**
196–8c.	$0{\cdot}839^{20}/_{0}$	**Dodecon, $C_{12}H_{20}$.**—Easily oxid.—Action of Br violent.
abt. 210–15		**Undecine, $C_{11}H_{20}$.**—Ammon. $AgNO_3$ gives white ppt.
213–215	0·785(20)	**Duodecylene, $C_{12}H_{24}$.**—(Fr. Canadian petroleum.)
233c.	0·845(0)	**Tridecylene, $C_{13}H_{26}$.**—(Fr. Burmese petroleum.)
245–8	0·814	**Triamylene, $C_{15}H_{30}$.**—Turpentine odor.—Adds Br_2 cold.
261	0·815(0)	**Heptyl Eth., $(C_7H_{15})_2$.O.**—Cf. Test 907!
274	$0{\cdot}784^{15}/_{4}$	**Cetene, $C_{16}H_{32}$.**—Br gives dibromide.—M. p. 4°.
280–5	$0{\cdot}804^{20}/_{4}$	**Cetylene, $C_{16}H_{30}$.**—M. p. 20°.
291–7	0·820(0)	**Octyl Eth., $(C_8H_{17})_2$.O.**—Cf. Test 907!
314–5	0·818(24)	**Eicosylene, $C_{20}H_{38}$.**

GENUS IX, HYDROCARBONS, ETC.

DIVISION B, SECTION 3,—LIQUID HYDROCARBONS AND ETHERS WITH SPECIFIC GRAVITY GREATER THAN 0·85 AT 20°/4°.

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS, ETC.** — Colorless Liquids with Specific Gravity greater than 0·85 at 20°/4°.
31·5	0·944(15)	**Furfurane, C_4H_4O.**—Peculiar odor.—I. aq.; e. s. alc. or eth.—Colors a pine splinter moistened w. conc. HCl emerald green!—Conc. HCl attacks vigorously giving a brown resinous body.
67	0·950(15)	**Hydrofurfurane, C_4H_6O** (?).—Adds Br_2 cold.—Not attacked by Na, KOH, or acetic anhyd.—PCl_5 gives furfurane.
80·36	0·879$^{20}/_{4}$	† **Benzene, C_6H_6.**—M. p. 5·42°.—Identify by Test 913!
93	0·903$^{17·7}/_{4}$	**2, 5(α)-Dimethylfurfurane, $Me_2.C_4H_2O$.**—I. aq.; misc. w. alc.—Conc. HCl changes to a resinous body.—Dil. HCl at 170° gives acetonylacetone.
111	0·866$^{20}/_{4}$	† **Toluene, $Me.C_6H_5$.**—Identify by Test 918!
114	0·913$^{0}/_{4}$	**Tropilidene, C_7H_8.**—CrO_3 mixture (cf. Test 905–2) gives benzoic ac. (cf. Test 312) and benzaldehyde.—Br gives an oily dibromide.
120–1	0·893$^{0}/_{0}$	**Cycloheptadiëne, C_7H_{10}.**—Odor garlicky.
136·5 (th. i.)	0·883(0)	† **Ethylbenzene, $Et.C_6H_5$.**—† Oxidize 1 grm. to benzoic ac. by Test 905–1!
138	0·880(0)	† **p-Xylene, $Me_2.C_6H_4$.**—M. p. 15°.—Identify by Test 920!
139·2	0·866$^{20}/_{4}$	† **m-Xylene, $Me_2.C_6H_4$.**—M. p. −54°.—Identify by Test 919!
141·6 (th. i.)	0·930$^{20}/_{4}$	**Phenylacetylene, PhC⋮CH.**—Test 906 w. ammon. CuCl gives a yellow flocculent ppt. fr. alc. sol., which when dry detonates on heating.—HNO_3 or conc. H_2SO_4 resinifies.—† Heated w. dil. H_2SO_4 gives acetophenone (Test 712).
142c.	0·893(0)	† **o-Xylene, $Me_2.C_6H_4$.**—M. p. −28°.—Identify by Test 921!
143–5	0·890(0)	**Crotonyl Eth., $(Me.CH{:}CH.CH_2)_2.O$.**
146	0·925(0)	**Styrene, $PhCH{:}CH_2$.**—I. aq.; misc. with alc. or eth.—Slowly polymerizes to glassy mass;—conc. H_2SO_4 polymerizes immediately.—Gives Test 903!—Odor aromatic and rather characteristic.
152·5–3	0·859(25)	**Cumene, $Ph.CH.Me_2$.**—Test 905–1 gives benzoic ac. (Test 312).
155		**Benzylethylene, $Ph.CH_2.CH{:}CH_2$.**—Unsat. (cf. Test 901).—Test 905–1 gives benzoic ac. (Test 312).
155	0·988$^{21}/_{4}$	**Anisol, Me.O.Ph.**—Aromatic odor!—I. aq.—W. conc. HI at 130°–40° gives phenol and methyl iodide.
156	0·86(20)	**Pinene (Terebenthene), $C_{10}H_{16}$.**—(The chief constituent of † oil of turpentine). The American or English, fr. Pinus Australis, is [+]; the French, fr. Pinus maritima, is [−].—Odor penetrating and characteristic.—Gives Test 901.—Fuming HNO_3 attacks w. almost explosive violence.—Well cooled and saturated w. dry HCl gas, gives hydrochloride ($C_{10}H_{16}.HCl$), stable volatile cryst. (m. p. 125°), fr. dil. alc., and of camphor-like odor ("artificial camphor").
158	0·870$^{9·8}/_{4}$	**Propylbenzene, $Pr.C_6H_5$.**—Test 905 gives benzoic ac.
158–9	0·873(16)	**o-Methylethylbenzene, $Me.C_6H_4.Et$.**—Oxid. by Test 905–3 gives phthalic ac.

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS, ETC.**—Colorless Liquids with Specific Gravity greater than 0·85 at 20°/4°.
158–9	0·869(20)	**m-Methylethylbenzene, Me.C_6H_4.Et.**—Test 905-1 gives isophthalic ac.
160–2	0-788$^{20}/_{0}$	**α-Terpenetetrahydride, $C_{10}H_{20}$.**—(Cf. IX, B, 1.)
162	0·865(21)	**p-Methylethylbenzene, Me.C_6H_4.Et.**—Test 905-1 gives terephthalic ac. (Test 318-3).
164	0·793$^{19}/_{0}$	**β-Terpenetetrahydride, $C_{10}H_{20}$.**—(Cf. IX, B, 1.)
164·5	0·869$^{9\cdot8}/_{4}$	**† Mesitylene, C_6H_3.Me_3(1:3:5).**—Identify by Test 914!
167–8	0·938(18)	**Methyl Benzyl Eth., C_7H_7.O.Me.**
168–8·5		**tert.-Butylbenzene, Ph.C.Me_3.**—Oxidation (cf. Test 905) gives benzoic ac.
169·8c.	0·879$^{20}/_{4}$	**† Pseudocumene, C_6H_3.Me_3(1, 2, 4).**—For coloration w. $AlCl_3$ cf. Test 904.—Identify by Test 917!
170–72	0·873(16)	**sec.-Butylbenzene, Me.CHEt.C_6H_5.**—Test 905 gives benzoic ac.
171–1·5	0·858(15)	**Isobutylbenzene, Ph.CH_2.$CHMe_2$.**—Test 905 gives benzoic ac.
171·3	0·996(0)	**o-Cresyl Methyl Eth., Me.O.C_7H_7.**
171–2	0·856(10)	[+] **Phellandrene, $C_{10}H_{16}$.**—(In fennel and other essential oils.)—I. alc.; s. eth.—Identify as nitrosite. (Cf. A, 246, 282; and 287, 374.)
170–5		**p-Methylstyrene, Me.C_6H_4.CH:CH_2.**—Unsat. (cf. Test 901).—Test 905-1 gives terephthalic ac. (Test 318).
172	0·982(0)	**Phenetol, Et.O.Ph.**—Odor aromatic.—I. aq.—At 400° gives phenol (Test 414) and ethylene.
173	0·846(23)	**Amenylbenzene, Ph.CH(Et).CH:CH_2.**—Gives Test 901.—Continued boiling gives diamenylbenzene, b. p. 208°–12°.—Test 905 gives benzoic ac. (Test 312).
174–5	0·918$^{15}/_{15}$	**Allylbenzene, PhCH:CHMe.**—Unsat. (cf. 901).—Dibromide, ndl. d. s. c. alc., m. p. 66·5°.
170–80		**Diamylene Oxide, $C_{10}H_{20}O$.**—Reduces ammon. $AgNO_3$ sol.
175 (th. i.)	0·853(25)	**Cymene, p-Me.C_6H_4.$CHMe_2$.**—Test 905-2 gives terephthalic ac. (Test 318).
175	0·987(0)	**p-Cresyl Methyl Eth., Me.O.C_7H_7.**
175–5·5		**1, 2, 3-Trimethylbenzene, C_6H_3.Me_3.**
175–6	0·862(20)	**m-Methylisopropylbenzene, Me.C_6H_4.Pr.**—Br substitutes readily cold.—Test 905-2 gives isophthalic ac. (Test 318).
176c.	0·957(15)	**1, 2-Hydrindene, C_6H_4:C_2H_4:CH_2.**—Br substitutes.—Sulphonated by cold conc. H_2SO_4. M. p. sulphonamide 91°–2°.
176	0·927(20)	**† Eucalyptol (Cineol), $C_{10}H_{18}O$.**—Agreeable odor like cardamon and camphor!—M. p. −1°–3°.—Unsat.; dibromide very unstable.—Dry HCl conducted into mixture of equal vols. eucalyptol and lgr. gives cryst. ppt. of unstable $(C_{10}H_{18}O)_2$.HCl.—Shaken w. saturated sol. of I in saturated KI sol. gives ppt. of minute cryst. w. greenish lustre.
176·5	0·853$^{10}/_{4}$	[+ or −] **Limonene (Hesperidene, Citrene, Carvene), $C_{10}H_{16}$.**—([+] in oil of lemons.)—General behavior in Test 901-3 as with pinene.—Dilute w. 4 vol. glac. $\bar{A}$c., cool well, and drop in Br as long as color disappears. Allow to stand until crystals separate. Drain, and then recryst fr. acetic ether. The tetrabromide formed melts at 104·5°. (A, 239, 3)!

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS, ETC.** — Colorless Liquids with Specific Gravity greater than 0·85 at 20°/4°.
176–7	0·851(16)	[+] **Sylvestrene, $C_{10}H_{16}$.**—(In Russian and Swedish turpentine oils.)—The sol. in acetic anhyd. is colored intensely blue by a drop of conc. H_2SO_4 (a reac. that may be interfered with by the presence of some other terpenes).—Br in Āc sol. (procedure as w. limonene above) gives tetrabromide, m. p. 135°–6°; but it is said to be preferable to identify as dihydrochloride, m. p. 72° (cf. A, 230, 241; 239, 25), obtained by action of dry HCl gas
176–8		**p-Butyltoluene, Bu.C_6H_4.Me.**—Oxid. by dil HNO_3 (Test 905-3), giving p-toluic ac.
176–8	0·901(15·5)	**Phenylbutylene, Ph.C_4H_7.**—Unsat. (cf. Test 901).—Test 905–1 gives benzoic ac.
178	0·873(21)	**Diethylphenylmethane, Ph.CH.Et_2.**—Test 905–1 gives benzoic ac.
180	0·864(15)	**Butylbenzene, C_4H_9.C_6H_5.**—Test 905–1 gives benzoic ac.
180c.	1·040(15)	**1, 2-Indene, C_9H_8.**—(In light coal-tar oils.)—Conc. H_2SO_4 gives brown resin.—Adds Br.—Forms picrate.—Dil. HNO_3 gives phthalic ac.
179–82		**Terpinene, $C_{10}H_{16}$.**—(In cardamon and other essential oils.)—Opt. inactive.—Resinifies on keeping, or by action of conc. H_2SO_4.—Unlike pinene is completely destroyed in the cold (except a few brown flocks) by a mixture of 6 pt. $Na_2Cr_2O_7$, 5 pt. H_2SO_4+30 pt. aq.—For identification as nitrosite, see A, 239, 36!
180–1	0·958	**o-Cresyl Ethyl Eth., Et.O.C_7H_7.**
181 (th. i.)		**Isobutenylbenzene, Ph.CH:CMe_2.**—Test 905–2 gives benzoic and acetic acids.—Br gives liq. bromide.
181–2	0·844(20)	**i-Limonene, $C_{10}H_{16}$.**—(Syn.-Dipentene, diisoprene, cinene, caoutchin, etc.)—Odor lemon-like.—Absorbs O fr. the air.—Prepare the tetrabromide, m. p. 124°–5°, by the procedure given under + or − limonene on p. 190!
181–2	0·860$^{20}/_{4}$	**m-Diethylbenzene, C_6H_4.Et_2.**—Oxid. by Test 905–1 gives isophthalic ac. (Test 318).
182–3	0·862$^{18}/_{4}$	**p-Diethylbenzene, C_6H_4.Et_2.**—Test 905–1 gives terephthalic ac.
183–4	0·878(20)	**1, 3, 4-Dimethylethylbenzene, Me_2.C_6H_3.Et.**—May be oxidized to xylic ac.
183–4	0·942(0)	**Pinol, $C_{10}H_{16}O$.**—Odor like that of eucalyptol!—Unsat.—Dissolved in 2 vols. glacial Āc and treated w. Br_2 gives stable dibromide which cryst. well fr. eth.-alc. w. m. p. 94°.
183–5c.		**Terpinolene, $C_{10}H_{16}$.**
185	0·866$^{18}/_{4}$	**o-Diethylbenzene, Et_2.C_6H_4.**—Test 905–1 gives some phthalic ac.
185		**Ethyl Benzyl Eth., Et.O.C_7H_7.**—Treatment w. P_2O_5 gives ethylene and anthracene (Test 912).
185	0·861(20)	**1, 3, 5-Dimethylethylbenzene, Me_2.C_6H_3.Et.**—Test 905–2 gives mesitylenic ac.
185		**Phenylallylene, Ph.C:C.Me.**—Tetrabromide, lft.fr. alc., m. p. 75°.
186–7		**1′-Butenylbenzene, Ph.CH:CHEt.**—Unsat. (cf. Test 901).—Test 905–1 gives benzoic ac. (Test 312).
186–8		**m-Pseudobutyltoluene, Me_3C.C_6H_4.Me.**—Test 905–2 gives isophthalic ac. (Test 318).
185–90		**Phenylcrotonylene, Ph.C_4H_5.**—Unsat. (cf. Test 901).—Test 905–1 gives benzoic ac. (Test 312).
185–90	0·892$^{22}/_{0}$	**Naphthaleneoctahydride, $C_{10}H_{16}$.**—Odor like turpentine.—Absorbs O fr. air.
189	0·966(0)	**p-Cresyl Ethyl Eth., C_7H_7.O.Et.**
189·5–91	0·874(15)	**Dimethylethylphenylmethane, Me_2(Et)(Ph).C.**—Br substitution product is oily.

Boiling-point (C.°).	Specific Gravity.	HYDROCARBONS, ETC. — Colorless Liquids with Specific Gravity greater than 0·85 at 20°/4°.
190–2		**1, 3-Ethylisopropylbenzene, Et.C_6H_4.Pr.**—Test 905-1 gives isophthalic ac. (Test 318-2).
193	0·885(18)	**Isoamylbenzene, Ph.C_5H_{11}.**—Slowly oxid. by Test 905-2 to benzoic ac. (Test 312).—Br in sunlight gives Br derivative, m. p. 128°-9°.
194–5		**Isopropyl-m-xylene, Pr.$C_6H_3.Me_2$.**
195		**m-Tolylbutylene, $C_7H_7.C_4H_7$.**—Unsat. (cf. Test 901); the dibromide is oily.
195–7	0·896$^0/_4$	**1, 2, 3, 5-Tetramethylbenzene, $Me_4.C_6H_2$.**—Test 905-1 gives only mellophanic ac., m. p. 238° d.
198–200		**p-Tolylpropylene, $C_7H_7.C_3H_5$.**—Unsat. (cf. Test 901).
199–200	0·879(20)	(s), **1, 3, 5-Diethyltoluene, $Et_2.C_6H_3.Me$.**—Test 905-3 gives uvitic ac., m. p. 287°-8°.
201	0·860(22)	**Amylbenzene, $C_5H_{11}.C_6H_5$.**—Test 905-2 gives benzoic ac. (Test 312).
201–3	0·923(21)	**Ethylphenylacetylene, $PhC \vdots CEt$.**—Unsat. (cf. Test 901). Test 905-1 gives benzoic ac. (Test 312).
200–5		**Ethylbutylbenzene, $C_{12}H_{18}$.**
204 (th. i.)		**1, 2, 3, 4-Tetramethylbenzene, $Me_4.C_6H_2$.**—Large cryst., m. p. −4°.—Test 905-3 gives prehnitic ac. (III, A, 1, m. p. 237°).
205 (th. i.)	0·981(12·5)	**Naphthalenetetrahydride, $C_{10}H_{12}$.**—Feeble odor.—Test 905 gives phthalic ac.—Conc. HNO_3 gives picric ac.—Oxid. on standing in air.—Br gives unstable substitution product.
abt. 205 (th. i.)	0·934$^{23}/_0$	**Naphthalenehexahydride, $C_{10}H_{14}$.**—Absorbs O fr. air.—HNO_3 or cold Br attacks w. violence.—Fuming H_2SO_4 sulphonates.
205–6	0·968$^{27}/_4$	**γ-Methylindene, $C_{10}H_{10}$.**—Naphthalene odor.—Absorbs O fr. air.—Conc. H_2SO_4 or HCl resinifies.—Forms very unstable picrate, m. p. 75°-6°.
205–6	1·086(15)	**Veratrol, o-$C_6H_4.(OMe)_2$.**—Solid at 15°.—Heated w. HI gives pyrocatechin and methyl iodide.
206–7		**Propyl-p-xylene, Pr.$C_6H_3.Me_2$.**
206–10		**s-Dimethylpropylbenzene, $Me_2.C_6H_3.Pr(3:5:1)$.** — Test 905-3 gives mesitylenic ac. (III, A, 2, m. p. 166°).
208–8·5		**Propyl-m-xylene, Pr.$C_6H_3.Me_2$(4, 3, 1).**
209		**Propyl-o-xylene, Pr.$C_6H_3.Me_2$(4, 2, 1).**
211–13c.	0·871(0)	**p-Propylisopropylbenzene, Pr.C_6H_4.Pr.**—Test 905-3 gives terephthalic ac. and propylbenzoic ac.
212		**Naphthalenedihydride, $C_{10}H_{10}$.**—Frozen at +15·5°.—Adds Br_2 in the cold; m. p. of unstable dibromide 74°.—Fuming H_2SO_4 sulphonates.
213	0·864(9)	**p-Isoamyltoluene, Me.$C_6H_4.C_5H_{11}$.**—Test 905-2 gives terephthalic ac. (Test 318-3).
214–15	0·857(16)	**Isohexylbenzene, Ph.$(CH_2)_3$.CHMe$_2$.**
214–15	1·080$^0/_4$	**Dimethyl Resorcinyl Eth., m-$(MeO)_2.C_6H_4$.**—Vol. w. st.
216·2	0·953(0)	**Methyl Thymyl Eth., Me.O.$C_{10}H_{13}$.**
214–18		**s-Triethylbenzene, $C_6H_3.Et_3$.**—Test 905-2 gives trimesic ac. (III, A, 1, m. p. 345°-50°).
215–20	0·920$^{21}/_4$	**Isoamyl Phenyl Eth., C_5H_{11}.O.Ph.**
220·5–1·5		**p-Dipropylbenzene, $Pr_2.C_6H_4$.**—Test 905-3 gives p-propylbenzoic ac. (III, A, 2, m. p. 140°).
223–8	0·911(0)	**Benylene, $C_{15}H_{28}$.**—Unsat. (cf. Test 901).
226·9	0·933(0)	**Ethyl Thymyl Eth., Et.O.$C_{10}H_{13}$.**—At 360°-400° splits to thymol and ethylene.
229–30	0·890(15)	**Allylisopropylbenzene, Me.CH : CH.$C_6H_4.C_3H_7$.**—Adds Br_2 to form dibromide, v. s. h. alc., m. p. 59°.

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS, ETC.** — Colorless Liquids with Specific Gravity greater than 0·85 at 20°/4°.
233	1·108(15°)	**Safrol**, $C_6H_3.(C_3H_5)(O_2CH_2)[1:(3, 4)]$.—Strong sassafras odor! M. p. after solidification by cold +11°; $N_D = 1{\cdot}53836$.—Quickly reduces a 1% neutral $KMnO_4$ sol. upon shaking. Is violently attacked and completely carbonized in Test 907 with conc. H_2SO_4.
233c.	0·989(28)	**Anethol**, $Me.O.C_9H_9$.—Cf. IX, A, m. p. 21·6°.
233		**Heptylbenzene**, $C_7H_{15}.C_6H_5$.—(Several compounds isomeric w. this substance w. b. p.'s between 225°-48° have been described.)
230–40		**Diisobutylbenzene**, $(C_4H_9)_2.C_6H_4$.
240–2 (th. i.)	1·001(19)	**α-Methylnaphthalene**, $C_{11}H_{10}$.—Freezes at −22°.—Long boiling w. conc. HNO_3 gives isonaphthoic acid, $C_{11}H_8O_2$.—Picrate fr. alc. forms yellow ndl., m. p. 116°.
242 (th. i.)		**β-Methylnaphthalene**, $C_{11}H_{10}$.—M. p. 32·5°.—The picrate forms yellow ndl. w. m. p. 115°.
244		**Dimethyl Orcinyl Eth.**, $(MeO)_2.C_6H_3.Me$.—Alm. i. aq.
250 (th. i.)		**1, 2, 4, 5-Tetraethylbenzene**, $Et_4.C_6H_2$.—M. p. 13°.—Oxid. gives pyromellitic ac. (III, A, 1, m. p. 264°).
251	1·008(0)	**β-Ethylnaphthalene**, $Et.C_{10}H_7$.—The picrate cryst. fr. h. alc. in fine yellow ndl. w. m. p. 69°–71°.
258 sl. d.	$1{\cdot}018^{10}/_{10}$	**α-Ethylnaphthalene**, $Et.C_{10}H_7$.—Forms a picrate, lemon-yellow ndl., m. p. 98°.
258–60		**Phenyltolyl**, $Ph.C_7H_7$.
261–2	$1{\cdot}001^{26}/_4$	**Diphenylmethane**, $Ph_2.CH_2$.—Ndl. m. p. 26°–7°.—Cf. Div. A of this genus.
261–3	0·849(15)	**Octylbenzene**, $C_8H_{17}.C_6H_3$.—M. p. −7°.—Test 905–2 gives benzoic ac. w. difficulty.—(Isomeric hydrocarbons exist w. b. p.'s between 230°–260°.)
262–4	1·020(12)	**1, 4-(α)Dimethylnaphthalene**, $Me_2.C_{10}H_6$. — Remains liq. at −18°.—Picrate forms orange ndl., m. p. 139°; s. h. alc.; v. s. eth.
263–7	1·015(27)	**p-Phenyltolyl**, $Ph.C_6H_4.Me$.—Freezes at −2°–3°.
265	0·990(0)	**β-Propylnaphthalene**, $C_{10}H_7.Pr$.—Picrate lemon-yellow ndl., m. p. 89°.
250–80	0·904–0·927	**Sesquiterpenes**, $C_{15}H_{24}$.—(Important constituents of many essential oils, like oils of cedar, calamus, cubebs, patchouli, etc.)—D. s. alc.; somewhat viscous.—Give solid hydrochlorides when HCl gas is passed into the cooled ethereal sol.
265	0·887(0)	**Diisoamylbenzene**, $(C_5H_{11})_2.C_6H_4$.—Liq. at −20°.
269c.	$1{\cdot}096^{14}/_4$	**Methyl α-Naphthyl Eth.**, $Me.O.C_{10}H_7$.—Gives red cryst. comp. w picric ac.—Split by conc. HCl at 150°.
270–5	0·933(20)	**Phenanthreneperhydride**, $C_{14}H_{24}$.—M. p. −3°.—Not attacked cold by fuming HNO_3, by H_2SO_4, or Br, and by CrO_3 only w. difficulty.
272–7	1·031(0)	**m-Phenyltolyl**, $Ph.C_7H_7$.—"Not attacked by $KMnO_4$."
275 (th. i.)	0·929(0)	**Cadinene**, $C_{15}H_{24}$.—(A sesquiterpene present in cubeb, patchouli, and some other essential oils.)—D. s. alc.—Resinifies easily.—Gives a solid dihydrochloride, m. p. 117°–18°.—When slightly resinified and dissolved in much glacial $\bar{A}c$ becomes green and then indigo-blue on addition of small successive portions of conc. H_2SO_4.
abt. 275		**o-o and o-p-Ditolyl**, $(Me.C_6H_4)_2$.
275·5 (th. i.)	0·997(17·5)	**m-Benzyltoluene**, $Ph.CH_2.C_7H_7$.—Much conc. HNO_3 at 90° gives nitro-compound, cryst. fr. h. glacial $\bar{A}c$, m. p. 141°.
277 (th. i.)	0·899(19)	**Pentaethylbenzene**, $C_6H.Et_5$.—Dec. by fuming H_2SO_4 to tetraethyl- and hexaethyl-benzene.

