

ism is termed *polymerism* (from *πολύς*, *polús*, many or much, and *μέρος*, part). Metastannic acid (*vide* p. 240) is a polymeric variety, or *polymeride*, of stannic acid. An illustration of a second variety of isomerism is seen in the case of cyanate of ammonium and urea, bodies already alluded to in connection with cyanic acid. These and several other pairs of chemical substances have dissimilar properties, yet are similar not only in elementary composition and in the centesimal proportion of the elements, but also in the fact that each molecule possesses the same number of atoms. But the reactions of these bodies indicate the probable nature of their construction; and this is shown in their formulæ by the disposition of the symbols. Thus cyanate of ammonium is represented by the formula NH_4CNO , urea by $\text{CO}(\text{NH}_2)_2$. Such bodies are termed *metamerie* (from *μετά*, *meta*, a preposition denoting change, and *μέρος*), and their condition spoken of as one of *metamerism*. Acetate of ethyl (p. 404) is metamerie with butyric acid (p. 493), for they have the same percentage composition and their vapors have the same specific gravity, and each therefore might be represented by the formula $\text{C}_4\text{H}_8\text{O}_2$; but their properties warrant us in assuming that their atoms occupy different positions in the two molecules—justify us in giving $\text{CH}_3\text{CO.OC}_2\text{H}_5$ as a picture of a molecule of acetate of ethyl, and $\text{C}_3\text{H}_7\text{COOH}$ as a picture of a molecule of butyric acid. Acetate of methyl ($\text{CH}_3\text{COO.CH}_3$), propionic acid ($\text{C}_2\text{H}_5\text{COOH}$),* and formate of ethyl ($\text{H.CO.OC}_2\text{H}_5$) are isomers of the metamerie variety, or *metamerides*; also quinine and quinidine, cinchonine and cinchonidine, and many of the volatile oils, etc. The isomerism of starch and dextrin may be of a polymeric or of a metamerie character; but we do not yet know which, and must therefore at present give them identical formulæ, though it is most probable that many of the carbohydrates are multiples of the mere empirical formulæ, since dextrin ($\text{C}_6\text{H}_{10}\text{O}_5$)_x by hydration produces maltose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, which would point to the formula of dextrin as being at least ($\text{C}_6\text{H}_{10}\text{O}_5$)₂. Substances similar in composition and constitution, yet differing in properties, are termed *allotropic* (*ἄλλος*, *allos*, another; *τρόπος*, *tropos*, condition). Thus ordinary phosphorus, kept at a temperature of about 450° F. in an atmosphere from which air is excluded, becomes red, opaque, insoluble in liquids in which ordinary phosphorus is soluble, oxidizes extremely slowly, and only ignites when heated to near 500° F. (red or amorphous phosphorus). A black allotropic variety of phosphorus is known. There are also three *allotropes* of carbon which are respectively crystalline, graphitic, and amorphous. Sulphur may be obtained in the viscous as well as in the hard, brittle condition. Another illustration of *allotropy* is seen in the varieties of tartaric acid, which have different optical properties, but otherwise are identical; they are in neither of the above-mentioned states of isomerism, but are allotropic modifications of the same substance. Occasionally one and the same substance crystallizes in two distinct forms; its state is then described as one of *polymorphism* (*πολύς*, *polus*, many;

* For explanation of formulæ, see chapter on Aldehydes and Acids.

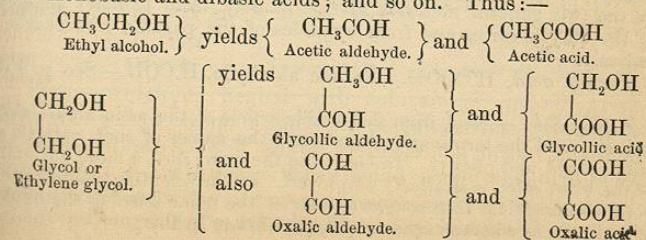
μορφή, *morphe*, form). Sulphur is polymorphous. It crystallizes by slow cooling in (1) prismatic crystals of sp. gr. 1.98, while in nature it occurs in (2) octahedra of sp. gr. 2.07. Melted and poured into water, sulphur takes up (3) the form of caoutchouc of sp. gr. 1.96. These differences warrant the statement that sulphur occurs in three distinct allotropic conditions. Possibly, such conditions result from the association of different numbers of atoms in the molecule of the element; that is, allotropic bodies may simply be *physically polymeric*, or in some other way be mere *physical isomerides*.