Boiling-point (C.°).	Specific Gravity.	**HYDROCARBONS, ETC.**—Colorless Liquids with Specific Gravity greater than 0·85 at 20°/4°.
277		**α-Diphenylethylene, $C_{14}H_{12}$.**—CrO_3 mixture oxid. to benzophenone. (Unsat.—Br addition product unstable.)
277–90c.	0·996(0)	**αβ-Diphenylpropane, Me.CHPh.CH_2.Ph.**
280		**β-Isobutylnaphthalene, $C_4H_9.C_{10}H_7$.**—The picrate forms yellow ndl., e. s. alc., m. p. 96°.
280–1		**3-Bitolyl, $C_7H_7.C_7H_7$.**—CrO_3 oxid. to isophthalic ac. (cf. Tests 905–2 and 318).
281c.	$1·075^0/_4$	**Ethyl α-Naphthyl Eth., Et.O.$C_{10}H_7$.**
281–2		**Dimethyldiphenylmethane, Me_2.C.Ph_2.**
283–4	1·043	**m-Ethylbiphenyl, Et.C_6H_4.Ph.**—CrO_3 oxid. to m-phenylbenzoic ac. (III, A, 2, m. p. 160°).
286	0·98	**p-Phenyltolylethane, Ph.$C_2H_4.C_7H_7$.**—M. p. 27°.
286		**Ditolylmethane, $CH_2.(C_6H_4Me)_2$.**—M. p. 22°–3°.—Slowly sulphonated by fuming H_2SO_4.—CrO_3 oxid. to dimethylbenzophenone.
288	$0·999^{16}/_4$	**o-m-Bitolyl, $C_7H_7.C_7H_7$.**—CrO_3 oxid. to isophthalic ac. (Test 318).
293–4	0·987(15)	**s-Benzyltolylethane, $C_7H_7.C_2H_4.C_6H_4$.Me.**
293–5		**p-Ethyldibenzyl, Ph.$CH_2.CH_2.C_6H_4$.Et.**—Shows bluish fluorescence.
294		**Benzyl-p-xylene, Ph.$CH_2.C_6H_3.Me_2$.**
294–5 (th.	0·985(18·9)	**Ethylbenzylbenzene, Et.$C_6H_4.CH_2$.Ph.**—E. s. alc., eth., or $CHCl_3$.
295–8	$0·974^{20}/_4$	**p_2-Ditolylethane, Me.CH.$(C_7H_7)_2$.**—Test 905–2 gives dimethyl phenyl ketone and tolylbenzoic ac.
295–8 (th. i.)	1·036(16)	**Benzyl Eth., $(Ph.CH_2)_2$.O.**—Heated above 315° yields benzaldehyde, toluene, and resinous matter.
304–5		**Ditolylethylene, $(Me.C_6H_4)_2$.C : CH_2.**—Test 905–2 gives ditolyl ketone, m. p. 94°.—Dibromide v. unstable, losing HBr.
308	0·969(15)	**Benzylcymene, $C_7H_7.C_6H_3$.(Me)Pr.**
310 (th. i.)	1·067(10·2)	**Phenanthrenetetrahydride, $C_{14}H_{14}$.**—Oxid. by CrO_3 in Āc sol. to anthraquinone (Test 1011).
a. 300	0·939	**Diterpenes, $C_{20}H_{32}$.**—(In copaiva balsam, etc.)—Very viscous; i. alc.
323–5	$0·966^{20}/_4$	**m-Dixylyl-ethane, $(C_6H_3.Me_2)_2$.CH.Me.**—Exhibits a blue fluorescence.
324c.		**α, β-Phenylxylylpropane, Ph,$(C_6H_3.Me_2).C_3H_6$.**
324–5		**α-Phenylnaphthalene, Ph.$C_{10}H_7$.**—Shows a feeble blue fluorescence.—Oxid. to o-benzoylbenzoic ac. in alkaline sol.
343–6	0·969(18)	**Diterebenthyl, $C_{20}H_{30}$.**—Absorbs O fr. air.—Is easily oxid. by oxid. agents.—Not attacked by cold H_2SO_4.—Fuming HNO_3 nitrates.—Br substitutes.
350		**Cuminyl Eth., $(C_{10}H_{13})_2$.O.**—Dist. w. partial dec. to cymene and cuminic aldehyde.
392–6	1·049	**Dibenzyltoluene, Me.$C_6H_3.(CH_2Ph)_2$.**
392–6		**Dixylylbenzene, $C_6H_4.(CH_2.C_6H_4.Me)_2$.**—E. s. alc., eth., or Āc.
390–400	0·871(0)	**Tetramylene, $C_{20}H_{40}$.**
396–400		**s-Triphenylethane, Ph.CH_2.CH.Ph_2.**—Shows a violet fluorescence.

NUMBERED SPECIFIC AND SEMI-SPECIFIC TESTS FOR SPECIES OF GENUS IX.

[TESTS 901–1000.]

901. Bromine Test for Unsaturation.

This test for unsaturation finds many applications, but is most frequently employed in connection with the species of Genera IX and III.

Dissolve or suspend 0.1 grm. of the pure compound—finely powdered, if it is an insoluble solid—in 2 cc. of dry carbon tetrachloride in a three-inch test-tube. Add three drops of a bromine solution * prepared by dissolving 2.0 cc. of bromine in 50 cc. of carbon tetrachloride. If decolorization does not take place at once, stopper the tube loosely, and allow to stand for three minutes in the cold, shaking occasionally if the body is insoluble. If the solution becomes colorless before the end of two minutes, drop in more bromine solution until a color that is permanent for a minute or two is produced. Then blow sharply across the mouth of the tube, and notice whether a white cloud (hydrated hydrobromic acid) makes its appearance.

If no signs of action in the cold are observed, hold the tube high above a small flame and boil very gently for two minutes. If decolorization results, drop in more bromine until the coloration remains permanent for nearly a minute when the solution is again boiled. Test for hydrobromic acid as before by blowing across the mouth of the tube.

Complete decolorization in either part of this test (either in the cold or after heating), if unaccompanied by evolution of hydrobromic-acid gas, shows that the compound under examination is unsaturated; that is, that it can add bromine.

The presence of double or triple bondings in hydrocarbons may in the great majority of cases be detected by use of the test in the cold only; but there are a few unsaturated hydrocarbons like stilbene which require short heating, and in tetraphenylethylene we have one which remains unchanged even when heated. Among the unsaturated acids, maleic and fumaric acids † also show an exceptional behavior in not decolorizing the tetrachloride solution after two minutes' boiling. Some other unsaturated acids, like aconitic, do not decolorize the solution until it has been heated, but the number of such species is not large.

Decolorization in either part of the test when accompanied by a copious evolution of hydrobromic acid always indicates substitution; but since addition may, or may not, have taken place at the same time, satisfactory inferences as to the existence of unsaturation in such cases can

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* Carbon tetrachloride is given the preference as the solvent, because bromine solutions prepared by its use may be kept for weeks without spoiling; because such solutions do not entirely lose their orange-yellow color on heating unless boiled for more than twice the time prescribed in the test procedure; and because the tetrachloride is such a poor solvent for hydrobromic acid that the gas escapes as soon as formed, and thus is easily detected by the fumes

† Fumaric or maleic acids will, however, decolorize hot bromine water. (Bromine water is as a rule a very unsatisfactory substitute for the carbon tetrachloride reagent, since it is frequently decolorized by acting as an oxidizing agent, holds back hydrobromic acid, and loses its color rather quickly on boiling.)

not be drawn. The appearance of scanty traces of hydrobromic acid towards the end of an experiment in which a considerable quantity of bromine has been consumed, may, however, be due to minor secondary reactions and may be disregarded.

In the heat, the number of compounds in Order 1 that are attacked by the treatment with bromine is greatly increased. The saturated hydrocarbons of the marsh-gas series, (C_nH_{2n+2}), *with unbranched carbon skeletons,* and the members of the acetic-acid series, ($C_nH_{2n}O_2$), are conspicuous examples of compounds unaffected under these circumstances. Some paraffin hydrocarbons like diisoamyl with branched carbon skeletons are, on the contrary, quite readily attacked in the heat, although not in the cold. Many of the aromatic hydrocarbons like mesitylene and anthracene are so easily substituted that decolorization occurs within a fraction of a minute in the cold; but pure benzene is so comparatively unreactive that it does not cause decolorization within the two minutes' limit on boiling.

Most phenols, and many aldehydes and ketones, cause decolorization cold within a few seconds. Whenever decolorization takes place readily in consequence of addition or substitution in a homogeneous compound, if the experiment is continued after the first disappearance of color, it will be found that the quantity of bromine eventually consumed will be at least several times greater than what was added at the beginning of the experiment.

902. Action of Fuming Sulphuric Acid.

Support a three-inch test-tube containing 1 cc. of fuming sulphuric acid (sp. gr. 1.89) by means of a small clamp in a nearly vertical position, but so that it shall be slightly inclined away from the operator. Drop in slowly from a medicine-dropper about five drops of the compound. If there are no immediate signs of solution or chemical action, shake the mixture cautiously for about one minute. Then allow to stand for a short time, and notice whether the compound added separates apparently unchanged as an upper layer.

If the substance does not dissolve, if heat is not evolved, and if the mixture does not become strongly discolored, the compound, if a liquid species of Genus IX, with a specific gravity less than 0.85 at 20°/4°, may belong to Section 1 (the paraffin section) of Division B.

903. Action of Fuming Nitric Acid.

[This test is dangerous unless performed cautiously as directed!]

In a three-inch test-tube, supported as in Test 902, place 1 cc. of fuming nitric acid of specific gravity 1.48. Then add from a medicine-dropper, held at arm's length, a single drop of the compound to be tested. A violent reaction often ensues, and there may be a slight explosion, or the substance may even ignite. If there are no signs of action, cautiously add a few more drops of the substance, and shake gently.

If the substance is a liquid species of Genus IX with a specific gravity at 20°/4° less than 0.85, and does not dissolve in the acid, and is not attacked by it (as will be indicated by absence of sputtering and evolution of heat, and by the non-appearance of a copious disengagement of red nitrous fumes), it is to be sought for in Section 1 (the paraffin section) of Division B.* It is improbable that any of the Species of Section 2 remains entirely unchanged after such treatment.

The liquid paraffins, although they are unattacked, and do not dissolve, always dissolve oxides of nitrogen so as to acquire a color much like that of the nitric acid. The presence of two layers after shaking may, therefore, be easily overlooked in a hasty observation.

904. Colorations with Aluminium Chloride.

Drop a hard lump of sublimed aluminium chloride weighing about 0.2–0.3 grm. into a clean 6–8-inch test-tube that has just been taken from a hot drying oven. Stopper the tube loosely. Hold it in a nearly horizontal position, and by means of a small flame placed

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* The tertiary paraffin diisopropyl is said to be violently attacked by cold nitric acid of specific gravity 1.52.

under one end slowly sublime the chloride until it forms a thin light-yellow coating covering a considerable portion of the glass surface. Allow to cool. Drop in 0.5 cc. of a solution containing 0.05 grm. of the hydrocarbon dissolved in 2.5 cc. of chloroform. Stopper the tube tightly. Lay it on its side upon a sheet of white paper that rests upon and partly covers the color standard. Then roll it back and forth so that the solution shall flow over and wet all parts of the sublimate. Observe the color after a few seconds, and again after 15–20 minutes.

Most aromatic hydrocarbons give colorations when thus treated. The colors are often very intense, and sometimes admit of employment as minor preliminary or confirmatory tests; but since the hue may be much modified by the presence of small quantities of impurities, too great importance ought not to be attached to the indications obtained by their use.

The initial colorations given by the liquid homologues of benzene approximate *orange;* e.g. pseudocumene, RO; m-xylene, O; benzene, OY (after five minutes). After standing fifteen minutes these colors will either remain unchanged, or will change by about one hue of the standard in the direction of the red end of the spectrum. The initial coloration with diphenylmethane and triphenylmethane is YO, darkening within a few minutes to YOT1; with anthracene it is OYS2–YS2.

Initial colorations of great intensity which persist unchanged for more than twenty minutes and approximate *blue,* are given by several important solid hydrocarbons; e.g. blue (B), by diphenyl; blue to green-blue (GB–B), by phenanthrene; and blue-green (BG), by naphthalene.

905. Oxidation of Side Chains.

The oxidation of the side chains in aromatic hydrocarbons to carboxyl groups by hot aqueous solutions of potassium permanganate, chromic acid, or nitric acid, has been employed in determining the constitution of many species of Genus IX. The most serious difficulty encountered in adapting these methods for use as practical specific tests arises from the extreme insolubility of all hydrocarbons in aqueous solutions. This renders the oxidations very slow. During the oxidation period—which is seldom less than several hours—the oxidation product, which is itself never entirely stable, is exposed to the destructive action of the oxidant. Hence the yield, which even under favorable circumstances falls much under the theoretical, is often very poor indeed. Hydrocarbons which are themselves stable, but give unstable oxidation products, are therefore the most difficult to treat successfully. Whenever it is suggested in the tables that some particular oxidant may be used in the identification of a hydrocarbon, it does not always follow that the oxidant mentioned is the best that could have been selected for the purpose, or that the yield will be good, but merely that the product named has been obtained by its use. It should also be understood that the following general directions are given as suggestions rather than mandatory procedures; and that what is said refers more especially to aromatic hydrocarbons having one or two side chains.

1. (*Oxidations with Potassium Permanganate.*)—The oxidation with permanganate, when applicable, will usually be preferred to either of the other methods. The reagent is a neutral aqueous solution containing 61.6 grms. of potassium permanganate to the liter. In organic oxidations it is said to be reduced according to the equation

$$2KMnO_4 + xH_2O = 2MnO_2.xAq. + 2KOH + 3O.$$

1 cc. of the solution accordingly contains 0.01 grm. of "available oxygen," and the alkali liberated is sufficient to combine with the full quantity of organic acid and carbon dioxide that will be produced in any ordinary oxidation. The latter fact makes it possible to perform these oxidations in closed vessels, and thus avoid the violent bumping that is one of the greatest objections to the use of permanganate when the oxidation is performed by boiling in flasks.

Calculate by aid of the equation given above how much permanganate solution will be theoretically needed to produce the desired effect, and place it in a strong wide flask or bottle of about one-liter capacity. If, as will sometimes happen, the hydrocarbon is lighter than water, and a liquid, the extended contact surface presented by the permanganate solution, which will be spread out in rather a thin layer, will do much to accelerate the reaction. When the oxidation product expected is benzoic, isophthalic, or terephthalic acid, about 1 grm. of the hydrocarbon should be enough for an experiment.

Suspend the bottle by a wire, so that the lower part will be immersed in a boiling water-bath; and, as soon as the air within has been expanded by the heat, and the hydrocarbon introduced, stopper tightly to prevent loss of substance by volatilization. Then heat until the red color of the permanganate is seen to have completely disappeared. This may require from two to eight hours, and some of the hydrocarbon will always remain unattacked. Separate the colorless alkaline solution from the bulky brown precipitate of hydrated manganese oxide by filtration. Evaporate to a small volume. Filter if necessary, and cool. Acidify the solution with a moderate excess of hydrochloric acid, and shake vigorously. Benzoic, isophthalic, and terephthalic acid will precipitate at this point. The two former may then be identified by their melting-points and specific tests, after a single crystallization from boiling water; the latter after being well washed with water. Phthalic acid being comparatively easily oxidized by hot permanganate, will not be detected, unless the hydrocarbon is one that oxidizes quite rapidly. The loss of benzoic acid in long-continued oxidations is also large, though less serious. In an oxidation of 1 grm. of ethylbenzene requiring six hours, the yield of pure benzoic acid was 0.20 grm. Benzoic acid is easily separated from any of the phthalic acids by treatment with chloroform, in which it is very soluble.

2. (*Oxidations with Chromic-acid Mixture.*)—Boil the hydrocarbon in a round-bottomed flask containing ebullator tubes (cf. p. 223) with the quantity of chromic-acid mixture theoretically required to produce the desired effect, until the chromic acid is completely reduced. The apparatus, chromic-acid mixture, and general procedure for the oxidation are the same as have been more fully described in Test 702 for the oxidation of ketones and alcohols, except that longer heating will be necessary. As the action of hot chromic acid on most of the aromatic acids is even more destructive than that of permanganate, it is advisable to use at least 2 grms. of the hydrocarbon for each experiment, and even larger quantities may sometimes be found necessary. Collect the insoluble residue of oxidation products, and unchanged hydrocarbon that separates from the well-cooled solution, on a small filter. Wash with a little cold water. Dissolve out the aromatic acids by boiling with a slight excess of sodium-carbonate solution. Reprecipitate with an excess of hydrochloric acid, and identify them by appropriate tests.

3. (*Oxidations with Dilute Nitric Acid.*)—Although nitric acid, being a milder oxidant than either permanganate or chromic acid, may be successfully employed in some cases in which the latter are inapplicable, and is occasionally mentioned in the tables, it has the disadvantage of being exceedingly slow in its action, and of giving products which sometimes consist largely of nitrosubstitution derivatives whose removal is troublesome. The proper procedure depends so much on the properties of the particular hydrocarbon to be oxidized, that in the few instances in which this method is referred to in the tables, it will always be best to consult the original literature relating to the subject before proceeding to the experiment. The following general statement and suggestions may, however, be of some assistance.

It is best to oxidize at least 2 grms. of the hydrocarbon with a large excess of acid. The nitric acid is usually a mixture of one part of concentrated commercial nitric acid with three parts of water, though in *some cases* a stronger acid can be used, shortening the time without causing much substitution.* The time of boiling varies from six to forty-eight hours. In general it is best to boil at least eight hours. If it is expected that a solid aromatic acid, not volatile with steam, will be formed, the excess of nitric acid should be removed by evaporation on a water-bath. The residue is next extracted with boiling sodium-carbonate solution, the solution filtered, and the organic acids precipitated from the filtrate by a moderate excess of hydrochloric acid. Nitro-acids may then be reduced by warming with tin and hydrochloric acid, so as to form soluble hydrochlorides of the corresponding amino-acids, which, upon filtration, will pass into the filtrate. Or, if the acid sought should also be soluble in dilute hydrochloric acid, it may be separated from the amino-acid by crystallization, after precipitating the tin with sulphuretted hydrogen.

906. Test for Triple-bonding in Compounds Containing the ($-C\equiv CH$) Group.

Dilute 1 cc. of ammoniacal cuprous chloride solution,† in a test-tube, with 5 cc. of cold water. Add a few drops of the hydrocarbon, if a liquid, and shake. If the hydrocarbon is a gas, conduct it directly into the copper solution. Collect the precipitate on a filter. Wash with cold water and observe the color.

The hydrogen atoms in compounds containing the $\equiv CH$ group are usually replaceable by copper when thus treated. These copper compounds appear as insoluble flocculent precipitates, varying in color, according to the body from which they are obtained, from a dark brick-red to a greenish yellow. When washed with alcohol and ether and dried with proper precautions, they often explode violently when struck a sharp blow or when strongly heated.

907. Saturated Ethers of Division B.

Drop 1 cc. of the compound slowly into 2 cc. of ice-cold sulphuric acid (sp. gr. 1.84) contained in a five-inch test-tube standing in a beaker of ice-water. Without removing the test-tube from the ice-water, shake briskly for half a minute or more. Then, after allowing to stand for a minute or two, observe whether the compound has dissolved completely to a colorless or nearly colorless solution. In case such a solution has been formed, pour it slowly into a second test-tube containing 3 cc. of cold water, shaking and cooling meanwhile, just as was done during the preparation of the acid solution. If the mixture on standing separates into two layers, remove and reject the lower layer, which will consist of dilute sulphuric acid, with the aid of a long capillary-pointed medicine-dropper. Wash the upper layer by shaking with 2 cc. of sodium-carbonate solution. If an emulsion forms, hasten the separation into layers by warming. Remove the carbonate solution as before by the aid of the dropper, and transfer the organic liquid to a dry three-inch test-tube. Add a small fragment of solid potassium carbonate, and heat nearly to boiling to hasten the drying action. Then after a few minutes, in order to ascert[illegible] product obtained is identical with the original substance, determine the [illegible] clear dried

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* Thus Fileti (G. 21, I, 5 and 22) used one part of acid to one of [illegible]izing p-propylisopropylbenzene, obtaining terephthalic acid with only a trace of a nit[illegible]

† **Ammoniacal Cuprous Chloride Reagent.**—This is the reagent used in gas analysis for the absorption of carbon monoxide.—It is prepared from an acid cuprous chloride solution as required for use. To prepare the acid solution, cover the bottom of a bottle with a layer of powdered copper oxide 1 cm. deep. Place in the bottle a number of pieces of rather stout copper wire, reaching from *top to bottom*, sufficient to make a bundle an inch in diameter, and [illegible] bottle with common hydrochloric acid of 1.10 sp. gr. Stopper, and allow to stand wi[illegible]sional shaking for some days, or until the solution becomes nearly or quite colorless. [illegible] about to make a test, decant a little of the clear acid solution, and add ammonia to it [illegible] present in slight excess, i.e., until the mixture has a distinctly ammoniacal odor. The space left in the stock bottle after every withdrawal of solution should be immediately filled with more hydrochloric acid (1.10 sp. gr.), and the bottle always be kept tightly stoppered to prevent absorption of oxygen from the air.

liquid by Siwoloboff's method. For a more detailed description of the manipulations involved in the washing and drying, and in the boiling-point determination, read the latter half of paragraph *i.* on the identification of soluble alcohols obtained in saponification tests (cf. p. 115).

Any species of Genus IX, Division B, that dissolves in sulphuric acid in this test to a clear, nearly colorless solution, which, upon dilution, gives a liquid identical in boiling-point with the original substance, is probably the oxide of a saturated hydrocarbon radical or, possibly, an "unsaponifiable ester." Unsaturated ethers and unsaturated hydrocarbons may also dissolve completely in the cold acid, or may be entirely decomposed by the reagent; but when a clear solution does result, dilution with water can not be expected to yield the original substance. Saturated hydrocarbons, even the aromatic ones, do not dissolve in the cold acid to any considerable extent.

911. **Acenaphthene.** (Properties tabulated on p. 177.)

Dissolve 0.05 grm. of the hydrocarbon and 0.10 grm. of picric acid in 2.5 cc. of boiling 95 per cent alcohol in a dry test-tube. Allow the solution to cool down to the temperature of the laboratory gradually. Acenaphthene under these conditions yields a beautifully crystallized orange-colored picric-acid compound, $C_{12}H_{10}.C_6H_3(NO_2)_3O$, whose slender flat needles shoot from the bottom of the tube to the surface of the solution. Collect on a small filter, and wash with 3 cc. of cold alcohol. Dry for fifteen minutes on a piece of porous tile at 100°, and determine the melting-point.

The color of the dry crystals is nearly the orange of the color standard (O–YO). They melt at 161°–162° (uncor.).

912. **Anthracene.** (Properties tabulated on p. 180.)

Place in a six-inch test-tube 0.05 grm. of the hydrocarbon, 1.5 grms. of chromic acid (CrO_3), 4 cc. of glacial acetic acid, and 1 cc. of water. Support the tube by a clamp so that its lower end shall rest in a circular perforation in a piece of asbestos board arranged as in Test 312–2, and boil for ten minutes over a small flame, so gently that the vapors shall all condense on the sides of the tube. Pour into 20 cc. of cold water. Collect the flocculent precipitate on a filter. Wash thoroughly with much water, and finally with 5 cc. of cold alcohol. Transfer the precipitate to a dry test-tube and boil with 10 cc. of strong alcohol. Cool. Collect the nearly white precipitate on a small filter. Wash with 5 cc. of cold alcohol. Boil up a second time with 10 cc. of strong alcohol, and again cool. Filter, and wash with 5 cc. of cold alcohol. Dry the residue fifteen minutes at 100° on a piece of porous tile, and determine the melting-point.

Anthraquinone, the product obtained in this test, is a pale yellowish compound, crystallizing from alcohol in minute needles which melt at 279°–280° (uncor.). For other characteristic pro[illegible]aquinone see Test 1011.

913. **Benz[illegible]**roperties tabulated on p. 189.)

Mix in a dry test-tube three drops of the hydrocarbon, 1 cc. of nitric acid (sp. gr. 1.42), and 1 cc. of sulphuric acid (sp. gr. 1.84). Heat the mixture until it begins to boil, and maintain it at this temperature for half a minute. Then pour slowly into 10 cc. of cold water. Cool quickly. Shake. Collect the bulky flocculent precipitate on a small [illegible]r, and wash until the washings are no longer colored. Dissolve in 8 cc. of boiling dilute [illegible]hol (1:1). Allow to stand until the solution has assumed the room temperature. The liquid will become filled with long, fine, nearly white needles of m-dinitrobenzene. Collect on a small filter. Wash with 5 cc. of cold dilute alcohol (1:1). Drain on a piece of porous tile and dry fifteen minutes at 50°.

The *dinitrobenzene* formed in this test melts at 89°–89.5° (uncor.).

914. **Mesitylene.** (Properties tabulated on p. 190.)

Allow one drop of the hydrocarbon to fall into a mixture of 2 cc. of sulphuric acid (sp. gr. 1.84) and 1 cc. of fuming nitric acid (sp. gr. 1.48) contained in a dry test-tube. Shake, and then boil very gently for one minute over a small flame. Break up any hard lumps that may form with a stirring-rod, and pour into 10–12 cc. of cold water. Collect the solid nitro-compound on a very small filter and wash well with cold water. Then wash once with 5 cc. of cold strong alcohol. Transfer to a test-tube and boil gently with 15 cc. of 95 per cent alcohol (*) until all dissolves. (The compound dissolves quite slowly.) Allow to cool. Shake vigorously. Collect the crystalline precipitate in the point of a very small filter. Wash with 5 cc. of cold 95 per cent alcohol (**). Drain on a piece of porous tile; dry for fifteen minutes at 100°, and determine the melting-point.

The product in this test, *trinitromesitylene,* is obtained in the form of minute colorless needles melting at 235° (uncor.).

915. **Naphthalene.** (Properties tabulated on p. 176.)

Dissolve 0.05 grm. of the hydrocarbon and 0.10 grm. of picric acid in 2 cc. of boiling 95 per cent alcohol. Allow the solution to cool gradually. Collect the long, hair-like yellow (Y–YT1) needles of the picric-acid compound, $C_{10}H_8.C_6H_3(NO_2)_3O$, on a small filter, and wash with 1 cc. of strong alcohol. After draining, transfer to a piece of porous tile, and press out adhering mother-liquor. Form the crystals into a little mound on a dry part of the tile; rinse them off with 5–10 drops of strong alcohol. Repeat the washing with alcohol twice more in the same manner, pressing out the adhering alcohol on a dry part of the tile each time with a small spatula. Spread out the crystals on a bit of dry tile and dry for 15–20 minutes at 50°. Then determine the melting-point.

The *picric-acid compound of naphthalene,* thus purified, melts at 150.5° (uncor.). (Long-continued drying at a high temperature is inadmissible since it causes a gradual loss of naphthalene.)

916. **Phenanthrene.** (Properties tabulated on p. 177.)

Dissolve 0.10 grm. of the hydrocarbon and 0.20 grm. of picric acid in 5.0 cc. of boiling 95 per cent alcohol. Allow to stand until quite cold. The picric-acid derivative of phenanthrene that forms separates in crystals. Collect on a filter, and allow to drain well without washing. Transfer to a piece of porous tile to absorb the last of the mother-liquor. Redissolve in 1 cc. of boiling alcohol. Allow to cool slowly as before. Collect the crystals on a piece of tile to absorb the mother-liquor, and wash with five drops of strong alcohol. When the alcohol has nearly all disappeared, place on a fresh piece of tile; dry fifteen minutes at 100°, and determine the melting-point.

The *picric-acid compound of phenanthrene,* $C_{14}H_{10}.C_6H_3(NO_2)_3.O$, obtained in this test, forms long, hair-like needles which are orange-yellow (OY) when dry, and melt at 143° (uncor.).

917. **Pseudocumene.** (Properties tabulated on p. 190.)

Nitrate two drops of the hydrocarbon by the procedure of Test 914 for mesitylene. Do not increase the quantities of acids and solvents prescribed, but follow the directions given literally, except that more than usual care must be taken not to overheat during nitration. During the operation the test-tube should be held at some distance above the flame, and the heating should be interrupted before the expiration of the minute if the mixture show signs of darkening, or if a sublimate should begin to appear on the sides of the tube.

The *trinitro-pseudocumene* formed in this test is a nearly white crystalline compound melting at 184° (uncor. .

918. Toluene. (Properties tabulated on p. 189.)

Dissolve three drops of the hydrocarbon in 1.5 cc. of the strongest fuming nitric acid. Then add at once, without cooling, 1.5 cc. of fuming sulphuric acid (concentrated sulphuric acid containing in solution about 10 per cent of sulphuric anhydride—the same reagent that is used for Test 902). After half a minute pour the mixture into 10 cc. of cold water in a test-tube. Cool well with running water. Close the tube with the thumb and shake vigorously and persistently until the nitro-compound separates in yellowish-white flocks, leaving the solution clear.

Collect the precipitate on a very small filter and wash with cold water. Dissolve in 8 cc. of boiling 50 per cent alcohol. Cool in running water. Shake vigorously. Filter. Wash the precipitate with 5 cc. of cold 50 per cent alcohol. Redissolve the washed precipitate a second time in 8 cc. of boiling 50 per cent alcohol. Cool. Shake. Wash with 5 cc. of 50 per cent alcohol. Dry, and determine the melting-point.

2, 4-*Dinitrotoluene*, the product in this test, is a nearly white precipitate of crystalline structure melting at 70°–71° (uncor.). (If the solution, in making the last crystallization, is allowed to cool slowly, the compound will separate out in the form of delicate white needles.)

919. m-Xylene. (Properties tabulated on p. 189.)

Nitrate *two* drops of the hydrocarbon by the procedure of Test 914 for mesitylene Do not increase the quantities of acids or solvents prescribed, but follow the directions given literally in every detail, except that the precipitate referred to at the point marked by the double asterisk (**) should receive one additional crystallization from 10 cc. of boiling 95 per cent alcohol before being dried.

The *trinitro-m-xylene* formed in this test is a nearly white crystalline compound melting at 181°–181.5° (uncor.).

920. p-Xylene. (Properties tabulated on p. 189.)

Nitrate two drops of the hydrocarbon by the procedure of Test 914 for mesitylene. Do not increase the quantities of acids or solvents prescribed, but follow the directions given literally in every detail, except that the quantity of 95 per cent alcohol used in crystallizing at the point marked by the single asterisk (*) should be reduced from 15 cc. to 5 cc.

The *trinitro-p-xylene* formed in this test is a nearly white crystalline compound melting at 138.5°–139° (uncor.).

921. o-Xylene. (Properties tabulated on p. 189.)

This hydrocarbon is easily distinguished from the meta and para compounds by the fact that when nitrated by the procedure prescribed in Tests 919 and 920, it gives an oily instead of a solid high-melting nitro-derivative. The following test may also be applied.

Sulphonate 0.25 cc. of the hydrocarbon by persistently shaking in a test-tube with 1 cc. of sulphuric acid (sp. gr. 1.84). During the shaking the tube should be *gently* warmed from time to time by dipping it for a second or two into boiling water. When the hydrocarbon has all dissolved (this will require 3–5 minutes), cool, and pour slowly into 10 cc. of a saturated solution of common salt. Cool well, and shake vigorously. The mixture will soon become pasty from the separation of a heavy precipitate of sodium o-xylenesulphonate. Filter, and wash with 10 cc. of a cold saturated salt solution. Press on a tile, and dry 10 minutes at 125°. Crush.

Mix 4 parts by weight of phosphorus pentachloride with 3 parts of the dry sulphonate in a test-tube, and heat for 10 minutes at about 100°. Cool, and pour in 5 cc. of ice-cold water. Shake. Allow to settle. Decant the water through a wet filter. Wash again by shaking with 5 cc. of cold water, followed by decantation. Return any precipitate that may have collected on the filter to the test-tube. Add 2 cc. of the most concentrated ammonia. Boil gently until the ammonia odor has almost disappeared. Dilute with 10 cc. of water. Heat to boiling. Filter hot. Cool the filtrate well with ice water. Shake vigorously, and collect the precipitate of the sulphonamide on a small filter. Wash with 5 cc. of cold water. Redissolve in 5 cc. of boiling water, and cool. Shake, filter, and wash as before. Repeat these operations twice more. Then dry for 15 minutes at 110° and determine the melting-point.

o-Xylenesulphonamide, the product of this test, crystallizes in pearly-white scales which melt at 143.5°–144°.

CHAPTER XII.

SUBORDER II.

THE COLORED COMPOUNDS OF ORDER I.

(Containing Carbon, Hydrogen, and Oxygen.)

THE CONTENTS OF SUBORDER II ARE INDICATED BY THE TITLE "COLORED COMPOUNDS." ANY CAREFULLY PURIFIED SOLID SPECIES OF ORDER I WHOSE COLOR EXCEEDS TINT 3 OF THE COLOR STANDARD (CF. PAGE 231) IN SATURATION, OR ANY YELLOW LIQUID SPECIES WHOSE COLOR WHEN VIEWED IN A LAYER 1 CM. THICK AGAINST A WHITE BACKGROUND IS MORE SATURATED THAN YT1 OF THE STANDARD, WILL BE CONSIDERED COLORED.

A very faint tinge of straw-yellow, caused by traces of impurities or decomposition products so small as to have no appreciable effect on the general chemical behavior of the substance, is often observed in specimens of compounds belonging to Suborder I. In doubtful cases the attempt should be made to decolorize such substances by boiling their solutions with purified bone-black. Compounds with colors less saturated than the tints of Series 3 of the color standard are described in Suborder I with the colorless compounds, but also sometimes receive mention in Suborder II.

Subdivisions of Suborder II.—The species described in Suborder II are arranged in two divisions, A for solids, and B for liquids; but are not numerous enough to require further subdivision into genera. They are all either ketones, quinones, or phenols.

The solid species are grouped in two sections. *The arrangement in Section* 1 is based upon melting-point, as is customary for solids in other parts of the work. Section 2 is virtually an appendix to Section 1, added to provide for the partial identification of certain important bodies, dyes, and acidimetric indicators, which have the common property of giving intensely colored solutions in alkali, but which fuse with so much decomposition, or at such high temperatures, or which are so difficult to isolate in a state of perfect purity, that their melting-points are unknown or have little practical significance. Some of these bodies are not met with except in the form of moist pastes and amorphous powders of rather variable composition, and are only admitted to the tables as compounds by courtesy because of the interest attaching to them as colors.

The arrangement of species in Section 2 is dependent on the color of the solution of the substance in dilute aqueous alkali, as is more fully explained on page 212. *To make the color comparison,* dissolve a few milligrams of the finely powdered substance by shaking in a test-tube with 5 cc. of 1 per cent cold sodium-hydroxide solution; and then dilute, if necessary, with water, until the mixture when held before a white background shows a depth of color that approaches either the normal tone, or the first tint of that hue of the standard which the color of the solution most closely resembles. The comparison should be made quickly, as many of the solutions absorb oxygen from the air, or change rapidly in both hue and tone on standing.

SUBORDER II, COLORED COMPOUNDS.

DIVISION A, SECTION 1,—SOLID SPECIES OF DETERMINED MELTING-POINT.

Melting-point (C.°).	**COLORED COMPOUNDS.**—Solid Species of Determined Melting-point.
28	† **Phoron, $C_9H_{14}O$.**—B. p. 198·5°.—Pale-yellow cryst.—Cf. VII, A, p. 136.
41	**Benzfuril, Ph.CO.CO.C_4H_3O.**—Fine yellow ndl. fr. h. dil. alc.—Volatile undec.—S. alkalies giving benzfurilic ac. (dec. 108°).—25 pt. c. Br give tetrabromide, yellow ndl. fr. alc., m. p. 127°–8°.
45·5	† **Thymoquinone, (Me).(Me_2CH).O_2.C_6H_2(1, 4, 2, 5).**—B. p. 232°.—Orange-yellow (OY) tbl. v. d. s. aq.; e. s. alc. or eth.—Odor sharp like quinone, but also like thymol!—S. without decomposition in c. conc. H_2SO_4 or HNO_3.—For characteristic color reactions cf. B. 18, 3196.—Heat 0·1 grm w. 5 cc. aq. and 0·2 grm. Br for ½ hr. on boiling water-bath. Wash the red oil with c. aq. until it is yellow and crystalline. Recryst. twice fr. 2 cc. h. alc. (adding a little eth. if oil should not crystallize readily). Gives dibromide, yellow lfts., m. p. 73°.
55	**1, 2-Dimethylquinone(3, 6), Me_2.C_6H_2.O_2.**—Sbl. in yellow ndl., d. s. aq.; e. s alc. or eth.
57–8	† **Benzylideneacetophenone.**—Pale yellowish pr.—Cf. VII, A, p. 137.
59–60	**Dioxybenzophenone, $(C_6H_4.OH)_2$.CO.**—B. p. 330°–40° d.—Light-yellow ndl. fr. lgr.—Alm. i. aq.; v. s. alc. or eth.; s. K_2CO_3 but ppt'd by CO_2.—Sol. in dil. alc. colored brown-red by $FeCl_3$.—Warming w. conc. H_2SO_4 or boiling w KOH sol. gives o-benzophenone oxide, ndl. fr. alc., m. p. 173°–4°, v. d. s. c. aq.
68	**Methyl Cinnamenylvinyl Ketone, $C_{12}H_{12}O$.**—Cf. VII, A, p. 137.
68–9	**Toluquinone(2, 5), Me.C_6H_3.O_2.**—Sbl. in rhombic-yellow lft., d. s. c. aq.; v. s. alc. or eth.—Odor pungent, quinone-like!—Aq. sol. is colored brown-red by alkalies.—Reduced by SO_2 to hydrotoluquinone, v. s. aq.; pearly lft. fr. bz.; m. p. 124°.
69–70	**Diphenylpropanetrione, $(PhCO)_2$.CO.**—B. p. 247° (60 mm.).—Golden-yellow ndl. fr. lgr.; e. s. alc.—Very hygroscopic.—Sapon. by NaOH gives benzoic and mandelic acids, benzoïn, and CO_2.—2 pt. boiled w. 5 pt. aniline and 10 pt. alc. give a dianil, yellow pyramids fr. bz., m. p. 148°.
71	**Phenoquinone, $C_6H_4O_2$.2C_6H_6O.**—Fine red ndl. w. green reflections!—S. c. aq.; e. s. alc. or eth.; s. lgr. (dif. fr. quinone and quinhydrone).—The red crystals become blue-black upon addition of alkali.—Reduced to hydroquinone (Test 411) by SO_2.
72–3	**1, 3-Dimethylquinone(2, 5), Me_2.C_6H_2.O_2.**—Yellow ndl.
83·5–4	**Diphenylene Ketone, $(C_6H_4)_2$.CO.**—B. p. 341·5°.—Large yellow tbl. fr. alc., i. aq.; v. s. alc. or eth.—Slowly oxid. by alkaline $KMnO_4$ to phthalic ac.—Oxime, m. p. 195°.—Well-cooled, fuming HNO_3 gives yellow nitro-comp. which sbl. easily, is d. s. c. alc., and melts at 220°.—Fusion w. KOH gives phenylbenzoic ac.
85	**Pseudodiphenylene Ketone, $C_{13}H_8O$.**—Dark-red cryst. fr. eth.—C. fuming HNO_3 gives dinitro-comp., ndl. fr. h. glacial Āc; i. alc.; m. p. 310°.—Boiled w. dil. alc. quickly gives diphenylene ketone (cf. above).
90	**Acetonephenanthrenequinone, $C_{17}H_{14}O_3$.**—Thin pale-yellow tbl. fr. eth.; i. aq.—Phenanthrenequinone separates upon boiling w. KOH sol.
90	**Retene Ketone, $C_{17}H_{16}O$.**—Vitreous sulphur-yellow cryst.; vol. w. st.; e. s. alc. or eth.; i. $NaHSO_3$.—Combines w. phenylhydrazine, but not w. hydroxylamine.—Ignition w. Zn dust gives retenefluorene.

Melting-point (C.°).	**COLORED COMPOUNDS.**—Solid Species of Determined Melting-point
92–3	**Acenaphthylene, $C_{12}H_8$.**—Golden-yellow cryst.—Cf. IX, A.
95	† **Benzil, Ph.CO.CO.Ph.**—B. p. 346°–8° c.—Fine pale-yellow (YT2) ndl., i. aq.; e. s. alc. or eth.—Dissolve 4 pt. in x's abs. alc.; add 1 pt. solid KOH and boil down in porcelain dish. An intense violet color (VR) appears, but disappears on continued boiling!—Sapon. w. NaOH gives benzilic ac. (quantitative).—Gives oximes.
98	**Benzocotoïn, $(OH)(COPh)(OMe)_2.C_6H_2$.**—Pale-yellow pr. fr. alc.; e. s. eth.; s. dil., but i. conc. NaOH.—$Pb\bar{A}c_2$ gives yellow ppt. w. NH_4OH sol.—Sol. gives dark-brown color w. $FeCl_3$.
102–3	**Cinnamyleneacetophenone, $C_{17}H_{14}O$.**—Golden ndl. fr. alc.—Colored cherry-red by conc. H_2SO_4.—Oxime, m. p. 131°.
103	**Oxy-m-xyloquinone, $Me_2.C_6H.(OH)_2.O_2$.**—Orange-red ndl., v. vol. w. st.—Sbl. in yellow ndl.—Odor like benzoquinone!—S. h. aq.; sol. colored red-violet by alkalies, even by $CaCO_3$!
103	**Methyl Oxynaphthyl Ketone, $Me.CO.C_{10}H_6.OH$.**—B. p. 325° sl. d.—Pale-green 6-sided pr. fr. bz.!—I. aq.; d. s. alc.; s. alkalies, but ppt'd by CO_2.—Oxime, m. p. 168°–9°.
103–4	**Pipitzahoïc Ac., (Perezon), $C_{15}H_{20}O_3$.**—Golden lft. fr. alc.—Sbl. undec.—S. in KOH w. intense purple color.—Ba salt purple and v. d. s. aq.—CO_2 separates ac. fr. salts.
104	**Santalin, $C_{15}H_{14}O_5$(?).**—Mic. red cryst. or red mass; misc. w. abs. alc. w. blood-red color; s. eth.—A weak acid, s. alkalies w. violet color.—Ammon. sol. gives dark-violet cryst. ppt. w. $BaCl_2$.—KOH fusion gives Āc and resorcin (cf. Test 418).
106	**Cinnamylenebenzylideneacetone, $C_{19}H_{16}O$.**—Yellow pr. fr alc.—Oxime, yellow lfts., m. p. 127°–8°.
109–10	**Phenylnaphthoquinone, $Ph.C_{10}H_5O_2$.**—Golden-yellow ndl. fr. alc.; s. eth.; d. s. lgr.—Polymerized quickly by sunlight.—An alc. sol. sat. w. NH_3 separates a comp. (red ndl. s. eth.) on standing, m. p. 174°.—Gives aniline derivative fr. h. alc. sol. w. aniline, dark-red ndl., m. p. 158°.
111	**1, 2, 4, 5-Tetramethylquinone, $Me_4.C_6.O_2$.**—Sbl. at 100° in golden ndl., d. s. c. lgr.; v. s. alc. or eth.—Very volatile with steam.
112–2·5	† **Dibenzylideneacetone, $(Ph.CH:CH)_2.CO$.**—Gives Test VII–1.—Yellow lft., d. s. alc.; s. eth.—S. in conc. H_2SO_4 w. deep orange-red color.—Colored dark vermilion by conc. HCl without being dissolved.—Adds Br_4 in $CHCl_3$ sol. to form comp. of m. p. 208°–11° d., ndl., v. d. s. alc. or eth.
115·7	† **Benzoquinone, p-$C_6H_4.O_2$.**—Peculiar, sharp irritating odor slightly suggesting that of chlorine!—Golden-yellow monoclinic pr. fr. h. aq.; d. s. c. aq.; e. s. alc. or eth.; s. h. lgr.—Sbl. easily in golden ndl.—Sol. in alkalies absorbs oxygen rapidly, becoming dark-colored.—Identify by Test 1012!
d. 115–20	**1, 2-(β)-Naphthoquinone, $C_{10}H_6O_2$.**—Small *odorless* red ndl. fr. eth., or orange lft. fr. bz.—Not vol. w. st.!—Unstable.—Sol. in dil. NaOH is yellow and absorbs O rapidly.—Add 1½ pt. aniline to a conc. sol. of 1 pt. of the quinone in h. alc.; anilinonaphthoquinone separates as red ndl. w. golden to greenish reflections, i. aq.; d. s. alc., m. p 240° (differs from aniline α-naphthoquinone in being s. in cold alkalies).—$KMnO_4$ oxidizes to phthalic ac.—Reduced by SO_2 to corresponding hydroquinone.
120–5	† **Absinthin, $C_{20}H_{28}O_4 + \frac{1}{2}H_2O$.**—(Fr. Artemesia absinthium.)—Yellowish (OYT2) mic. cryst. fr. alc. w. bitter taste and wormwood odor (sample fr. Merck)!—Alm. i. c. aq.; e. s. alc or eth.—Sol. in NaOH is brown-red.—Sol. in H_2SO_4 is brownish and then green-blue liq.—Reduces ammon. $AgNO_3$, but not Fehling's sol.—Alc. sol. gives ppt. w. tannic ac.
125	**Benzohydroquinone, $Ph.CO.C_6H_3.(OH)_2$.**—Long yellow ndl. fr. dil. alc.; e. s. alc. or eth.
125	**1, 4-Dimethylquinone(2, 5), (Phloron), $Me_2.C_6H_2.O_2$.**—Long golden-yellow ndl. fr. alc.; d. s. h. aq. or c. alc.—Sbl. undec.—Reduced by SO_2 to hydrophloron.—Br aq. gives dibrom-derivative, golden lft. fr. h. alc., m. p. 184°.—Aniline derivative yellow-green ndl., m. p. 264° (A, 255, 171).