QUESTIONS AND EXERCISES.

774. How is wheat-starch or potato-starch isolated?
775. Define gluten and gluten.
776. Enumerate the proximate principles of wheaten flour.
777. Is starch soluble in water?
778. Which is the best chemical test for starch?
779. Distinguish physically between the varieties of starch.
780. Into what compound is starch converted by heat?
781. What occurs when a mixture of starch and water is allowed to flow into hot diluted sulphuric acid?
782. If two equal amounts of starch with water be heated, one containing a small quantity of ground malt, what effects ensue?
783. Write a short article on the chemistry of malting.
784. What is the nature of gum arabic? and how is it distinguished from "British gum"?
785. Mention the properties of the products of the action of nitric acid of various strengths on cellulose.
786. How is pyroxylin prepared?
787. Explain *isomerism*, giving several illustrations.
788. Give examples of polymeric bodies.
789. State the formula of a body metamerie with urea.
790. Define allotropy and polymorphism, giving illustrations.

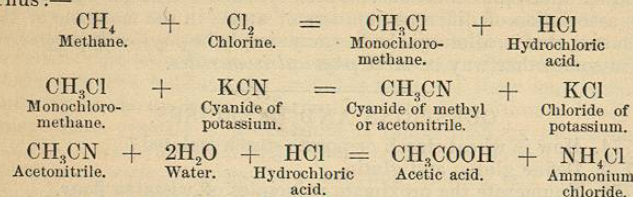
ALDEHYDES AND ACIDS.

General Formation.—The aldehydes and acids may be artificially formed by oxidation of the primary alcohols, glycols, etc. Monohydric alcohols, having only one hydroxyl (OH) group, form monobasic acids, dihydric alcohols (glycols), having two hydroxyl groups, yield monobasic and dibasic acids; and so on. Thus:—



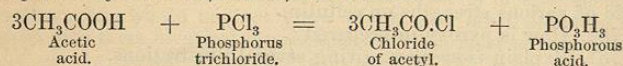
It will be seen that the groups COH and COOH denote respectively an aldehyde and an acid, the H in the COOH group being replaceable by a metal, such as $\text{CH}_3\text{CO.ONa}$ (acetate of sodium).

Acids may also be obtained by acting on the *nitriles* or cyanides of the hydrocarbon radicals with hydrochloric acid and water. Thus:—

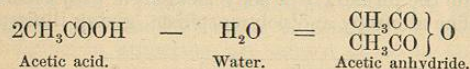


Many aldehydes and acids occur in nature; for example, oil of meadowsweet (salicylic aldehyde), oil of bitter almonds (benzoic aldehyde), citric acid in lemons.

General Reactions.—Aldehydes all form crystalline compounds with acid sulphite of potassium; by oxidation they yield an acid, and by the action of nascent hydrogen they yield an alcohol; while acids, by nascent hydrogen, yield an aldehyde, and then an alcohol. With oxides, hydrates, carbonates, and sometimes with metals, acids form metallic derivatives. With the alcohols, acids yield alkyl* or ethereal salts, as, for instance, acetic ether. By the action of the chloride, iodide, or bromide of phosphorus their hydroxyl group is replaced by chlorine, iodine, or bromine:—



Like inorganic acids they form anhydrides by the elimination of water:—



The important aldehydes and acids will now be mentioned.

The Acetic Series.

Acids of the Acetic Series, $\text{C}_n\text{H}_{2n+1}\text{CO.OH}$ (Monobasic).—Formed by the two general methods given—namely, from primary alcohols of the ethylic series and from cyanides of the paraffin hydrocarbon radicals.

Formic acid, H.CO.OH . *Formic aldehyde*, H.CO.H .—See p. 404.

* *Alkyl Salts.*—*Alkyl*, from the Arabic article *al*, the, as in alkali, alcohol, etc., and the termination common to the names of such radicals as ethyl, amyl, and phenyl. In Germany the word *ester*, a mere variation of the word *ether*, is similarly employed. In the scientific chemistry of both countries it is thus sought to restrict the name *ethers* to the oxides of radicals, as common ether ($\text{C}_2\text{H}_5)_2\text{O}$, (*Ether*, B. P.).