Melting-point (C.°).	**COLORED COMPOUNDS.**—Solid Species of Determined Melting-point.
125	† **1, 4-(α)-Naphthoquinone, $C_{10}H_6O_2$.**—Yellow (Y) ndl. w. pungent quinone-like odor, which is, however, much less intense than that of benzoquinone.—E. vol. w. st. (dif. fr. β-comp.).—S. alc.; e. s. eth.; d. s. aq.—Sol. in alkali is red-brown.—Identify by Test 1013!
127	**Oxylapachol(α), $C_{15}H_{14}O_4$.**—Yellow ndl. e. s. alc., eth., or alkalies.—$Ag\bar{A}+H_2O$, chestnut-brown cryst. ppt.
129	† **αβ-Dibenzoylstyrene, Ph.CO.CPh:CH.CO.Ph.**—Pale-yellow ndl. (YT2) fr. alc., v. d. s. c. alc. or eth.; e. s. h. alc —Odor faint aromatic.—M. p. of nitro deriv. 155°.
abt. 130	**Oxypipitzahoïc Ac., $C_{15}H_{20}O_4$.**—Reddish-yellow lft.—Sol. in KOH is violet-red.
130–1	† **Cotoïn, $MeO.C_6H_2(OH)_2.CO.Ph$.**—(In coto bark.)—Pale-yellow pr. fr. h. aq.—Sulphur-yellow (sample fr. Schuchardt YT2) tbl. fr. alc.—Taste sharp and biting; dust provokes sneezing.—V. d. s. c. aq.; e. s. alc., eth., NaOH, or Na_2CO_3, but ppt'd by CO_2.—Reduces ammon. $AgNO_3$ sol. cold and Fehling's sol. on heating.—In conc. aq. sol. $FeCl_3$ gives brown-black ppt. and in alc. sol. brown-red color.—Warming w. conc. H_2SO_4 gives benzoic ac. and phloroglucin.—Sol. in ammonia gives yellow amorphous ppt. w. $Pb\bar{A}c_2$.—Yields a cryst. oxime.
132·5	**Chrysoketone, $C_{17}H_{10}O$.**—Silky yellow ndl. or orange-red pr.
133–4	**Salicyloresorcin, $HO.C_6H_4.CO.C_6H_3.(OH)_2$.**—Yellow lft. fr. h. alc.—S. h. Na_2CO_3 sol., but ppt'd by CO_2.—Fusion w. KOH gives resorcin and salicylic ac.
135	† **Furoïn.**—When pure, slightly yellowish; usually buff colored. Sol. in NaOH violet-red.—Cf. Genus IV, A.
140	† **Hæmatoxylin, $C_{16}H_{14}O_6+3H_2O$.**—Melts w. loss of aq.—Taste sweet!—Colorless tetragonal pr. when pure and freshly prepared, but soon changed by sunlight to dark red-brown.—D. s. c. aq.; e. s. alc., eth., or h. aq.; s. alkalies and alkali carbonates w. intense beautiful purple-red color, changed by acids to a clear orange-yellow (OY).—Thin layers of the very intensely colored alkaline sol. are V; largely diluted VR and R.—Gives dark color w. $FeCl_3$ and finally a ppt.—W. alum sol. gives rich RV color, which largely diluted gives VR.—Reduces ammon. $AgNO_3$ sol. in the cold.
140	**Lapachol, $C_{15}H_{14}O_3$.**—Small yellow pr. fr. eth. or bz.—Sbl. w. much difficulty.—S. NaOH or Na_2CO_3 w. red color.—Dissolved by shaking w. 5 pt. conc. H_2SO_4 and ppt'd by aq. gives β-lapachon, which cryst. fr. alc. in flat orange-red ndl., m. p. 155°–6°.—Readily oxid. to phthalic ac. by HNO_3 (sp. gr. 1·38).
140–1	† **Alizarin Yellow A (Trioxybenzophenone), $(HO)_3.C_6H_2.CO.Ph$.**—(Cryst. w. 1 aq.).—Yellow ndl., d. s. h. aq.; e. s. alc. or eth.; ppt'd fr. Na_2CO_3 sol. by CO_2.—Sol. in conc. H_2SO_4 yellow.—Warming w. conc. H_2SO_4 gives benzoic ac.
142	**Pyrene Ketone, $C_{13}H_8O$.**—Golden-yellow tbl. fr. alc.—Gives $NaHSO_3$ comp.—Fuming HNO_3 dissolves w. deep purple-red color.—$KMnO_4$ oxid. to naphthalic ac.
142	† **Dicinnamenyl Vinyl Ketone, $C_{21}H_{18}O$.**—Golden-yellow ndl. fr. abs. alc.; d. s. c. alc. or eth.
143–4	**Perezinon, $C_{15}H_{18}O_3$.**—Pale-yellow ndl. s. alc. or eth.—Garnet-red on warming with Millon's reagent.
143–4	**2, 4′-Dioxybenzophenone, $(C_6H_4.OH)_2.CO$.**—Pale-yellow lft. fr. h. aq.; e. s. alc. or eth.; s. alkalies, but ppt'd by CO_2.—Fusion w. KOH gives phenol and p-oxybenzoic ac.
146–7	**1-Oxyxanthone, $C_{13}H_8O_3$.**—Clear-yellow ndl. fr. alc.; d. s. h. aq.—Fusion w. KOH gives resorcin and salicylic ac.—W. Br in $\bar{A}c$ sol. gives dibrom-derivative, yellow ndl., m. p. 222°.
146–8	† **Barbaloïn, $C_{16}H_{18}O_7$** (dried at 100°).—(Before drying, yellow ndl., w. xH_2O, m. p. 70°–80°).—Taste sweetish and then *very bitter*.—S. 60 pt. aq., 20 pt. alc., or 470 pt. eth.; v. s. NaOH to deep orange-red sol.; e. s. acids.—A trace of $FeCl_3$ gives fine red-violet color w. aq. sol.; more $FeCl_3$ gives a greenish black!—Br water added drop by drop w. a pause of ½ min. between each addition gives a fine VRT2 color. An x's of Br immediately changes the color to yellow, and then gives a yellow ppt. of tribromaloïn.—A little of the powder stirred into a drop of HNO_3 (sp. gr. 1·2) gives a deep carmine-red, soon changing to orange. (The carmine color w. nataloïn is permanent, but is not given at all by socraloïn.)

Melting-point (C.°).	**COLORED COMPOUNDS.**—Solid Species of Determined Melting-point.
148	**Vulpic Ac., $C_{19}H_{14}O_5$.**—(In Cetraria vulpina.)—Yellow monoclinic lft. fr. alc., v. d. s. alc.; e. s. eth.—Heated above 200° gives MeOH and pulvic anhyd.—Sapon. by boiling $Ba(OH)_2$ gives MeOH, oxalic, and α-toluic ac.
149	**2, 3, 4, 2′-Tetraoxybenzophenone, $(OH)_3.C_6H_2.CO.C_6H_4.OH$.**—Cryst. w. $1H_2O$ in greenish-yellow lft.; e. s. alc. or eth.—W. warm conc. H_2SO_4 splits to salicylic ac., etc.
152	**Paracotoïn, $C_{12}H_8O_4$.**—Pale-yellow lft., d. s. h. aq.; e. s. eth. or h. alc.—S. in alkalies, sapon. giving a yellow i. ac., m. p. 108°.—Fusion w. KOH gives piperonylic ac.—Br substitutes in c. $CHCl_3$ sol. giving comp. cryst. fr. alc., m. p. 200°-1°.
151-4	**5-α-Oxynaphthoquinone (Juglon), $HO.C_{10}H_5.O_2$.**—Yellowish to brick-red ndl. fr. $CHCl_3$.—Begins to darken on heating to abt. 125°.—Somewhat vol. w. st.—I. aq.; e. s. alc.; s. conc. H_2SO_4 w. intense blood-red color, s. in very dil. NaOH w. purple color, changing to brown.—Boiling w. aq. gives i. greenish-brown powder, s. in alkalies w. deep-violet color.—$Cu\bar{A}c_2$ added to alc. sol. gives dark-violet mic. pr. w. metallic lustre.
156-8d.	**Euxanthic Ac., $C_{19}H_{18}O_{11}$.**—Straw-yellow ndl., anhydrous when fr. alc.—D. s. c. alc.; e. s. eth.—$Pb\bar{A}c_2$, yellow gelatinous ppt.—Dist. w. HCl gives furfurol (Test 115).
162	**Furil, $C_4H_3O.CO.CO.C_4H_3O$.**—Golden-yellow ndl. alm. i. aq.; d. s. eth. or c. alc.; e. s. $CHCl_3$.—Sapon. gives furilic ac. (v. unstable).—E. dec. by conc. HCl.—Reduced to furoin by Na amalgam.
160-70d.	† **Anthranol.**—Cf. Genus IV, A.—Color YT2-YT3. D. s. in alkali w. bright-yellow color.
170	**Diphenylbutanoltrion, Ph.CO.CH(OH).CO.CO.Ph.**—Yellow pr.; e. s. alc. or eth.
170-1	**Dioxydimethyltriphenylmethane, $(Me.C_6H_3.OH)_2.CH.Ph$.**—Pale-yellow ndl. fr. dil. alc.; d. s. aq.; e. s. alc. or eth.; e. s. dil. NaOH.—Gradually turns red on exposure to air, especially if warmed. Diacetate by boiling w. x's acetic anhyd., yellow ndl. fr. alc., m. p. 94°.
171	† **Quinhydrone, $C_6H_4.O_2.C_6H_4.(OH)_2$.**—Dark-green pr. w. metallic lustre, red-brown by transmitted light!—Sbl. w. slight dec.—S. h. aq.; e. s. alc. or eth. w. yellow color; i. lgr.—Boiled w. aq. splits to quinone and hydroquinone.—Reduces ammon. $AgNO_3$ sol.—Reduced by SO_2 to hydroquinone (Test 411).
171-2	**6-Phenyl-3-benzoylpyronon, $C_{18}H_{12}O_4$.**—Yellow ndl. fr. alc.; d. s. c. alc., e. s. eth.—Boiled w. alc. KOH gives acetophenone, benzoic, and acetic ac.—$FeCl_3$ gives orange-red color w. alc. sol.—Sol. of NH_4 salt gives a scarlet-red ppt. w. $FeCl_3$.—Sol. in conc. H_2SO_4 is olive-green, becoming violet when warmed.
170-78	† **Chrysarobin, $C_{30}H_{26}O_7$.**—Yellow ndl. or lft. fr. acetic ac. (sample fr. Merck YS1 powd.).—Sbl. w. dec. in yellow lft.—I. aq. or NH_4OH; s. in not too dil. KOH w. yellow color and green fluorescence.—Air passed through sol. oxid. to chrysophanic ac., m. p. 162°.—Ignition w. Zn dust gives methylanthracene.—Sol. in conc. H_2SO_4 is yellow.
177	**2-Methylanthraquinone, $Me.C_{14}H_7.O_2$.**—Pale-yellow lustrous ndl., s. eth.; v. d. s. alc.; s. conc. H_2SO_4 w. blood-red color, changing to violet on heating!—Ignition w. Zn dust gives 2-methylanthracene.
177	**2-Naphthyl-1, 4-Naphthoquinone, $C_{10}H_7.C_{10}H_5.O_2$.**—E. s. alc. or bz.; s. conc. H_2SO_4 w. indigo-blue color!
178	**Curcumin, $C_{14}H_{14}O_4$.**—Yellow or orange-yellow pr.; i. aq.; d. s. alc.—Sol. in eth. fluoresces green.—S. alkalies w. intense red-brown color.—Sol. in conc. H_2SO_4 is fine reddish purple.—Alc. sol. gives bright-red ppt. w. $Pb\bar{A}c_2$ sol.—Place piece of filter-paper in alc. sol. and evaporate to dryness at 100°. Saturate paper w. boracic ac. sol. A red color appears at once or on evaporating. A drop of NaOH sol. will give series of fine colors, green and purple most prominent; HCl will give a red color changed to green and blue by x's of alkali.
178(?) or 190	**Dioxymethylanthraquinone (Chrysophanic Ac.), $C_{15}H_{10}O_4$.**—6-sided tbl. fr. bz.; golden yellow ndl. fr. alc.; s. eth. or h. alc.; v. d. s. NH_4OH or alkaline carbonates; v. s. NaOH; in each case w. deep-red color.—Salts dec. by CO_2.—Ignition w. Zn dust gives methyl anthracene.

Melting-point (C.°).	COLORED COMPOUNDS.—Solid Species of Determined Melting-point.
181–2	**Fluorenequinone, $C_{13}H_8O_2$.**—Yellowish granules fr. bz.—Hot KOH sol. gives brown product w. odor like diphenyl.
185·5	**Picylene Ketone, $C_{21}H_{12}O$.**—Golden-yellow cryst. powder, e. s. h. bz.—Fusion w KOH gives picenic ac.
188	**Fluoranthenequinone, $C_{15}H_8O_2$.**—Small red ndl.; s. alc. or $NaHSO_3$ sol.—Quickly oxidized to CO_2 by CrO_3 mixture (dif. fr. fluorenequinone).—Ignition w. soda-lime gives diphenyl.
187–92c.	**Sinapic Ac., $C_{11}H_{12}O_5$.**—Pale-yellow ndl., e. s. h. alc.; i. eth.—Na salt gives red ppt. w. $FeCl_3$
a. 190	**Rutin, $C_{27}H_{32}O_{16}+2H_2O$.**—(In leaves of rue: Ruta graveolens.)—Clear yellow silky ndl. fr aq.—Loses $2H_2O$ at 150°–60°.—E. s. h. aq.; i. eth.; s. alkalies.—Sol. colored dark green by $FeCl_3$!—Hydrolyzed by boiling w. dil. ac. to quercetin and rhamnose.
191–2	**o-Diphenyleneketonecarbonic Ac., $C_{14}H_8O_3$.**—Orange-red ndl. fr. dil. alc., alm. i. aq.; e. s. eth.—Ignition w. Zn dust gives fluorene. Warmed w. fuming HNO_3 gives nitro ac., m. p. 245°–6°.
195	**Caffeic Ac., $C_6H_3.(OH)_2.CH{:}CH.CO_2H$.**—(Cryst. w. $\frac{1}{2}H_2O$.)—Straw-yellow pr. fr. aq.; e. s. alc.—Aq. sol. becomes grass-green w. $FeCl_3$, changing to blue or violet upon addition of Na_2CO_3.—Alkaline sols. brown in the air.—Aq. sol. reduces h. $AgNO_3$ and gives a yellow ppt. w. $Pb\bar{A}c_2$.—Dist. gives pyrocatechin, Test 416.
195–6	**α-Usnic Ac., $C_{18}H_{16}O_7$.**—(Fr. various lichens.)—Sulphur-yellow pr. fr. h. alc.; d. s. c. alc. or eth.—Very weak acid.—Salts are yellow.—$FeCl_3$ gives a dark brownish-red color w. alc. sol.
197–7·5	**Retenequinone, $C_{18}H_{16}O_2$.**—Flat orange ndl.; s. h. alc.; d. s. h. eth. or lgr.; i. c. NaOH; s. conc. H_2SO_4 w. green color!—A drop of alc. KOH added to an alc. sol. gives dark Bordeaux-red color which disappears on shaking w. air! Upon warming w. exclusion of air, color reappears.—Ignition w. Zn dust gives retene, m. p. 94°.
199–201	**Carbousnic Ac., $C_{18}H_{16}O_7$.**—(In lichens.)—Yellow pr. similar in properties to α-usnic ac. (cf. m. p. 195°–6°).
200d.	**Eupittonic Ac., $(MeO)_6.C_{19}H_8O_3$.**—Hair-like orange ndl. fr. ethyl alc.—Dibasic.—The blue solution in NaOH gives blue ppt. of Na salt with x's alkali which changes to green cryst. after 24 hrs.
200–1	**Bithymoquinone, $C_{20}H_{24}O_4$.**—Long clear yellow silky ndl., not vol. w. st.—V. d. s. solvents; i. abs. eth.; s. undec. in h. fuming HNO_3.—Dist. gives much thymoquinone (cf. p. 205)!—Not reduced by SO_2, but gives hydrothymoquinone when dist. fr. Zn dust.
200–2	**Euxanthonic Ac., $[C_6H_3.(OH)_2]_2.CO$.**—Yellow warts or cryst. fr. h. aq., s in KOH w. yellow color which darkens rapidly in the air.—Red-yellow ppt. w. $Pb\bar{A}c_2$ sol.—Fusion splits to euxanthone and H_2O.—$FeCl_3$ gives red color.
202	**Quinacetophenone, $Me.CO.C_6H_3(OH)_2$.**—Pale yellow-green cryst.; v. d. s. c. aq.—Reduces Fehling's sol.—$FeCl_3$ gives transient deep-blue color w. aq. sol.
202	† **Phenanthrenequinone, $C_6H_4.CO.CO.C_6H_4$.**—B. p. a. 360°.—Yellow-orange (YO) ndl.; sbl. in cryst.; d. s. h. aq.; d. s. alc. or eth.; e. s. h. $\bar{A}c$; e. s. warm $NaHSO_3$ sol.!—Ignition w. Zn dust gives phenanthrene; w. soda-lime, diphenyl.—Identify by Test 1014!
206d.	**α-Anthracenecarbonic Ac., $C_{15}H_{10}O_2$.**—Cf. III, A, 2.
202–19d.	**Scoparin, $MeO.C_6H_3.(OH).C_{13}H_8O_3.(OH)_5+5H_2O$.**—(In Spartium scoparium.)—Small clear yellow cryst. fr. 70% alc.; v. d. s. c. aq.; e. s. h. aq.; i. eth.; e. s. NaOH or Na_2CO_3 giving greenish-yellow sol.—Bleaching powder colors dark red —HNO_3 gives picric ac.—Fusion w. KOH gives phloroglucin, vanillic, protocatechuic, and acetic acids.
211–12	**Isoanthraquinone, $C_{14}H_8O_2$.**—Pale-yellow ndl.—Fusion w. KOH gives blue mass.—More s. in H_2SO_4 than anthraquinone.
214–15	**Pulvic Ac., $C_{18}H_{12}O_5$.**—Orange pr. fr. alc. which efflorescе to orange powder· s. aq., eth., $CHCl_3$, or bz.—Adds Br, and is oxid. by alkaline $KMnO_4$.

Melting-point (C.°).	**COLORED COMPOUNDS.**—Solid Species of Determined Melting-point.
216–17	† **Piperic Ac., $CH_2.O_2.C_6H_3.CH:C_2H_2:CH.CO_2H$(3, 4, 1).**—Pale-yellow (YT2) ndl., alm. i. aq.; s. h. alc. or eth.—† The sol. in dil. Na_2CO_3 when gently oxid. by warming on a watch-glass w. a few drops of $KMnO_4$ sol. emits the delicate heliotrope aroma of piperonal!—$Ba\bar{A}_2$, i. c. aq.
219	**Purpurin-1-carbonic Ac., $C_{14}H_4(OH)_3O_2.CO_2H$.**—Red lft., i. c. aq. or alc.; d. s. h. $CHCl_3$.—Sol. in Na_2CO_3 is orange-colored.—Boiling w. aq. or alc. gives CO_2 and purpurin.
d. 220	**α-Dioxyanthracene, $C_{14}H_{10}O_2$.**—Yellow lft. or ndl., v. s. alc; the yellow sol. fluoresces strongly blue.—$FeCl_3$ or Br gives blue-green color w. alc. sol.
220	**Oxylepidene** ("Needle-shaped"), **$C_{28}H_{20}O_2$.**—Yellow ndl., i. aq.; d. s. h. alc.; alm. i. eth.
227c.	**Diphenyleneketonecarbonic Ac., $CO.C_{12}H_7.CO_2H$.**—Yellow ndl. fr. alc.; i. aq.; s. conc. H_2SO_4 w. yellow color.—Gives oxime, m. p. 263°.—$Ag\bar{A}$ yellow ppt.
231	**Purpurinxanthinecarbonic Ac., $C_{14}H_5(OH)_2O_2.CO_2H$.**—Golden lft. fr. glacial Āc, s. eth. or h. aq.; s. in NaOH w. red color, or in conc. H_2SO_4 w. intense yellow color.—Dec. above m. p.
231	**2-Oxyxanthone, $C_{13}H_8O_3$.**—Yellowish ndl. fr. dil. alc.—Acetyl deriv., m. p. 161°.
232	**Oxylepidene** ("Octahedral"), **$C_{28}H_{20}O_2$.**—Yellowish octahedra fr. h. Āc, alm. i. alc.; i. h. alcoholic KOH.—Heated nearly to boiling gives isomer, s. alc., w. m. p. 136°.
235	**Chrysoquinone, $C_6H_4.CO.CO.C_{10}H_6$.**—Orange-red ndl.; s. h. alc.; v. d. s. eth.; s. in cold H_2SO_4 w. corn-flower-blue color, ppt'd by aq. (delicate). Sbl. in red ndl. Oxid. by $KMnO_4$ to phthalic ac.—Ignition w. Zn dust gives chrysene.
240c.	† **Euxanthone, $C_{13}H_8O_4$.**—Pale-yellow (YT1) lft. or ndl.; sbl. w. dec.—I. aq.; c. s. h. alc.; d. s. eth.; s. NaOH or conc. NH_4OH w. yellow color.—Green color w. $FeCl_3$.—$Pb\bar{A}c_2$ gives ppt. w. alc. sol.—Gives no oxime or phenylhydrazone.
abt. 250	† **Brazilin.**—Cf. Gen. IV, A!—Cryst. red-brown after exposure to air and light. Sol. in NaOH intense red! Taste sweet!
253–6d.	† **Daphnetin, $C_9H_4O_2.(OH)_2$.**—When strongly heated on a watch-glass has a faint coumarin-like odor.—Pale yellowish ndl. fr. dil. alc. (preparation fr. Schuchardt YT3); s. h. aq.; v. d. s. eth.—$FeCl_3$ added to a 1:4000 aq. sol. gives a permanent green (G) color, changing to red (RS2) when Na_2CO_3 is added (cf. Test 401).—Reduces ammon. $AgNO_3$ or Fehling's sol. instantly.—Gives a yellow gelatinous ppt. w. $Pb\bar{A}c_2$.
256	† **Purpurin, 1, 2, 4-Trioxyanthraquinone, $C_6H_4.(CO)_2.C_6H.(OH)_3$.**—Deep-red ndl. fr. abs. alc.—Long orange ndl. (+H_2O) fr. dil. alc.—S. aq. w. deep-yellow color (no absorption bands).—Sol. in eth. shows absorption bands at E and F.—Sol. in NaOH or Na_2CO_3 is bright red w. two absorption bands in the green.—Sol. in conc. H_2SO_4 is cherry-red.—Oxid. by HNO_3 (cf. Test 905–3) gives phthalic ac.—W. alumina mordant dyes scarlet.
261	**Acenaphthenequinone, $C_{12}H_6O_2$.**—Sbl. in yellow ndl.—V. d. s. alc. or c. Āc.—Dissolved to an acid by boiling w. KOH.—Reduction w. Zn dust in boiling Āc sol. gives acenaphthenon.
262–3	**Xanthopurpurin, $C_6H_4.(CO)_2.C_6H_2.(OH)_2$.**—Yellow ndl. fr. Āc.—Sbl. in orange ndl.—S. in $Ba(OH)_2$ sol. (dif. fr. alizarin and anthrachryson).—S. in NaOH is red.—Boiled w. KOH in air gives purpurin (cf. spectrum above).—Ignition w. Zn dust gives anthracene.—Does not color fibre mordanted w. alumina.
266–8	**Resorcinphenylaceteïn, $C_{20}H_{16}O_4$.**—Mic. brown plates, green by reflected light, fr. alc. + Āc.; i. eth. or bz.—Dil. sol. in NaOH shows intense-green fluorescence.—Diacetate, silky ndl. fr. Āc., m. p. 150° d.
267	**Gentianine, $C_{13}H_7O_5.Me$.**—Pale-yellow silky ndl., d. s. h. aq., alc., or eth.; e. s. alkalies w. golden-yellow color, reprecipitated by CO_2. Diacetate (boiling w. acetyl chloride), hair-like ndl. fr. alc., m. p. 196°.—Reduces Tollen's reagent.

Melting-point (C.°).	**COLORED COMPOUNDS.**—Solid Species of Determined Melting-point.
275 (284·5c.)	† **Anthraquinone, $C_6H_4.CO.C_6H_4.CO$.**—B. p. 380° c.—Sbl. in pale-yellow ndl.—S. 44 pt. h. alc.; v. d. s. c. alc. or eth.—V. stable, not attacked by boiling NaOH or oxid. agents.—Ignition w. Zn dust gives anthracene.—Identify by Test 1011!
275	**1, 3-Dioxyflavone, $C_{15}H_{10}O_4$.**—Thin pale-yellow tbl.—Sbl. in ndl.—Alm. i. aq.; s. h. Āc.; e. s. alkalies w. intense-yellow color.—Alc. sol. is dirty violet w. $FeCl_3$.—Split by boiling KOH to acetophenone, phloroglucin, etc.
276	**2, 3-α-Dioxynaphthoquinone, $(HO)_2.C_{10}H_4.O_2$.**—Orange-red lft., green by reflected light!—Sbl. in ndl. w. metallic lustre.—D. s. h. aq.; v. d s. alc. or eth.—Sol. in NaOH is corn-flower blue; in Na_2CO_3 violet-blue.—E. oxid. to phthalic ac. by Test 905-3.
280	**1, 5-Dioxyanthraquinone (Anthrarufin), $C_{14}H_6O_2.(OH)_2$.**—Sbl. in light-yellow toothed lft., alm. i. aq.; d. s. alc.; s. eth.; alm. i. NH_4OH, Na_2CO_3, or $Ba(OH)_2$; e. s. KOH w. violet-red color.—S. conc. H_2SO_4 w. very intense-red color and fluorescence, distinct even at dilution of 1 : 10,000,000!—Continued fusion w. KOH gives salicylic ac., etc.—Ba salt is carmine-red.
282d.	**Pyrenequinone, $C_{16}H_8O_2$.**—Sbl. w. slight dec. in light purple-red ndl., v. d. s. alc., eth., or CS_2; s. $NaHSO_3$; s. conc. H_2SO_4 w. brown color.—Alc. sol. + 1 drop NaOH is dark wine-red, unchanged upon shaking w. air.—Ignition w. Zn dust in H gives pyrene.
283	**β-Anthraquinonecarbonic Ac., $C_6H_4:(CO)_2:C_6H_3.CO_2H$.**—Yellowish pr. fr. alc., v. d. s. alc. or eth.—Sbl.—Boiled w. Zn dust and KOH gives intense-red color.
289–90	† **Alizarin, $C_6H_4.(CO)_2.(C_6H_2.(OH)_2$.**—B. p. 430°.—T.t. partly immersed in oil-bath at 200° sbl. slowly in OR and O. ndl.—I. aq., v. d. s., alc. or eth.—S. in v. dil. NaOH; sol. has red-violet (RV) color. More conc. sols. intensify the color, but the hue remains the same.—NaOH sol. is ppt'd by CO_2 (dif. fr. isopurpurin). Alkaline sol. is ppt'd by $BaCl_2$; not soluble in $Ba(OH)_2$.—Sol. in conc. H_2SO_4 is purple-red.—Ignition w. Zn dust gives anthracene.
291–3	**1, 7 (m-)Benzdioxyanthraquinone, $C_{14}H_8O_4$.**—Sbl. w. dec. in yellow ndl., s. eth. or alc.; s. NaOH w. deep-yellow color.
295c.	**Diacenaphthylidendione, $C_{24}H_{12}O_2$.**—Sbl. brownish-red ndl., v. d. s. bz.—Adds Br_2 (comp. i. alc., lft. fr. $CHCl_3$ and lgr.) m. p. 237°.—Phenylhydrazone, brown-red cryst. powder, m. p. 105°–10°.
302	**2-(m)-Oxyanthraquinone, $C_6H_4.(CO)_2.C_6H_3.OH$.**—Yellow lft. or ndl. fr. alc.—Sbl.—Alm. i. aq.; e. s. alc. or eth.; e. s. ammonia giving red-yellow sol.; s. $Ba(OH)_2$ sol., and K salt s. alc. (dif. fr. alizarin).—Ignition w. Zn dust gives anthracene (Test 912).
305	**Alizarin-β-carbonic Ac., $(HO)_2.C_6H_2:C_2O_2:C_6H_3.CO_2H$.**—Sbl. in red ndl., s. alc.—The sol. in alkalies is blue.
308	**Naphthalfluoresceïn, $C_{24}H_{14}O_5$.**—Large yellow rhombic pr. fr. eth.—Sol. in dil. NaOH is reddish yellow w. green fluorescence.—Acetyl derivative (fr. acetic anhyd.), m. p. 191°.
310	**Anthragallol, $C_{14}H_5O_2.(OH)_3$.**—Sbl. at 290° in orange-red ndl.—Brown sol. in alc. or eth.—S. alkalies w. green color.—Spectrum, cf. B. 19, 2331.—Ignition w. Zn dust gives anthracene.—Pb salt, violet-brown ppt. fr. alc. w. $Pb\bar{A}c_2$.
340	**2, 3-Anthraquinonedicarbonic Ac., $C_{16}H_8O_6$.**—Yellow ndl., e. s. alc.—Salts reddish, alm. i. aq.—Warmed w. Zn dust and NH_4OH is easily reduced to anthracenedicarbonic ac.

COMPOUNDS CONTAINING C, H, AND O [ORDER I].

SUBORDER II, COLORED COMPOUNDS.

DIVISION A, (SUPPLEMENTARY) SECTION 2,—SOLID SPECIES, MOSTLY OF HIGH OR ILL-DEFINED MELTING-POINT, GIVING INTENSELY COLORED SOLUTIONS IN DILUTE ALKALI.

[The arrangement of species in this section of the tables is such, that compounds follow one another in the order that the hues obtained by dissolving them in dilute caustic soda occupy in the spectrum or color standard, beginning with red, and proceeding through orange, yellow, green, blue, and violet.—Since the *hue* as well as the intensity of these colors depends very much on the concentration, the colors should be produced and observed under the conditions prescribed on page 204. The exact order of succession is reasonably well established only for those compounds whose color reactions have actually been examined by the author with the aid of the color standard. The colors thus determined are distinguished from those based on the verbal description of other authorities by being followed by a color symbol (e.g., red = R). The preparations used in most of the writer's experiments on the species of this supplementary section were commercial products—sometimes pastes—from reliable manufacturers. The best preparations of this class are, of course, liable to slight differences in composition, and are never absolutely homogeneous.]

Color of Solution in very dilute NaOH.	**COLORED COMPOUNDS.**—Solid Species, giving intensely colored solutions in dilute Alkali.
R-RV. Intense VB in conc. NaOH.	**Hæmatoxylin, $C_{16}H_{14}O_6+3H_2O$.**—Brown cryst. (colorless when pure).—Taste sweet.—Sol. in conc. NaOH, deep violet (V or BV), becoming (R) on acidification w. HCl.—Sol in conc. H_2SO_4 orange (O).—Cf. Sec. 1, m. p. 140°.
Red (R).	**Brazilin.**—Red-brown cryst (colorless when pure).—Taste sweet.—Cf. Gen. IV, A, m. p. abt. 250°.
Red (R) (slightly RV).	**Flavopurpurin, $C_{14}H_5O_2.(OH)_3$.**—Yellow ndl. or YOS1 paste.—D. s. h. aq.; e. s. h. alc.—Sol. in conc. H_2SO_4 is red.
"Deep red."	**2, 7-Dioxyanthraquinone, $C_{14}H_6O_2.(OH)_2+H_2O$, [Isoanthraflavic Ac.].**—Yellow cryst.; m. p. a. 330° after losing cryst. aq. at 150°.—Sbl.—Sol. in conc. H_2SO_4, deep red.—S. c. $Ba(OH)_2$ sol ; s. alc.; alm. i. eth.
"Fine red."	**Trioxyaurine, $C_{19}H_9O.(OH)_5$.**—Dark-red lft. fr. eth.-alc.
Red (R).	**Purpurin, $C_6H_4.(CO)_2.C_6H.(OH)_3$.**—[Cf. Sec. 1, m. p. 256°.]—Orange-red (ORS1) paste or ndl.—Sol. in conc. H_2SO_4, R-OR, changing to YO on dilution w. aq.
Fuchsine red.	**Cresolaurine, $C_{22}H_{18}O.(OH)_2$.**—Amorph. red powder; i. aq.; d. s. eth.—Sol. in Ac, yellow.
Intense red to brown (yellow-green fluorescence).	**Resorcinoxaleïn, $C_{20}H_9O_2.(OH)_5$.**—Red powder.—S. in conc. H_2SO_4 w. emerald-green color.—The alkaline sol. diluted to a pale-yellow shows moss-green fluorescence.
Red (w. green-yellow fluorescence).	**Orcinaurine, $C_{22}H_{15}O_2(OH)_3$.** — Red-brown grains, v. d. s. alc.
Red.	**Carminic Ac., $C_{17}H_{18}O_{10}$.**—Red pr. fr. alc., or red-brown powder. E. s. aq.; sol. yellowish red.—Aq. sol. gives purple ppt. w. baryta sol.—Alc. sol. heated w. aniline gives ruby-red cryst. anilide, m. p. 190° d.
Carmine-red.	**Brazileïn, $C_{16}H_{12}O_5$.**—Cryst. w. $1H_2O$. Powder reddish-brown. D. s. aq.; sol. rose-red w. orange fluorescence.—Alkaline sol. browns in air.—Triacetyl deriv., yellow lft. fr. alc., m. p. 203°-7°.

Color of Solution in very dilute NaOH.	**COLORED COMPOUNDS.**—Solid Species, giving intensely colored solutions in dilute Alkali.
Brownish red (fluorescent).	**Fisetin, $C_{15}H_{10}O_6 + 4H_2O$.**—Cryst. in lemon-yellow ndl. w. 4 aq. (lost at 110°). M. p. a. 360° d.—S alc ; alm. i. aq.—PbĀc$_2$ gives orange-yellow ppt. in alc. sol.—Reduces Fehling's sol. hot.—Tetraacetate, ndl. fr. alc., m. p. 200°–1°.
Orange-red (OR) (not fluorescent).	**Aurine, $C_{19}H_{12}O.(OH)_2$ and Rosolic Ac., $Me.C_{19}H_{11}O.(OH)_2$.**—Commercial article a mixture w. very variable m. p (sometimes as low as 90° or 100°), and w. strong odor of phenol.—Color of powder RO. Lumps show conchoidal fracture and greenish metallic reflections.—Sol. in conc. H_2SO_4 yellow (OY–Y).—A (1:5000) sol. in very dil. NaOH shows absorption band at D½E to b. More conc sol. shows one-sided absorption fr. violet to D line —Sol. in alc. orange (O).
Yellow-red (not fluorescent).	**Resaurine, $C_{19}H_{11}O.(OH)_3$.**—Amorph. light brick-red powder; e. s. alc.; alm. i. eth.
Orange.	**2, 6-Dioxyanthraquinone (Anthraflavic Ac.), $C_{14}H_6O_2.(OH)_2$.**—Sbl. in yellow lft., m. p. a. 330°.—Sol. in conc. H_2SO_4 yellow, showing broad absorption band between blue and green.—D. s. c. alc.; i. eth.
Red to yellow (according to dilution). Intense yellow-green (YG) fluorescence.	**Fluoresceïn, $C_{20}H_{10}O_3.(OH)_2$.**—Yellow-orange (YOS1) powder.—Sol. in conc. H_2SO_4 (Y) w. slight greenish fluorescence.—I. c. aq.; d. s. alc. or eth.—Paper stained a pale yellow by dil. sol. in Āc becomes pink when held in steam from boiling Br water.—The very dil. sol. in dil. NaOH shows a distinct absorption band from a little to right of E to just beyond F.
Yellow-orange (YO).	**Phenacetolin (Phenaceteïn), $C_{16}H_{12}O_2$.**—Chocolate or red-brown powder. M. p. a. 330°. Sol. in conc H_2SO_4 (YOS1–2) —I. aq.; sol. in alc. orange; in dil. HCl yellow; in dil ammonia violet-red (VR). (Colors as given by a sample purchased from Merck.)
Yellowish brown.	**Resorcinbenzeïne, $C_{38}H_{22}O.(OH)_8$.**—Pr. or lft . violet- or brownish-red; yellow by transmitted light E s h. alc. when freshly precipitated, otherwise v d. s.—Loses aq. at 130°.—Dil. ammon. sol. red-violet and fluorescent.
Yellowish brown.	**Galloflavin, $C_{13}H_6O_9$(?).**—Greenish-yellow lft. Sol. in conc. H_2SO_4 orange.—D. s. h. alc.; sol. clear yellow w. faint-green fluorescence.
Orange-yellow.	**Alizarin Yellow "C," $CH_3.CO.C_6H_2(OH)_2$.**—Yellowish paste, e. s. h. aq.—Sol. in conc. H_2SO_4 yellowish.—Cf. Gallacetophenone (IV, A, m. p. 168°).
Orange-yellow (OY).	**Alizarin Yellow "A," $Ph.CO.C_6H_2.(OH)_3$.**—Paste, gray yellow (light YA). E. s. h. aq.—Sol. in conc. H_2SO_4 clear yellow (Y).
Orange-yellow.	**Quercetin, $C_{15}H_{10}O_7 + xH_2O$.**—Lemon-yellow cryst. powder. Loses H_2O at 130°.—S. 280 pt. h aq. or 229 pt. c. alc.—M. p. a. 250° (r. h.).—Alc. sol. dark green w. $FeCl_3$, turning dark red on warming; gives brick-red ppt. w. PbĀc$_2$.
Yellow.	**Croconic Ac., $CO:C:C:(CO_2H)_2 + 3H_2O$.**—Pale sulphur-yellow ndl. or grains, e. s. aq.; s. alc.—Sbl. after losing aq. at 100°.—$BaCl_2$ gives lemon-yellow ppt. of BaĀ + 1½H_2O.—Ag salt, orange-red ppt.
Deep yellow.	**Luteolin, $C_{15}H_{10}O_6 + 2H_2O$(?).**—Yellow ndl., m. p. a. 320° d.—Sbl.—S. 14,000 pt. c. aq., 37 pt. alc., or 625 pt eth.—Taste, bitter-astringent.—Sol. green w. little $FeCl_3$, brown-red w. larger quantity.—Sol. in conc. H_2SO_4 yellowish green giving violet ppt. on dilution.—$CaCl_2$ gives orange ppt., which becomes red and cryst. on boiling.
Green.	**α-Naphtholbenzeïne, $C_{54}H_{34}(OH)_4.O$.**—Brown powder, i aq.; s. alc., eth., or bz. w. yellow-red color.—The green sol. in alkalies is turned reddish yellow by acids.

Color of Solution in very dilute NaOH.	**COLORED COMPOUNDS.**—Solid Species, giving intensely colored solutions in dilute Alkali.
Intense G–YG.	**Cœruleïne, $C_{20}H_8O_6$.**—Black powd. or paste, i. aq. or alc.—Sol. in conc. H_2SO_4 "dirty yellow-brown" (broken OY much darker than dark OYÂ).
Blue.	**Alizarincyanin "R," $C_{14}H_3O_2.(OH)_5$.**—Brown lft. or paste.—Dist. undec.—Sol. in conc. H_2SO_4 blue w. red fluorescence.
Cornflower-blue.	**2, 3-Dioxyanthraquinone, $C_{14}H_6(OH)_2.O_2$.**—Orange-yel. ndl. fr. Āc, v. d. s. h. alc. or eth.—Sol. in conc. H_2SO_4 blood-red.—Ba salt dark-blue ppt.
Cornflower-blue.	**5, 6-β-Dioxynaphthoquinone(1, 4),(Naphthazarin), $C_{10}H_4O_2.(OH)_2$.**—Sbl in red-brown ndl.—Sol. in conc. H_2SO_4 fuchsine red.—D. s. h. alc.; cryst. fr. alc. sol. in "green-brown" ndl.—Diacetate, yellow ndl., m. p. 192°.
Intense blue.	**Pyrogalloquinone, $C_{18}H_{14}O_9$.**—Sbl. in garnet-red ndl. M. p. a. 220°.—D. s. alc.; s. eth.—Sol. in conc. H_2SO_4 carmine-red or on addition of trace of nitrous acid, intense violet. Br in Āc sol. gives clear red tetrabrom-derivative, m. p. 202°–4°.
Intense blue (B).	**Alkannin, $C_{15}H_{14}O_4$.**—Dark red-brown resinous mass (softens below 100°).—I. aq.—Sol. in alc. orange-red (OR), and when dilute shows conspicuous absorption bands, one at Eb, the other at $D\frac{1}{3}E$; also two easily overlooked bands, one at F, and the other at $D\frac{1}{2}C$. The sol. in ammonia is blue with conspicuous absorption bands D and $D\frac{2}{3}C$.
Intense Blue to VRT2 (according to concentration).	**Galleïne, $C_{20}H_{10}O_7$.**—Dark red-brown powder, or small cryst. w. green metallic reflections (also described as violet paste or powder). S. w. red-brown color in warm alc.—Heated w. *fuming* H_2SO_4 gives olive-yellow sol. (containing cœruleïne) from which olive flocks separate on dilution w. aq.; the ppt. dissolves w. intense green color (G–YG) in dil. NaOH.
Impure Violet. Blue (B) w. conc. NaOH.	**Rufigallic Ac., $C_{14}H_2O_2.(OH)_6$.**—Orange-red (ORS2) cryst. or brown-red powder, i. aq.—Sol. in conc H_2SO_4 intense red, becoming yellow on dilution.
Blue-violet.	**Alizarin Bordeaux, $C_{14}H_4O_2.(OH)_4$.**—Sbl. in deep-red ndl. (green w. metallic lustre by reflected light).—Not melted at 275°.—Sol. in c. conc H_2SO_4 has intense blue-violet color.—Baryta water gives blue ppt. w. alc. sol.—Tetra acetyl deriv , m. p. 201°.
Red-violet (RV).	**Alizarin, $C_{14}H_6O_2.(OH)_2$.**—(Cf. Sec. 1, m. p. 289°–90°.)—Sbl. in orange (O) ndl.—("Paste" OYS1–YOS1).—Sol. in conc. H_2SO_4 is red (R); dilution w. aq. gives OY ppt.
Violet-red.	**Benzaurine, $C_{19}H_{13}(OH)_3$.**—Brick-red powder, e s. alc. or eth.; i. aq.—Color of alkaline solution changed to yellow by acids.
Violet-red.	**Resorcincinnamyleïne, $C_{21}H_{13}O.(OH)_3+H_2O$.**—Brown amorph. powder; at 100° becomes green w. metallic lustre —Alc. sol. red.
Violet-red (VR).	**Iso or Anthrapurpurin, $C_{14}H_5O_2.(OH)_3$.**—Orange ndl. fr. alc., m. p. a. 330°.—(Paste YOS1). E. s. alc.; d. s. h. aq. or eth.—Sol. in conc. H_2SO_4 red, giving OY ppt. on dilution w. aq.
RV (Intense VB–V w. conc. NaOH).	**Hæmateïne, $C_{16}H_{12}O_6$.**—Thin, mic., gray-green, water-free cryst. w. yellowish-green metallic lustre; commercial product a dark-brown powder. D. s. aq. or alc.; v. d. s. eth.—Sol. in conc. NaOH deep violet or blue-violet (V or BV), becoming red (R) on acidification w HCl. Sol. in conc. H_2SO_4 orange (O).—Cryst. darken and decompose abt. 250° (dif. fr. hæmatoxylin).

COMPOUNDS CONTAINING C, H, AND O [ORDER I].

SUBORDER II, COLORED COMPOUNDS.

DIVISION B,—LIQUID SPECIES.

Boiling-point (C.°).	Specific Gravity.	**COLORED COMPOUNDS.**—Liquid Species.
87·5-8	0·973(22°)	† **Diacetyl, Me.CO.CO.Me.**—Yellow (Y) liquid of peculiar sweetish-pungent odor! Vapor w. color of Cl.—S. 4 pt. aq. at 15°. —Treatment w. alkali by Test IV, 2 gives an opaque brown sol.! —† To identify: Mix in a 3-inch test-tube 1 drop of the ketone, 1 cc. of aq., and 0·5 grm. of hydroxylamine hydrochloride. Boil. A heavy cryst. ppt. of the pure white dioxime separates at once. Cool. Collect on a small filter. Wash w. c. aq. Dry at 100° for 15 min. The diacetyldioxime formed melts at 234·5° (uncor.)!
108	0·948(19)	**Acetylpropionyl, Me.CO.CO.Et.**—Color, odor, and behavior towards alkali as w. diacetyl above.—S. in 15 pt. c. aq.—M p. of dioxime 170°-2°!
115-16		**Acetylisobutyryl, Me.CO.CO.CH.Me$_2$.**—Color, odor, and behavior towards alkali as w. diacetyl above; but d. s. aq.
128	0·934$(^{19}/_4)$	**Acetylbutyryl, Me.CO.CO.Pr.**—Color, odor, and behavior towards alkali as w. diacetyl above.—M p. of dioxime 168°!
138	0·908$(^{22}/_4)$	**Acetylisovaleryl, Me.CO.CO.Bu.**—Properties as for preceding comp.—M. p of dioxime 171°-2°!
163	0·881$(^{19}/_4)$	**Acetylisocaproyl, Me.CO.CO.(CH$_2$)$_2$.CH.Me$_2$.**—Properties as for preceding comp —M. p. of dioxime 172°-3°!
175-6	1·072$(^{14}/_4)$	**Phenyldiacetyl, Me.CO.CO.CH$_2$.Ph.**—Viscous yellow oil. Odor honey-like, but pungent
216-18·	1·104$(^{14}/_4)$	† **Acetylbenzoyl, Me.CO.CO.Ph.**—Yellow oil of peculiar sweetish-pungent odor. Vapors yellow. Browns w NaOH in Test IV, 2.—M. p. of dioxime 239°-40° (cf. B. 22, 2129).

NUMBERED SPECIFIC TESTS FOR SPECIES OF SUBORDER II.

[TESTS 1011–1100.]

1011. Anthraquinone. (Properties tabulated on p. 211.)

Boil together in a test-tube for half a minute, a mixture of 5 cc. of an aqueous sodium-hydroxide solution (1 : 20), 0.01 grm. of the finely powdered quinone, and 0.2 grm. of zinc dust. Filter quickly while hot through a plaited filter. Anthraquinone gives a deep-red (about OR) colored filtrate, which quickly becomes decolorized on shaking in contact with the air, in consequence of absorption of oxygen; while a flocculent precipitate of light-colored anthraquinone separates. Upon adding more zinc dust, heating, filtering, and shaking, the phenomena described may be repeatedly reproduced.

This color reaction, which in the modified form as described by Claus (B. 10,926), is still more delicate and striking, although less convenient, is, in connection with its physical properties, the only test that will usually be needed for the identification of anthraquinone.

1012. Benzoquinone. (Properties tabulated on p. 206.)

Dissolve 0.05 grm. of the substance in 5 cc. of hot alcohol. Add 10 drops of aniline. Boil one minute. Cool. Filter. Wash the precipitate with 3 cc. of hot alcohol. Transfer to a test-tube, and boil with 20 cc. of glacial acetic acid. Cool. Filter. Dry, and observe the behavior of the compound on heating in a melting-point capillary.

2, 5-Dianilinoquinone, the product in this test, is obtained in the form of very insoluble and lustrous scales of a peculiar violet-red color, which, when dry, give a brownish "streak." It sublimes without melting at 325°–330° (uncor.).

1013-α-Naphthoquinone. (Properties tabulated on p. 207.)

Boil together for one minute in a test-tube 0.05 grm. of the quinone, 5 drops of aniline, and 2 cc. of alcohol. Cool. Add 10 cc. of water and 1 cc. of acetic acid, and shake. Filter off the precipitate, and wash with cold water. Recrystallize from 10 cc. of boiling dilute alcohol (1 : 1). (Very vigorous shaking is sometimes necessary to start the separation of crystals from the well-cooled solution.) Wash with 3 cc. of the dilute alcohol. Press on a porous tile. Dry 15 minutes at 100°, and determine the melting-point.

2-Anilinonaphthoquinone, the product in this test, is obtained as a fluffy dark-red (R–RS1) powder consisting of micro-crystalline needles, and melts at 190° (uncor.).

1014. Phenanthrenequinone. (Properties tabulated on p. 209.)

1. (Color reaction.)—Apply the reaction with caustic and zinc dust described in Test 1011. The color produced by phenanthrene is a quite pure and intense green. It is seen to the best advantage on the edges of the plaited filter. The green filtrate when vigorously shaken absorbs oxygen from the air (less rapidly than in the test for anthraquinone), and becomes yellowish.

2. Dissolve 0.05 grm. of the quinone in a mixture of 2 cc. of fuming nitric acid (sp. gr. 1.48) and 2 cc. of sulphuric acid (sp. gr. 1.84). Boil gently for one minute. Cool, and pour into 10 cc. of cold water. Collect on a filter, and wash thoroughly with hot water. Dissolve the washed precipitate in 15 cc. of boiling glacial acetic acid. Cool, and filter. Wash the precipitate with 3 cc. of glacial acetic acid. Dry 15 minutes at 125°, and determine the melting-point.

The product in this test *a-2, 7-Dinitrophenanthrenequinone* is a yellowish crystalline precipitate which begins to turn brown about 270° (uncor.), decomposes to a sticky mass at 285° (uncor.), and completely liquefies to a black drop at 294° (uncor.).

CHAPTER XIII.

SPECIAL METHODS, APPARATUS, AND REAGENTS.

EVERY department of experimental science gradually acquires a more or less considerable body of special laboratory methods which experience has proved are best adapted to meet its peculiar requirements. These constitute its *special technique*. The purpose of the present chapter is to bring together for explanation or comment a few methods of this kind which will be helpful to persons using the procedures of this volume. It is assumed that the reader is already familiar with the simpler manipulations of analytical and organic chemistry, and of experimental physics.

MELTING- AND BOILING-POINTS.

The numerical values of the melting- and boiling-points of organic compounds have such a wide range, and can be approximately determined with so little difficulty, that they are more regularly met with in the original descriptions of new species than any other physical constants. Unfortunately, however, only a very small fraction of these values are the result of fully corrected thermometric measurements, or of observations made under conditions that can be exactly duplicated.

In using published data of this kind we have no choice but to assume that all necessary corrections for irregularities in the bore of the thermometer capillary, the value of its scale unit, and the position of its zero-point at different times have been made, though it is to be feared that chemists are often very negligent in this particular. But a very serious uncertainty always exists as to the proper interpretation to put upon values obtained at higher temperatures that are not followed by the word "corrected" or "uncorrected." In the neighborhood of 300°, a melting-point that has been corrected for stem-exposure is very likely to be about 10° higher than if uncorrected—a difference which is several times greater than the probable combined error from all other causes. What proportion of the great body of these unclassified melting- and boiling-points in chemical literature has been corrected for stem-exposure can only be surmised; but the author's experience inclines him to accept the conclusion of Meyer and Jacobson's "Lehrbuch der organischen Chemie" (Vol. I, pp. 115, 116), that among organic chemists the unqualified "melting-point" has come generally to mean one uncorrected for stem-exposure; while the unqualified "boiling-point" (boiling-points often being taken in long-necked distilling flasks or with short-stemmed thermometers) is in most cases substantially "corrected." The confusion arising from this unfortunate and unscientific practice can only be entirely remedied by the careful redetermination of all the unqualified data.

The melting-points given in the "numbered specific tests" of this volume are all uncorrected for stem-exposure; but they may be readily converted into "corrected" melting-points by simply adding the proper correction from the following empirical table. This table is applicable only to observations made in an apparatus of approximately the form and dimensions shown in Fig. 5, and the larger corrections may even then leave a residual error of about half a degree.

[Table of stem-exposure corrections to be added to the direct readings of an otherwise corrected 360° rod thermometer, with a diameter of 5 mm., and a degree length of 0.85 mm., when immersed in a liquid bath from the −10° point, and with 100° of the stem within the air-space of the inner tube of an apparatus of the form and dimensions described below.]

Observation (C.°).	Correction (C.°).	Observation (C.°).	Correction (C.°).	Observation (C.°).	Correction (C.°).
50	0.1	140	2.0	230	6.7
60	0.2	150	2.3	240	7.2
70	0.3	160	2.7	250	7.8
80	0.5	170	3.1	260	8.4
90	0.7	180	3.6	270	9.0
100	0.9	190	4.1	280	9.6
110	1.1	200	4.6	290	10.2
120	1.4	210	5.3	300	10.9
130	1.7	220	6.0		

The Usual Method for Determining Melting-points.—These determinations are most conveniently made in the apparatus figured, because the closed flask prevents the free escape of fumes into the laboratory when high temperatures are being used, and also excludes dust and moisture from the bath to such an extent that frequent renewal of the liquid is unnecessary. In a laboratory where melting-points are frequently taken, it is well to have two such flasks, one for high and the other for low temperature determinations, always in readiness for immediate use.

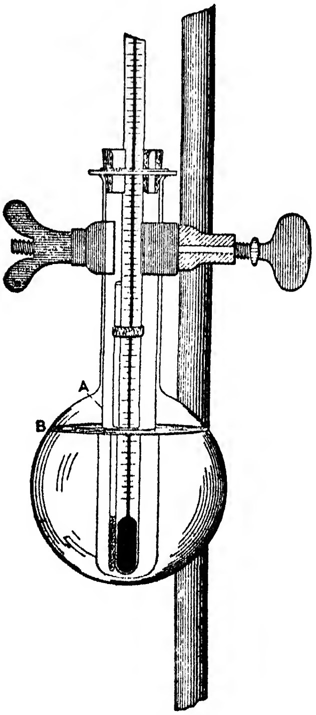

Fig. 5.

The flasks should be round-bottomed, with bulbs 65 mm. in diameter, and with necks 75 mm. in length and 20 mm. in diameter. Their capacity is about 200 cc. The inner tube, *A*, is a test-tube with a diameter of 15 mm., which hangs freely suspended by its flanged lip. Both the inner tube and the flask are filled with a clear liquid to the level *B*, it being a very bad practice to use the test-tube as an air-bath.

The best bath for temperatures between 0° and 220° is probably colorless sulphuric acid of 1.84 specific gravity. The acid in the inner tube is, it is true, easily browned by contact with organic matter of any kind, and so must be renewed occasionally; but it has the advantage over dissolved or molten solids that when splashed upon the cool upper parts of the tube it drains back quickly without leaving any cloudy film to interfere with a clear view of the lower part of the thermometer scale.

A bath highly to be recommended for temperatures between 220° and 320°, in connection with the foregoing,—and which may be used, though less advantageously, for the entire range of temperature between 15° and 320°,—is prepared by cautiously heating in a porcelain casserole under a hood until boiling ceases at the higher temperature, a mixture of 70 parts by weight of concentrated sulphuric acid and 30 parts of neutral potassium sulphate, and stirring constantly until the sulphate is completely dissolved; or by similar treatment of a mixture of 55 parts by weight of the acid with 45 parts of acid potassium sulphate. The mixture has the consistency of glycerine,* and does not fume so badly as to prevent the use of rubber bands for attaching melting-point capillaries to the thermometer. It is less corrosive and less easily discolored by traces of organic matter than sulphuric acid.

The phenomenon of fusion is observed in a thin-walled glass capillary, sealed at the lower end †, which is occupied by a few milligrams of the substance. These melting-point tubes should have a length of 6 to 7 cm. and an internal diameter of 1 mm. They are most readily made from rather soft glass tubes having an internal diameter not less than 1 cm.—not, as is often done, from small-bore tubing. A piece of such tubing, of convenient length, is supported at both ends and rotated in a blast-lamp flame until a ring 2 cm. long has been heated to dull redness. Then, upon separating the hands rather slowly, until both arms are outstretched at full length horizontally from the shoulders, a capillary of the desired diameter, and nearly two meters in length, may be drawn out in a single operation.

To charge the melting-point capillary, force its open end downward into a small mound of the finely powdered substance. Then, holding upward the open end, which will now be closed by a short plug of the compacted powder, draw the flat side of a file horizontally across the tube a little below the substance. The powder, loosened by the vibrations set up in the glass, will quickly slide down into the desired position. The charged capillary is now attached to the thermometer by a narrow rubber band sliced off from a piece of rubber tubing. The band should be placed 2 cm. above the surface of the bath, and the substance in the capillary should be situated opposite the middle of the thermometer-bulb. If a sulphuric acid bath should be used at temperatures above 170°, a piece of fine platinum wire, which will not be attacked by the hot acid fumes, should be wound spirally around tube and thermometer, as a substitute for the band. With the potassium

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* After long exposure to the air it may become semi-solid through absorption of water, but is easily liquefied again by heat. When a melting-point above 300° is to be taken with a bath that has not been heated much above 250° for some weeks, it is advisable first to boil it for a few minutes. Otherwise the bubbles of steam given off in the neighborhood of 300° will cause bumping and interfere with the observation. Under certain obscure conditions the mixture may solidify to a hard mass, with a considerable rise of temperature. But this is a rare occurrence, and when it happens a short boiling will bring the bath back to its normal state.

By increasing the proportion of neutral sulphate from 30% to 40% this bath may be used for temperatures up to 370°. Such a bath remains pasty until the temperature has fallen to 90°-60°. Either of these sulphate baths if slightly darkened by organic matter may be cleared by a short heating above 300°

As a bath for temperatures between 370° and 500° fused zinc chloride, *free from dust*, may be employed. Since it is very apt to crack any flask in which it may be allowed to solidify on cooling, it should be poured out upon a clean tile as soon as the temperature has fallen to about 280°.

† The melting-points of a few compounds which fuse at high temperatures with decomposition and loss of water, carbon dioxide, or ammonia, have been found to be sharper when observed in capillaries sealed at both ends. These melting-points are, however, of very little value unless accompanied by a statement of all the dimensions of the capillary, and of the quantity of substance fused; for they will be found often to vary many degrees with a change in these conditions, because of differences in the gas pressures of the decomposition products.

sulphate bath, however, rubber bands are not seriously attacked, even when the bath is at 300°.

For general convenience in manipulation, and because it is probable that a majority of the organic melting-points on record have been obtained by instruments of approximately these dimensions, the use of a thermometer with a graduation extending from $-25°$ to $+360°$, with degree-marks about 0.85 mm. apart, is to be preferred. A thin stem (diameter about 5 mm.) is advantageous, as it saves space and acquires the temperature of the bath quickly. The direct readings of such a thermometer may be sufficiently corrected for stem-exposure by means of the table on page 218. (For a discussion of the other thermometric corrections cf. Crafts, Am. V, 309.)

The proper rate for heating in a melting-point determination depends somewhat on the behavior of the compound. Substances that melt without any decomposition are always to be heated very slowly, as the melting-point is approached. An average rise of 2° per minute for the last 5° is fast enough; for it is only by proceeding slowly that we can feel reasonably sure that the substance and thermometer are both at the same temperature. On the other hand, with substances that begin to decompose slightly before fusion, slow heating increases the quantity of decomposition products, and gives mixtures which will begin to melt much too low. Substances of this class should be heated rapidly to within a few degrees of their probable melting-point, and then at a rate of about 5° per minute.

As has been shown by Reissert* and others, the true melting-point of compounds that melt without decomposition, when the fusion is observed in capillary tubes, lies much nearer to the temperature observed at the moment when minute droplets are first formed from particles of fine powder in actual contact with the capillary wall, than that at which a more considerable portion of the mass has become liquid; for, while the temperature of the melting compound must remain constant during the period between incipient and complete fusion,—in obedience to the well-known law,—that of the bath and thermometer is meanwhile gradually rising. The temperature recorded just before the moment of complete liquefaction will, however, generally be nearer its true melting-point for any compound that melts with slight decomposition, or contains traces of impurities. Differences of 2° between melting-points obtained by different methods of observation are quite possible.

In taking the melting-points of compounds that fuse to mobile liquids, a very common practice among organic chemists—regardless of theoretical considerations—seems to be to observe the thermometer at the moment when the first clear drop of sufficient size to detach itself from the solid mass and roll down the capillary under the influence of gravity makes its appearance. As this moment is usually easier to fix than that of the appearance of the first minute droplets, and with pure stable compounds gives values nearer the true melting-point than

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* A. Reissert, B. 23, 2239.

The true melting-point of a compound is its temperature of fusion as recorded by a thermometer immersed in a considerable quantity of the melting mass, as is described on page 225. It usually differs somewhat from the melting-point that would be found by using the capillary method. The melting-points of the specific descriptions in this volume are all capillary melting-points.

the moment of complete fusion, or than the moment of incipient fusion with compounds that are not free from every trace of impurity, this method of observation is to be recommended as on the whole the most satisfactory for analytical use.

The Usual Method for Determining Boiling-points.—The apparatus required is shown in Fig. 6. The bulb of the distilling-flask has a capacity of 10 to 15 cc., and the volume of liquid to be distilled is preferably 5 to 10 cc. The bottom of the flask rests in a circular opening cut by a brass cork-borer in a square piece of asbestos board, *A*, having a thickness of 3 mm. The perforation should have a diameter of about 2 cm. and be slightly beveled by a file on the upper edge, to make it fit closely to the surface of the flask. If the contact is not good at all points when the flask is pressed down into the opening, it may be improved by the use of an annular washer of thin asbestos paper, *B*, which will prevent the upward leakage of hot gases from the flame. *C* is a threefold wrapping of asbestos paper reaching to a point 1 cm. above the side tube. Its object is to prevent sudden condensation of vapor and consequent thermometric fluctuations, if the apparatus should happen to be exposed to a draft of cold air. The thermometer should be thin-stemmed, and inserted along the central axis of the neck of the flask, with its bulb well below the side tube. If there is a stem-exposure, a light auxiliary thermometer—not shown in the cut—will be attached to the main thermometer by rubber bands with its bulb opposite to the middle of the exposed mercury column. The neck of the distilling-flask *above* the side tube should be as short as possible, since, if the space which it contains is large, it will not be entirely filled with vapor at the temperature of the boiling liquid.

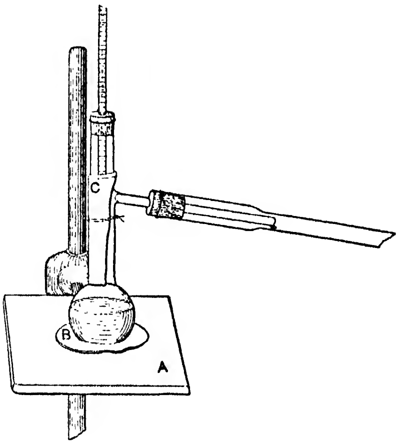

FIG. 6.

Unless the substance shows marked signs of decomposition when boiled, distil slowly, i.e., at a uniform rate of about 0.5 cc. per minute. Since some time will elapse before the thermometer can acquire the temperature of the vapor, little significance should be attached to readings taken before the end of the first minute after the fall of the first drop of distillate. Interrupt the distillation when the liquid remaining in the flask has fallen below the level of the asbestos diaphragm. Any reading taken after this point has been reached, when less than 1 cc. will remain in the flask, will be influenced by superheating,* and should be rejected.

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* **Superheating.**—The great advantage to be derived from the use of asbestos screens in this determination is not generally appreciated; and it will surprise many to learn that a boiling-point taken in a 10-cc. flask with the simple precautions given, will be more worthy of confidence than one made with a tenfold greater quantity of substance in which they are omitted. Much time and material would be saved if such screens were generally utilized in fractional distillations whenever the quantity of material to be boiled is rather small. As practical illustrations of the danger of superheating the vapor of liquids boiling in unscreened flasks, the following instances, which are copied from the author's note-book, will be of interest.

(1) 5 cc. of "frozen," thiophene-free benzene was distilled in a 10-cc. distilling-flask of the usual pattern; first, rapidly, the flask being unscreened; then, slowly, with the bottom of the

In the case of pure compounds that boil without decomposition, the difference between the first and last significant readings (after being corrected for stem-exposure, if the temperature of the auxiliary thermometer rises considerably during the experiment) ought not to amount to one degree. The boiling-points of substances that suffer slight decomposition during distillation are often expressed as falling between two limits.

The stem-exposure correction may be found by substitution in the formula $N(T-t)\times 0.000154$; in which N represents the length of the exposed thread of mercury (expressed in degrees); T, the observed boiling-point; t, the temperature of the auxiliary; and 0.000154, the apparent coefficient of expansion of mercury in glass.

To reduce boiling-points taken under pressures between 720 and 780 mm. to their approximate values at 760 mm., apply a correction of 0.1° C. for every 2.7 mm., the correction having a plus sign below 760 mm., and a minus sign with higher pressures.

Determination of Boiling-points of Small Quantities.*—If only a few drops of liquid can be spared for a boiling-point determination, the following procedure should be used: About three drops of the liquid are introduced into a narrow glass tube, *A*, by means of a medicine-dropper having a long capillary point. The tube *A* should have a length of 6 to 7 cm. and an internal diameter of 2.5 to 3 mm. It is sealed at the lower end; attached to the thermometer by a rubber band; and is heated in the bath used for determining melting-points (page 218, Fig. 5). To prevent the super-heating, and violent boiling that would otherwise occur on heating, the slender capillary *B* is dropped into the liquid. These tubes are made from narrow pieces of melting-point capillary (cf. page 219), by heating the glass at the point *C* in the edge of a flame, the tube being supported at both ends, until the walls melt and fuse together. This leaves a little chamber under *C*, closed above, but open below, which is to be cut off so as to have a length of 3 mm.

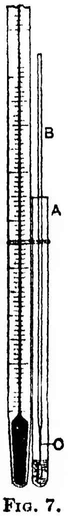

Fig. 7.

To make the determination, the temperature of the bath is gradually raised until the single air-bubbles that begin to rise from the capillary chamber some degrees below the boiling-point are replaced by *an apparently uninterrupted thread* of small vapor-bubbles. The lamp should now be removed, until boiling ceases and the liquid is seen to be about to recede into the capillary chamber. *The temperature at the moment of recession is that at which the liquid remaining in the tube would begin to boil.* In the case of compounds that are not quite pure it is not necessarily

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flask resting in an asbestos diaphragm 12 mm. in diameter. The temperatures observed at intervals of one minute in the case of the unscreened flask were—80.3°, 81.0°, 82.2°, 86.0°, and, as the last drops disappeared, 93°. With the screened flask the minute observations noted were—79.8°, 80.0°, 80.0°, 80.0°, 80.0°, 80.0°, 80.1°, 80.1°, 80.2°, of which the last two readings were taken after the liquid had reached the level of the screen, and of which the first was probably registered before the thermometer had quite acquired the temperature of the heated vapor.

(2) 17 cc. of pure water was rapidly distilled from an unscreened 50-cc. flask. The precaution was taken not to allow the *visible* flame of the burner to play on the glass above the surface of the liquid, and boiling was stopped when 5 cc. of water remained in the flask. The readings obtained were 100.2°, 102.0°, 106°, 108.0°, 108.0°. The intervals between all these readings, with the exception of that between the last two, which was 30 seconds, were 1 minute, as in the experiment with benzene.

* Siwoloboff's method (slightly modified), B. 19, 795.

identical with that of the chief constituent of the mixture. Hence, after noting the temperature at which recession begins, heat should always be applied again until the continuous thread of bubbles reappears, and the boiling then continued until nearly half the liquid has evaporated from the tube. If the temperature of the second recession is identical with the first, it is probably the boiling-point of a pure compound. *If it differs a few degrees from the first, it may be accepted as the most probable boiling-point of the chief constituent of the mixture.*

If the capillary chamber should entirely fill with liquid while the observation of the first recession is being made, it will have to be emptied, or the capillary replaced by a fresh one before the experiment can be repeated; for a tube containing neither air nor vapor affords no protection against superheating, and gives no thread of bubbles when the boiling temperature is passed.*

THE THERMOMETRIC INDICATIONS OF CHEMICAL PURITY.

Two kinds of tests for chemical purity will be discussed under this head. The evidence of homogeneity that may be furnished by those of the first class is identity of the melting- or boiling-point of the original substance with the melting- or boiling-points of all portions into which a given mass of it may be subdivided by any method of fractionation that, without causing decomposition, would naturally tend to bring about a difference in the proximate composition of the fractions if the substance were a mixture. Tests of this class will be distinguished as "*fractionation tests.*"

Tests of the second class, which it will be convenient to call "*sharpness tests,*" depend on the fact that it is rather unusual to meet with mixtures of two or more compounds that can be completely melted or distilled within a fraction of a degree of the temperature at which fusion or boiling begins, while it is characteristic of pure stable compounds to melt or boil at definite temperatures and not between limits.

The temperature interval between incipient and completed fusion or boiling, when measured under fixed conditions, is a definite property of every stable mixture, which may be given the name of "*fusion-interval*" or "*boiling-interval.*" The magnitudes of these "*intervals,*" in the case of a substance of doubtful chemical homogeneity, are often highly significant in their indications. Examples illustrating their interpretation as purity indices are given in the tables on pages 226 and 227.

The sharpness tests have the advantage of being applicable to all stable substances without any preliminary operations. The fractionation tests involve more operations, but when completed are more conclusive.

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* The fact that light glass tubes containing a small chamber for air or vapor at one end prevent bumping and promote regular boiling is capable of many applications. With their aid even such troublesome liquids as concentrated sulphuric acid and concentrated potash solution may be safely boiled in narrow test-tubes, if care is taken never to permit the vapor-chamber to fill by a temporary cessation of the boiling. The only precautions necessary to this end are to *carefully shield the flame and the vessel from drafts of cold air after boiling first begins, and to make the vapor-chamber of such a length that it will at all times be entirely covered by the boiling liquid.* Such *ebullator-tubes* are, like melting-point tubes, best made (cf. p. 219) by drawing out large-bore tubes at the blast-lamp. They must be long enough to find support against the walls of the flask or test-tube in which they are used, but so thin and light as not to endanger its safety. The diameter of the *vapor-chamber* will generally be 1.5 to 3 mm., and *its height always less than that of the liquid* in which it is to be used. If a chamber of small diameter becomes accidentally filled, it is most quickly emptied by being passed slowly through a flame. It should then be allowed to cool before being used.

Fractionation Tests.

[*For Solids.*]

(1).—Determine the melting-point of the substance. Recrystallize it from some volatile solvent in which it is not very soluble in the cold. (Crystallization from a hot saturated solution is the most rapid method.) If necessary, concentrate the mother-liquors by evaporation. When about three-quarters of the substance has been recovered in solid form, collect the crystals all in one portion and drain them. Press; dry; and determine the melting-point. If this melting-point differs slightly from that obtained before crystallizing, repeat the treatment. If it remains unchanged, repeat, using a different solvent. Reject the mother-liquors; or unite them and recover the dissolved matter by evaporation.

If the substance is chemically homogeneous, the melting-points of the several successive crystallizations should be identical. If it is a mixture, some constituents will probably pass into the mother-liquors more rapidly than others, and the melting-points of the several crystallizations will differ. This procedure is almost always used when the quantity of substance is very small, and is shorter than the method which follows.

(2).—Prepare a saturated solution of the substance in some chemically inactive solvent. By cooling, or by evaporation, crystallize out the entire quantity in three fractions, of which the middle one (2) should be the largest. Wash, drain, and dry the fractions (1) and (3), and determine their melting-points carefully. If these two melting-points are identical with that of the original substance (especially if they are sharp), the substance is quite probably homogeneous. The test may be made more rigorous by recrystallizing each of the end fractions, and determining the melting-points of the first crystals separating from fraction (1), and of those that separate last from the mother-liquor of fraction (3); or the test may be repeated with other solvents.

[*For Liquids.*]—Distil the substance, if practicable, through a fractionating tower, and collect three fractions, of which the middle one (2) should be the largest. Carefully determine the boiling-points of fractions (1) and (3), and compare them with that of the original liquid. A more elaborate fractionation is of course often necessary.

Sharpness Tests.

Three procedures for tests of this class will be given: two for solids, and one for liquids.

(1).—[*Fusion-interval for Solids in Capillary Tubes.*]

This procedure is identical with "The Usual Method for Determining Melting-points" already described on page 218. The "interval" is the difference between the temperature when the first clear droplets can be distinguished on the capillary walls, and that at which the substance becomes entirely liquefied. On account of its simplicity it is in constant use in organic laboratories; but it is a crude method, and in general cannot be depended upon to do more than indicate the existence of gross impurity, apparent intervals of more than one degree often being obtained in the examination of very pure compounds, even when great pains are taken to raise the temperature regularly and slowly. The deficiencies of the method are not difficult to explain. The thermometer registers the temperature of the bath, and not that of the melting substance in the capillary. The substance, according to its thermal conductivity, heat capacity, state of subdivision, and the diameter of the capillary, melts more or less slowly—but, *if chemically homogeneous*, without changing its temperature. The temperature of the bath and thermometer are, however, meanwhile slowly but constantly rising.

(2).—[*Fusion-interval for Solids with Thermometer Immersed in the Melting Substance.*]

This procedure has been comparatively little used, but is more satisfactory in its results than (1). When the necessary apparatus has once been set up, it can be applied to compounds of low melting-point without any special difficulty.

The apparatus required is shown in Fig. 8. *A* is a 7-inch test-tube, supported within a thin glass air-jacket *B* by cork or asbestos rings *CC*. Through the cork *D* pass the thermometer *E* for registering the melting-point, an auxiliary thermometer *F* for use in the correction for stem-exposure—when this correction is necessary—and a light but strong stiff stirrer *H*. The whole arrangement is heated by immersion in a bath of water, glycerine, or molten paraffin, contained in a tall narrow beaker provided with a stirrer.

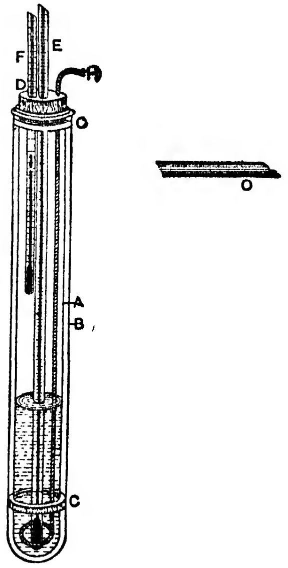

FIG. 8.

Bring 10 to 15 grams of the dry *powdered* substance into *A*. Heat the outer bath quickly to a temperature 10° to 15° higher than that of the melting-point, and then hold it nearly constant during the remainder of the experiment. Set the inner stirrer in motion as soon as the substance melts enough to allow it to be worked freely. This will usually be several minutes after the powder shows the first signs of shrinkage and softening. Take the first reading a minute or two later, when the bulb of the thermometer is surrounded by a pasty mass in which all interstices are evidently filled by liquid; and continue to record observations at intervals of one minute, until not more than one or two centigrams of substance remain unfused. About fifteen or twenty readings in all will be made. To prevent parallax errors, that would otherwise render the readings nearly worthless, make all observations through the horizontal tube *O*. A brass cork-borer (diameter 5–10 mm.), thrust through a large cork and supported by an iron clamp, is an admirable arrangement for the purpose. It has been shown that the average of several readings of the same temperature taken in this way by practised observers, on thermometers whose degree divisions are 1 mm. in length, contains a probable error of only a few hundredths of a degree.

The *fusion-interval* in this method is the difference between the means of the first and last three accepted observations; or, if there are not more than ten observations in a series, between the means of the first and last two observations. The first and last reading in a series should, however, always be rejected, if they show a considerably more rapid change of temperature during the minute in which they were taken than occurred during other periods of equal length; for such a behavior usually indicates that the thermometer has either not been long enough in contact with the bath at the beginning of an experiment to acquire its temperature, or else that the quantity of solid substance remaining unmelted near the end of the test was too small to prevent a measurable rise in temperature in those portions of the liquid with which it was not in immediate contact.

Perfectly pure crystalline compounds that melt without decomposition should give an "interval" by this method that is not greater than the unavoidable error of observation. The true melting-point of a slightly impure compound may be assumed to lie nearest to the higher limit, since impurities cause depression. The following table* of fusion-intervals illustrates the kind of information that may be derived from the application of this test.

TABLE OF MELTING-POINTS (CORRECTED) AND FUSION-INTERVALS.

No.	Substance.	M. P. (C.°)	Interval.
1	Naphthalene, specially purified	80·08	0·00
2	" best commercial	79·55	0·20
3	Benzophenone, specially purified	47·93	0·06
4	" +1% of No. 1	46·83	0·54
5	Salicylic Acid, good commercial	157·81	0·04
6	Thymol " "	49·51	0·21
7	Stearic Acid, sold as "C. P."	63·7	2·8
8	" " (once recryst. from Alcohol)	65·65	1·70
9	" " (twice " " ")	67·80	0·80
10	" " (thrice " " ")	68·80	0·00
11	Cane-sugar Crystals (melts with decomposition)	153·8 (?)	8·8 (?)

(3).—[*Sharpness Test for Liquids.*]

Distil 5–8 cc. of the liquid from a 10–15 cc. (or larger) distilling-flask, with all the precautions mentioned in the directions given for boiling-point determinations on page 221, recording thermometer readings at intervals of one minute. The readings must be made through a narrow horizontal tube, mounted and used as in the determination of the fusion-interval (cf. Fig. 8, page 225). The "boiling-interval" will be the difference between the mean values of the first two and the last two significant readings.

Results by this method are of the same order of reliability as those for the fusion-interval by procedure 2, but are so much more easily obtained that procedure 3 is of far greater practical importance. The significance that may be safely attached to boiling-intervals in special cases will be best understood from an inspection of the following table, in which a considerable number of such data obtained from typical pure and commercial preparations and mixtures have been collected.

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* The results in this table, as well as those on the boiling-interval on page 227, were obtained by Mr. Arthur Davis in the author's laboratory, by the use of a 360° thermometer, the length of whose degree was slightly less than one millimeter. The last significant figure in all these results was secured by the process of averaging, and has a probable error of about three units.

Substances 1 and 3 had been brought to a condition of exceptional purity by distillation and repeated recrystallization from alcohol. Their behavior is that of the typical, pure stable compound. 2 and 4 illustrate the effect of slight impurity in the case of the same substances. 2, 5, and 6 are good examples of what may be expected from high-grade commercial preparations of good stability. 11 shows the uselessness of sharpness tests for pure compounds that decompose noticeably in melting. Numbers 7–10 show the progressive changes in the interval that occur in the crystallization of an impure substance by a suitable method.

TABLE OF BOILING-INTERVALS OF TYPICAL COMPOUNDS AND MIXTURES ILLUSTRATING PROCEDURE (3).

Substance.	Boiling-interval (C.°).
Benzophenone, specially purified.	0·00
Benzene, free from thiophene, "frozen"	0·05
Para Toluidine, Kahlbaum's.	0·03
Ortho Toluidine, Kahlbaum's.	0·28
Nitrobenzene, Merck's, from cryst. Benzene.	0·13
" " commercial grade	0·25
Dimethylaniline, Merck's, free from mono compound	0·13
" " commercial grade.	0·85
Resorcin, Kahlbaum's.	0·23
Acetone, from the bisulphite compound	0·35
" "56–58 chemically pure," Merck's.	0·38
Ethyl Alcohol, 95%	0·25
Aniline, Kahlbaum's intermediate grade.	0·52
Phenol, Merck's "Synthetic".	0·83
Paraldehyde, Kahlbaum's.	1·25
Methyl Acetate, Kahlbaum's.	1·33
Benzaldehyde, originally "C. P.," but slightly oxidized.	1·80
Glacial Acetic Acid, containing about 2% water.	2·50
Acetoacetic Ether, Kahlbaum's (boiled with some decomposition)	3·00
Cinnamic Acid, Merck's (boiled with decomposition)	3·45
Amyl Acetate, Kahlbaum's, a mixture of isomers	3·70
Ethyl Ether, commercial, U. S. P., containing much alcohol and water	40·85
Benzene containing 5% Toluene.	2·32
Nitrobenzene containing 5% o-Nitrotoluene	0·97
Acetone containing 5% Methyl Alcohol.	0·92
Para Toluidine containing 5% o-Toluidine.	0·69
"Constant-boiling Mixture" of Methyl Alcohol and Benzene *.	0·15

SPECIFIC GRAVITIES.

The specific gravity of solid organic compounds has been determined for comparatively few species, and is consequently not at present a property of great analytical importance. The specific gravity of liquid compounds, on the contrary, has been determined with almost the same regularity as the boiling-point, and sometimes affords the simplest possible means for the arrangement of such species into "Sections." The recorded values for the specific gravities of organic liquids are usually reliable in the second decimal place, often in the third, but very rarely in the fourth.

As the analyst will often have too little of a pure compound to enable the determination of its specific gravity by the Westphal balance or hydrometer, two other methods for the determination, which are also rapid and usually sufficiently accurate for his purpose, will now be described in detail.

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* Ryland, Am. 22, 384 [1899].—This mixture is an example of many known cases of two miscible liquids, that, when once brought together in certain proportions, boil like a pure compound, and can not be separated by the usual method of fractional distillation. The analyst is not very likely to meet such mixtures ready formed in commercial preparations, the chances all favoring the presence in excess of some one constituent. He may, however, somtimes prepare such mixtures for himself, while attempting to resolve a mixture into its constituents by fractional distillation. Such mixtures have a constant boiling-point only under the atmospheric pressure at which they were prepared, so that the absence of homogeneity may be detected by distilling over one half *in vacuo* and then determining the boiling-interval under the ordinary pressure of what remains in the flask—provided both constituents do not have the same vapor-tension at all temperatures, which is a coincidence that is very unlikely to occur.

Determination of the Specific Gravity of Small Quantities of Liquids.

(1).—[*Method for* 0.20 *cc. of Substance.*]

Prepare a pycnometer for this purpose by bending a piece of thick-walled glass tubing 28–30 cm. in length, into the form shown in Fig. 9. The tubing should be of the kind used in gas analysis for transferring gases from one container to another, and have an internal diameter of 1 mm. and an external diameter of about 5 mm. The part between *A* and *B* should be drawn out to form a narrow-bored but thick-walled capillary, 8 cm. long. The zero-point of the instrument is a short, thin horizontal scratch made at *C*.

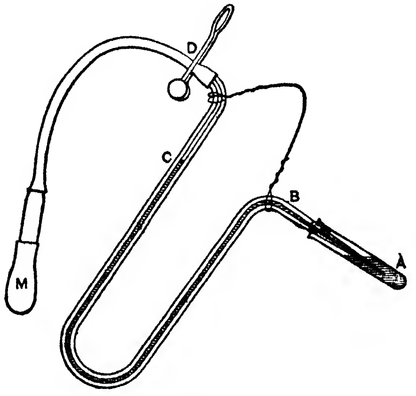

Fig. 9.

To calibrate the pycnometer begin by attaching a few centimeters of clean rubber tubing at *D*. Slip the point of an ordinary medicine-dropper *M* into the open end of the rubber tube, and then a light brass burette-clip over the latter, so that it may be quickly clamped off at any time at *D*. Next incline the instrument as shown in the figure, so as to immerse the point of the capillary in cold water contained in a 3-inch test-tube. The manipulation will be facilitated by having the test-tube held in a clamp. Open the clip at *D*. Compress the rubber bulb of the dropper to expel air. Then allow the bulb to expand slowly again, so as to suck water into the pycnometer. When the latter has filled to the horizontal arm above the zero-mark, close the clamp. Separate the dropper from the rubber tube. Then take off the clamp and separate the rubber tube from the pycnometer. Next suspend the pycnometer for some time in the air from the hook of the analytical balance, or for five minutes in a beaker containing cold water having the desired temperature. When the instrument and its contents have acquired the temperature of their surroundings, touch the edge of a bit of dry filter-paper to the tip of the capillary *A*, which must be filled by the water. As the water is absorbed by the paper, its level in the longer arm of the pycnometer will gradually fall. Bring this level exactly to the zero-mark. [If care is taken in subsequent operations not to incline the capillary *AB* much below a horizontal position, no water will flow out.]—The pycnometer is now ready to be weighed, unless it has been suspended in water, in which case it must first be carefully wiped dry.

To determine a specific gravity by this method, fill the pycnometer with the organic liquid by the manipulations described above in connection with the calibration. If we then represent the weight of water required to fill the instrument to the reference-mark by *w*, and the weight of the same volume of the organic compound by *o*, the specific gravity, uncorrected for temperature, will be $\frac{o}{w}$. The result should not differ from the true gravity by a full unit in the second decimal place.

After use, the pycnometer should be washed out at once with alcohol or ether, and thoroughly dried by an aspirated current of dry air. When not in use, it should be kept in a clean box along with a carefully adjusted counterpoise made from thick sheet lead, and a card giving the weight of water which it contains at the room temperature. As long as the counterpoise continues to balance the dry piknometer, its capacity may be assumed to have undergone no change.

(2).—[*Method with* 1 *cc. Pipette.*]

This very rapid method has an accuracy limit of about a unit in the third decimal place.

Calibrate a pipette (*A* in Fig. 10), to contain (not deliver) one cubic centimeter when filled to the reference-mark. If the determinations are to be made at about 20°, scratch the reference-mark on the pipette stem at the level of the lowest point of the meniscus seen when the pipette contains 0.9982 grm.* of distilled water at that temperature. Then the weight in grams of any liquid having the same volume at 20° will be the number expressing its specific gravity at 20°/4°.

The pipette is to be manipulated as follows: Suck in the liquid until it stands about half a centimeter above the reference-mark. Wipe off any traces of the liquid adhering to the outside of the stem. Then allow it to run out until the meniscus just touches the reference-mark. Wipe off the fraction of the last drop that hangs from the narrow outlet of the pipette, by touching it with the finger. Stand the pipette in the recipient tube *B*. Support the apparatus by the aid of the attached platinum wire on the balance-pan, as shown in the cut, and weigh at once. If an accurately adjusted lead counterpoise for the entire apparatus is kept in readiness and placed upon the opposite pan of the balance, the weights that have to be added to produce equilibrium give the desired gravity directly without any calculation.

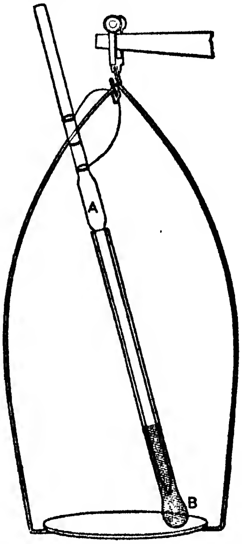

FIG. 10.

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* The correct location for this mark is most easily ascertained (as suggested in Ostwald's "Physico-chemical Measurements") by gumming a strip of millimeter-paper to the stem of the pipette and determining the weight of water corresponding to two points on the scale, one on each side of the true position and 10 mm. apart. "Then, on the justifiable assumption that the stem is cylindrical throughout this short piece, we can calculate the proper position of the mark from these two weighings." If, for instance, one weighing is 1·0222, the other 0·9930, and the desired weight 0·9982, then the reference-mark should lie $\frac{1\cdot0222-0\cdot9982}{1\cdot0222-0\cdot9930}\times10=8\cdot3$ mm. below the upper mark on the paper scale.

If it is desired to calibrate the pipette for use in comparing the density of a liquid at some other temperature than 20° with that of water at 4°, the proper weight of water to be used may be taken from the accompanying table of the density of water at various temperatures.

DENSITY OF WATER BETWEEN 15° AND 30°.

Temperature (C.°).	Densities.	Temperature (C.°).	Densities.	Temperature (C.°).	Densities.
15	0·9991	21	0·9980	26	0·9968
16	0·9990	22	0·9978	27	0·9965
17	0·9988	23	0·9976	28	0·9963
18	0·9986	24	0·9973	29	0·9960
19	0·9984	25	0·9971	30	0·9957

COLOR.

According to Aubert there are at least one thousand hues in the solar spectrum which may be distinguished by the human eye as different. Each of these hues may again be varied many times by changes in luminosity and admixture with white light, giving in the aggregate, it is estimated, as many as two million color differences that are recognizable under favorable circumstances. Yet, although the color of a chemical compound is often its most salient physical property, and the changes which this color experiences when treated with reagents may furnish the simplest test that can be applied for its identification, careful analysts have always very properly refused to attach the same importance to verbal descriptions of subjective color phenomena as a means for specific characterization, that they willingly grant to the recorded values of melting-points, boiling-points, specific gravities, and other physical constants whose determination requires the use of comparatively slow and elaborate methods of measurement.

The chief causes for the disrepute into which color tests have fallen are: the customary failure, except in spectroscopic work, to refer colors to any well-defined standard; the loose use made of the terms constituting the popular nomenclature of color; the imperfect development of the color memory; and, finally, the frequent omission of minor but essential experimental details from the directions given for the performance of color reactions. To minimize these defects in the original color descriptions and tests of this work, it has been considered desirable, whenever possible, to consistently adhere to a more definite color terminology than has before been used for chemical purposes. It has been necessary, however, to leave all copied color descriptions recorded in terms of the crude popular standard in which they were found; i.e. a standard in which red might signify anything from violet-red to orange, or from pink to russet.

The Terminology of Color.—To prevent possible misunderstandings, before proceeding to the subject of color comparisons, it will be necessary to define the sense in which certain common color terms will be used. It should be remarked that the restricted meanings that will be accepted for the terms have the sanction of good authority, though they are sometimes used popularly, and by artists, with very different meanings.

A *Pure*, *Full*, or *Saturated Color* is the most intense expression of that color without admixture of white, black, or gray.

No pigmentary color is absolutely pure. A surface painted with artificial ultramarine blue, for example, reflects with the blue about 25 per cent of white light, the effect of which is to soften the color and reduce its action on the eye. In the color-standard cards A and B in the back of this volume, the third horizontal series of color rectangles, counting from the top of the sheet, approach most nearly to the corresponding colors of the spectrum; and, as the pigmentary types of the pure colors, will sometimes be referred to as the "pure" or "full-color series" of the standard.

The *Luminosity* of a color is that constant of it which is dependent on the quantity of light which it transmits to the eye, and is nearly equivalent to brightness. Two colors may be equal in *purity*, each reflecting, we will say, 75 per cent of blue and 25 per cent of white light, but can not be made to match except by exposing the brighter surface to a feebler illumination than the other.

The *Hue* of a color is in some respects its most fundamental quality. It is dependent entirely on the refrangibility, or wave length, of the kinds of light producing the sensation. The purity and luminosity of colors may be absolutely equal, but one may appear red and the other yellow. The difference is one of hue. Each color in the standard, in going from red to violet, is a distinct hue.

A *Tint* of a color is the result obtained by reducing a pure or full color by the addition of white light. In the standard, the two color rectangles immediately over each full color are its "tints." Tint 1 contains less white than Tint 2. *Tint* 3, which is sometimes referred to in descriptions, is not a tint actually represented in the standard, but is to be imagined as a tint of about half the saturation of Tint 2.

A *Shade* of a color is the result obtained upon viewing a full color in shadow. With pigments, shades of most colors are obtained by adding black. The two shades corresponding to each full color of the standard are placed vertically under it.

Each of the upper five colors in the same vertical column of the standard—two tints, two shades, and one full color—is called a *tone* of that particular color scale. The full color of the scale is sometimes called the "normal tone" of the color.

A *Broken Color* is the subdued effect obtained by mixing a full color with neutral gray (black and white), viewing the tint of a color in a shadow, or a shade of a color in strong sunlight. The lowest horizontal series of colors in each of the sheets of the standard contains "medium" tones of the broken colors. Tints and shades of these "medium tones" will sometimes be referred to in the text as "light" or "dark" broken colors, respectively. It has not been considered necessary to represent them on the color sheets. The russets, browns, citrenes, and olives, are typical broken colors. All pigmentary colors, including the so-called full-color series of the standard, are somewhat broken; and in many color reactions, particularly where intense violets are under observation, it will be found that the colors to be compared are distinctly more saturated than the purest corresponding color of the standard. This will not often prevent the recognition of the fundamental hue of the color, however.

The Use of Pigmentary Color Standards.—Every colored substance illuminated by ordinary daylight owes its color to its selective absorption of rays of certain definite wave lengths from the white light that penetrates its surface. The light that escapes absorption and is transmitted to the eye is, almost without exception, a mixture of rays of many different wave lengths together with more or less unchanged white light. The subjective effect is, however, the perception of a simple color. Red and yellowish-green lights, for instance, give an orange which looks in all respects like the orange of the spectrum. Unaided by the spectroscope, it is impossible for the eye to detect in it the presence of either red or yellowish green. In the same way the original ingredients of every subjective color entirely elude visual analysis, and it is therefore theoretically possible, by the use of a suitable mixture of pigments, to prepare a systematically graduated scale of apparently homogeneous colors, that may be used as a color standard, and with which all other subjective colors, however simple or complex the light rays producing them may be, can be compared. As the colors of all natural objects are somewhat "broken," the fact that the colors of pigmentary standards are less "saturated" than the corresponding hues of the spectrum, is often an advantage rather than otherwise, and in other cases merely limits, but does not destroy, their usefulness.

The exact color descriptions of this work are all expressed in terms of the Bradley Color Standard. This standard, mounted in a special compact form, to facilitate its use in the laboratory, will be found on the two cards,* A and B, in a pocket in the back cover of this volume. It contains eighteen pure colors; and of derived tones, thirty-six tints, thirty-six shades, and twelve medium broken colors.

Color Symbols are only used in the tables for describing such colors as have been actually compared with the Bradley Standard in the author's laboratory. These symbols are as follows:

R=RED; OR=ORANGE-RED; RO=RED-ORANGE; O=ORANGE; YO=YELLOW-ORANGE; OY=ORANGE-YELLOW; Y=YELLOW; GY=GREEN-YELLOW; YG=YELLOW-GREEN; G=GREEN; BG=BLUE-GREEN; GB=GREEN-BLUE; B=BLUE; VB=VIOLET-BLUE; BV=BLUE-VIOLET; V=VIOLET; RV=RED-VIOLET; VR=VIOLET-RED.

The *Tints* of any color are represented by the symbol of the normal tone of the color followed by the symbol T1, T2, or T3; in which the numeral stands for the number of the tint, Tint 1 coming next to the normal tone of the color in saturation. The *Shades* of a color are in like manner represented by adding S1, or S2, to the symbol of the normal tone.

The following examples will illustrate the use of these color symbols: YS2= the second shade of yellow; YT1=the first tint of yellow; OT1-OYT1=a color between the first tint of orange and the first tint of orange-yellow.

Comparisons with the Color Standard.—All comparisons with the Standard should be made near an unscreened window through which light reflected from the sky—not direct sunlight—falls upon the colored object and standard from behind the observer.

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* The colors used on these sheets are those of the Bradley Standard, as described in Milton Bradley's "Elementary Color", (Springfield, Mass.). The fundamental colors, red, orange, yellow, green, blue, and violet are claimed to be careful pigmentary imitations of the hues seen at certain definite points in the solar spectrum. The wave lengths of the light emitted by the portions of the spectrum selected for imitation are, according to the measurements of Prof. A. H. Pillsbury: 6571 for red; 6085 for orange; 5793 for yellow; 5164 for green; 4695 for blue; and 4210 for violet. This series of six fundamental normal hues is increased to eighteen, by introducing twelve additional colors in such a way as to bring two new hues, separated by equal chromatic intervals, between each of the original colors. The values for these intermediate hues were determined, by blending the adjacent hues of the original series of six in pairs, by Maxwell's method, on a rotating color-wheel on which the areas of the two colored sectors were in the ratio of two to one. Yellow-orange, for example, is the subjective color resulting from the blending in the eye of the light from two superficial units of the fundamental orange and one of the yellow; orange-yellow, of two parts of the yellow and one of the orange. Two "tints" and two "shades" were then derived for each of the eighteen "normal tones" by dilution with white or black.

Additional copies of these color sheets, to replace the originals as they become soiled or injured, can be procured at any time from Messrs. John Wiley & Sons, the publishers of this volume. A comparison of the new color sheets with well-preserved samples of the Bradley colored papers prepared at different times during the last dozen years, indicates that the colors used are stable, and that much care has always been taken by the manufacturers to faithfully reproduce the colors of their first standard.

If the substance is a solid, it should be placed upon a piece of white paper, and laid upon the perforated shield accompanying the Standard, close to the rectangular window. The object of the screen is, partly to protect the Standard from accidental injury, and partly to prevent the confusion that is apt to arise from presenting many kinds of colored light to the eye at the same time. It is important to remember in color descriptions, that the color of a solid substance in masses is often different from its "streak," or color of its fine powder; and that the color of a moist precipitate is usually different from that of the same substance after drying. It is only occasionally that a color is met with which exactly matches one of the color squares of the Standard. The statement in descriptions, that a compound has a light orange-yellow color (YOT1), is therefore to be understood to mean nothing more than that its color more closely resembles this color of the Standard than any other. If the color to be described obviously lies *between* two colors of the Standard, the fact is, however, often indicated by the symbol; e.g. YOT-OYT1.

To examine a solution, lay the perforated screen upon the Standard so as to expose to view one or two color patches that resemble the color to be described, and hold or support it in an upright position, so that diffused sky light, coming from behind the observer, will fall upon it. Then hold the test-tube containing the solution vertically in front of the shield at a distance of about twice or thrice its diameter, and just above or to one side of the perforation. The comparison will thus be made by transmitted white light reflected through the solution from the screen. In observing the color of a fluorescence, replace the white screen by one coated with lamp-black. The light reaching the eye is in this case reflected back from the solution and not from the screen.

The color of a solution depends not only upon the nature of the substances dissolved, but also upon its concentration, the thickness of the colored layer, and sometimes upon the temperature. No description of an unfamiliar color reaction in a solution is entirely satisfactory unless all these conditions are given. In the greater number of cases, it is true, the result of dilution is chiefly to reduce the saturation of the original color; i.e., to produce a lighter tint of the original hue. But some change in hue is of very common occurrence, and in tests, like that for acroleïn (Test 112), where the change in hue upon continued dilution with water is from orange-yellow to violet-blue, it is the most striking and essential feature of the test.

The temperature is sometimes a very important condition, as in Test 401 for phenols with ferric chloride, where a pronounced yellow color is communicated to the solution in blank experiments by the reagent alone, unless the test is made cold. Unless otherwise indicated by the context, all color comparisons with solutions which are referred to the color standard in this work relate to solutions of approximately definite concentration, the colors being observed, as above stated, in three- to six-inch test-tubes at the temperature of the laboratory. Many color reactions, especially among those with ferric chloride for the phenols, and for the Species of Suborder II, Division A, Section 2, give colors which change rapidly on standing. In the absence of directions to the contrary, such colors should always be observed as soon as possible after their appearance.

It is more difficult to match the colors of solutions with a pigmentary standard than those of solids; for the colors in the Standard often appear distinctly "broken" and muddy by contrast, particularly if the solution happens to be a brilliant purple. But the fundamental *hue*, which is the most important color element, will still usually be distinguishable. Such comparisons are sometimes facilitated by using a solution of the colored substance so dilute that it will approximately match the first "tint" of a hue, rather than the "full" or "normal" color of the scale.

THE MANIPULATION OF SMALL QUANTITIES.

As has been stated on page 2, most of the specific tests in this volume depending upon the isolation of a pure derivative of a compound, are made with only a decigram or less of substance. The use of these small quantities not only saves valuable material, but also greatly shortens the time required to complete an experiment; so that, in many instances, a derivative may be prepared, filtered off, washed, recrystallized, and dried ready for a melting-point determination within half an hour. Some of the conditions and expedients that have been found conducive to success in such preparations in the small way deserve special mention.

Solid Precipitates.—In making the selection of a characteristic solid derivative suitable for preparation on the small scale in specific tests, it is desirable to choose one that will separate in a bulky but crystalline condition from the solvents used; and which may be recrystallized quickly by cooling its hot saturated solutions. Precipitates that are both crystalline and voluminous may be removed from glass surfaces and filters, and washed, recrystallized, dried, and handled with much less loss than those that are either too compact, slimy, or gelatinous.

Precipitates that are very soluble in the cold, and which form only after evaporation of a considerable portion of the solvent, are poorly adapted for these tests; evaporation being a slow operation, and the difficulty in separating crystals that are uncontaminated by by-products from the small mother-liquor being usually greater than in the method by cooling. Among the numbered specific tests are many examples of derivatives that combine all the good qualities just mentioned in a high degree. A single decigram of some of the aromatic nitro-derivatives, for example, upon separating from a hot saturated solution in dilute alcohol, is sufficient to fill entirely a five-inch test-tube with a mass of hard interlacing crystals. Some sticky resinous precipitates of equal weight would be entirely lost as inconspicuous adhesive smears on the test-tubes or filters.

If no precipitate should appear upon cooling what is supposed to be a hot saturated solution of a solid derivative, always close the mouth of the test-tube firmly with the thumb, and shake vigorously and persistently. Many compounds whose preparation is directed in the numbered specific tests, tend to form supersaturated solutions; but upon being thus treated, give bulky crystalline precipitates. This final precautionary shaking should never be omitted.

Small precipitates should be collected on correspondingly small filters and funnels. A large filter retains so much mother-liquor as to require excessive washing; and the precipitate, if at all adhesive, will be very difficult to separate from the large paper surface. A supply of cut filters, 5 cm. in diameter, and a few very small funnels are therefore indispensable for the performance of the specific tests.

When hot filtration of a saturated solution is necessary, the funnel and filter are most easily and effectively heated by first pouring through them some of the boiling liquid that is to be used as the solvent in the experiment. Clogging of the funnel-tube by separation of solid matter may be prevented by cutting off its lower end so that only about 1 cm. remains. If the solid begins to crystallize out at a temperature very little below the boiling-point of the solvent, a comparatively large filter and funnel are to be preferred to a small one, as they will give more rapid filtration. On a very small filter there is greater danger that the free passage of the solution may become obstructed by the deposition of solid matter in the pores of the paper.

In filtering from one test-tube into another, hang a short piece of thick bent copper wire over the lip of the test-tube in which the funnel is placed, so as to leave a passage for the escape of air from the tube. For mixtures that filter slowly, fit the recipient test-tube with a doubly perforated rubber stopper and use it as a filter-bottle, placing a small filter-cone in the funnel and applying gentle suction with the filter-pump.

In washing small precipitates with a liquid in which they are rather soluble, the danger of using an unnecessarily large volume of solvent has been provided against in the more important procedures by the specification of some definite volume. These directions should be closely followed. The solvent should be dropped upon the precipitate in such a manner as to detach it from the sides of the filter and wash it down into the point, so as to facilitate its subsequent separation from the paper. Very small precipitates which do not require much washing, and which it is thought undesirable to bring upon a filter, may be separated from most of the supernatant solution by decantation, and then shaken out upon a piece of porous tile. When the adhering solution has disappeared in the tile, it may be sprayed or moistened as many times as desired with the solvent, waiting after each treatment until the liquid disappears before adding more.

If it becomes necessary to redissolve a precipitate that is very small and firmly attached to the filter, open the filter, tear off the sector to which the solid adheres, and boil it with the solvent. Do not boil up the whole filter, or the pulpy mass formed may cause explosive boiling and loss of the substance.

Precipitates whose melting-points are not too low are directed to be dried in a drying-oven at some definite temperature and for a definite time. Solids of very low melting-point are air-dried at the ordinary temperature, or supported in a warm place over a drying-oven, on a piece of porous tile or filter-paper. Drying in the oven should always be preceded by rubbing the moist substance over the surface of a porous tile with a small spatula, or pressing it between filter-paper to remove all the mother-liquor.

Liquids.—The preparation of liquid derivatives is not often recommended in specific tests, because the purification of such compounds on the small scale generally presents special difficulties. The procedure for the isolation and identification of liquid alcohols from the saponification of a gram or two of an ester (p. 114), the Siwoloboff boiling-point method for two or three drops of liquid (p. 222), and the method of page 228 for the determination of the specific gravity of liquids having a volume of only 0.2 cc., are, however, examples which show that the difficulties connected with the manipulation of small quantities of liquids may sometimes be satisfactorily overcome. Test-tube experiments with less than a centimeter of a liquid must be made in very narrow tubes. With a tube of 5 mm. internal diameter, five drops of a substance are all that is required to enable a satisfactory observation of the action of sodium on alcohols in Test VIII–2.

The separation of very small volumes of two liquids of different specific gravities is best made with a pipette. The mixture is placed in a narrow test-tube, and all but a few drops of the substance that is present in the greater quantity are removed by a large pipette and rejected. The remainder of the liquid, measuring perhaps 1 cc., is then sucked up into a small pipette made from a piece of glass tubing that has been drawn out so as to have an average internal diameter of only about 2 mm. in the long tapering portion. The suction is most easily controlled if applied by the rubber nipple of a medicine-dropper. When both liquids have been brought into the pipette, and appear in two layers after standing, they may be separated to a fraction of a drop by slowly ejecting them, successively, into separate tubes.

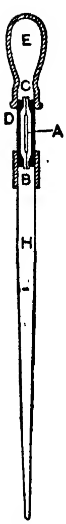

Fig. 11.

The most perfect control over the rate of flow in careful experiments is gained by the employment of the safety pipette shown in Fig. 11. This pipette is provided with a regulator *A*, 3 cm. in length, made by drawing out a piece of thermometer tubing at the blast-lamp until the capillary at *B* and *C* is narrowed almost to complete closure; and then cementing it with melted wax, *D*, into a short section of glass tube of the same diameter as the upper part of the pipette stem. The capillary, if sufficiently constricted, offers so much resistance to the passage of gas from the air-space, *E* to *H*, that the contents of the pipette can not be discharged in less than several seconds, even when the bulb is suddenly and forcibly compressed. By the use of this device the transfer of a small measured volume of a valuable or corrosive liquid in work at the balance (as in weighing out acetic anhydride for Test VIII–3) is made a safe and simple operation.

SPECIAL REAGENTS.

The following is a complete list of the less common chemicals and solutions required for the performance of the ordinal, generic, sectional, and numbered specific tests of this volume. All these reagents can be purchased, or easily prepared by following the directions given in these pages. Most of them are already used in analytical laboratories.

[*For Ordinal Tests.*]

Metallic Sodium. The best commercial sodium, free from particles of salt.
Sodium Nitroprusside. In small crystals or powdered.
Nitrosylsulphuric Acid. Preparation described on page 13.
Fluorescein Paper. Preparation described on page 14.

[*For Generic Tests.*]

Fuchsine Aldehyde Reagent. Preparation described on page 15.

α-Naphthol Solution. A 10 per cent solution in chloroform. See page 26.

Decinormal Sodium Hydroxide (aqueous)	Carefully standardized.
Decinormal Hydrochloric Acid (aqueous)	
Normal Sodium Hydroxide (aqueous)	
Normal Sulphuric Acid (aqueous)	

Approximately Normal Sodium Hydroxide (alcoholic). Unless the alcohol is very free from aldehyde it will become colored on keeping, and hence should not be prepared in large quantities.

Phenolphthaleïn. A 1 : 300 solution in 50 per cent alcohol.

Ferric-Chloride Solution. A 10 per cent aqueous solution made from the sublimed chloride.

Hydroxylamine-hydrochloride Solution. Prepared as described on page 133.

Alcoholic Sodium-hydroxide Solution for Test VII, A. Prepared as described on page 133.

Phenylhydrazine. Redistilled if the color is not very light.

Acetic Anhydride.

[*For Sectional Tests.*]

Phenylhydrazine Hydrochloride. Prepared as described on page 32.

Fehling's Solution. Prepared as described on page 33.

Bromine Solution. 2 cc. bromine in 50 cc. dry carbon tetrachloride. See page 195.

Fuming Sulphuric Acid. An acid of sp. gr. 1.89, which may be prepared by dissolving sulphur trioxide or a solid Nordhausen acid in oil of vitriol.

Fuming Nitric Acid. Specific gravity 1.48.

[*For Occasional Use in Numbered Specific Tests.*]

Acetyl Chloride.

Aluminium Chloride. Dry, sublimed.

Ammoniacal Silver-nitrate Solution. Prepared as described on page 22.

Ammoniacal Cuprous-chloride Solution. Prepared as described on page 197.

Aniline.

Benzaldehyde.

Benzoyl Chloride.

Bromine.

Chromic Anhydride.

3, 5-Dinitrobenzoic Acid. Prepared by Kahlbaum, and for sale by dealers.

Iodine Solution. Prepared as described on page 166.

Mercuric Oxide.

β-Naphthol.

Phosphorus Pentachloride.

Phloroglucin Solution. Prepared as described on page 33.

Resorcin.

Para-toluidine.

SPECIAL APPARATUS.

Ignition-tubes of Hard Glass or Iron. Description and cut on page 10.

Asbestos-board Screens. Size 4″×4″. Thickness 3/16″. Used in the sodium fusion (page 10, Fig. 1); the determination of boiling-points (page 221, Fig. 6); and in specific tests (e.g., Test 311–2).

"Medicine-droppers." As shown in Fig. 1, page 10.

Lipped Test-tubes. In addition to the usual assortment of test-tubes of the larger sizes, a good supply of tubes with a height of 3 inches and diameter of ½ inch, with cork stoppers to fit, and a few with a height of 3 inches and diameter of 3/16 inch, should always be kept in readiness. (Cf. page 112, Fig. 3, and page 152, Fig. 4.)

Mounted Burettes for Decinormal and Normal Alkali and Acid. Mounting shown in Fig. 2, page 78.

Pipettes with Bulbs and Long Stems. Of the usual pattern and calibrated to *deliver* 2 cc., 25 cc., and 50 cc., respectively.

1-cc. Pipette Graduated to Hundredths. Straight, without bulb; graduated by the manufacturer.

1-cc. Pipette for Specific Gravities. Page 229, Fig. 10.

10-cc. Graduated Cylinders. With lip and foot for general use in rough measurements. Graduation to half centimeter.

Capillary Piknometer. Page 228, Fig. 9.

Safety Pipette. Description on page 236, Fig. 11.

Covered Heating-bath. Page 152, Fig. 4. Recommended for use in several generic tests.

Bath for Melting-point Determinations. Page 218, Fig. 5.

Melting-point and Ebullator Capillaries. Pages 219 and 222, Fig. 7.

Apparatus for Determination of True Melting-point and Fusion Intervals. Page 225, Fig. 8.

Glass Funnels. Diameter 2 cm.

Cut Paper Filters. Diameters 3 cm. and 5 cm.

ALPHABETICAL INDEX.

The alphabetical index relates primarily to classification, analytical methods, numbered tests, reagents, and apparatus, but also contains the names of such compounds—about 15 per cent of the total number described—as will be most frequently sought in the tables. To find the description of any compound of minor importance, consult the complete "Formula Index" on page 244.

FORMULA INDEX.

The Formula Index gives the page, and usually the part of the page, on which any compound of known empirical formula described in this volume will be found. The numerals following a dash—which is commonly preceded by a melting-point or boiling-point—are the page numbers. The compounds are arranged according to the kind and number of atoms represented in their symbols. This form of index—already used in Richter's Lexicon and many of the leading chemical journals—is so simple that detailed explanations are not necessary. Polymers and compounds of unknown molecular weight are mentioned under the simplest formula expressing their percentage composition. Water of crystallization is always omitted from the formulæ. To facilitate access to the original literature, the names applied to compounds are generally literal English translations of names used in the indexes of the third edition of Beilstein's Handbuch der organischen Chemie. Incidentally it is possible to use this index in identifying compounds by the "Method of the Empirical Formula."

C_{13} GROUP.

NOTE ON REAGENTS FOR REDUCTION TESTS.

(To face page 17 of " The Identification of Commercial Dyestuffs.")

While the original descriptions of all color discharges obtained in **Tests 8** and **11** that are tabulated in Volume III are based on the use of a solution of Rongalite C, practically identical results under the same experimental conditions are secured by the employment of a reducing mixture prepared by the following empirical procedure:

Place in a 300-cc. flask 15 grams of dry sodium bisulphite and 8 grams of zinc dust. Add 75 cc. of distilled water. Shake to dissolve the bisulphite and wet the zinc. Then add from a burette 7.5 cc. of commercial " formalin " (40 per cent formic aldehyde solution). After mixing thoroughly, heat quickly to boiling on a wire gauze over a Bunsen flame, and boil moderately for just 5 minutes. Dilute at once with 45 cc. of cold distilled water, and then cool and filter. Or, double all the quantities mentioned may be taken, and the mixture boiled for the same period of 5 minutes.

The commercial dry sodium bisulphite of the quality placed on the American market by reputable manufacturers as the " U.S.P. viii " grade, if taken from full recently purchased bottles, is generally suitable for the preparation of this reagent, even when not absolutely fresh. The finished reagent should not be preserved for more than a few days, and should not smell of formic aldehyde when warmed. It should be understood that the times required for discharges in reduction tests and the color-returns in oxidation tests as stated in the tables are only approximations, and will be found to vary slightly in independent experiments with the same dyestuff whichever reagent is employed.

In **Tests 6, 11,** and **21** it is permissible to substitute any good commercial sodium hydrosulphite for Blankit T.

PHARMACEUTICS