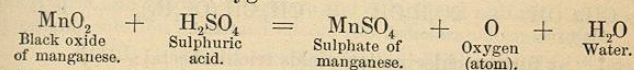
Acetic Acid, CH_3COOH (Methylformic acid).—Obtained by the oxidation of alcohol. See p. 294.

Aldehyde, or Acetic Aldehyde, $\text{C}_2\text{H}_4\text{O}$ or $\text{CH}_3\text{CO.H}$.

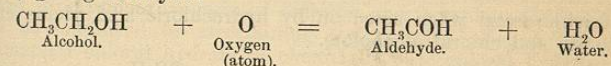
Preparation.—Place together, in a capacious test-tube or flask, about four parts of spirit of wine, six of black oxide of manganese, six of sulphuric acid, and four of water, and gently warm the mixture; aldehyde (*alcohol dehydrogenatus*), a highly volatile liquid, is immediately formed and its vapor evolved, recognized by its peculiar, somewhat fragrant odor. Adapt a cork and rather long bent tube to the test-tube, and let some of the aldehyde slowly distil over into another test-tube, the condensing-tube being kept as cool as possible. Set the distillate aside for a day or two; the aldehyde will have nearly all disappeared and acetic acid be found in the tube. Test the exposed liquid by litmus-paper; it will be found to have an acid reaction: make it slightly alkaline by a drop or two of solution of carbonate of sodium, then boil to remove any alcohol and aldehyde present, add sulphuric acid, and notice the characteristic odor of the acetic acid evolved.

These experiments will enable the process of acetification described in connection with acetic acid to be more fully understood. Pure diluted alcohol is not oxidized by exposure to air, but in presence of fermentive matter or vegetable matter undergoing decay or change it is oxidized first to aldehyde and then to acetic acid.

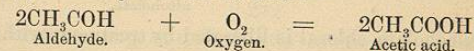
In the above process the black oxide of manganese and sulphuric acid furnish nascent oxygen:—



The nascent oxygen then acts on the alcohol, just as the oxygen of the air acts on the alcohol in fermented infusion of malt, beer, or wine, giving aldehyde:—



The aldehyde rapidly, even when pure (more rapidly when impure), absorbs oxygen and yields acetic acid:—



Tests.—Aldehyde heated with solution of potash gives a brownish-yellow resinous mass of peculiar odor. Its aqueous solution reduces salts of silver, giving a mirror-like coating to the sides of a test-tube. When acted on by phenol dissolved in sulphuric acid it gives a red color. Aldehyde on keeping yields polymerides, metaldehyde, and paraldehyde.

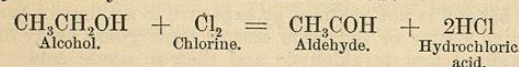
CHLORAL.

Chloral or *Trichloraldehyde*, CCl_3COH , is a chlorine substitution-derivative of aldehyde, though it cannot directly be obtained by acting on aldehyde by chlorine, because condensation-products are formed.

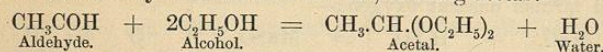
Process.—Pass a rapid stream of dry chlorine into pure absolute alcohol so long as absorption occurs. During the first hour or two the alcohol must be kept cool; afterward gradually warm till ultimately the boiling-point is reached. The preparation of a considerable quantity occupies several days. The crude product is mixed with three times its volume of sulphuric acid and distilled, again mixed with a similar quantity of sulphuric acid, and again distilled, and finally rectified from quicklime.

The formation of chloral would at first sight seem to be due to the production from the alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) of aldehyde (CH_3CHO), through the removal of hydrogen by the chlorine, and the substitution of chlorine for hydrogen in the aldehyde (CH_3COH), with formation of *chlor-aldehyde* or *chloral* (CCl_3COH). But the reactions are far more complicated, being as follows:—

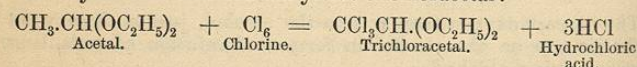
Aldehyde and hydrochloric are first formed:—



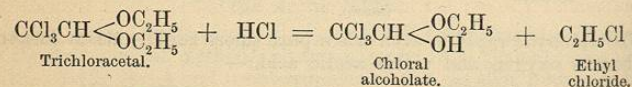
The nascent aldehyde unites with alcohol, forming acetal:—



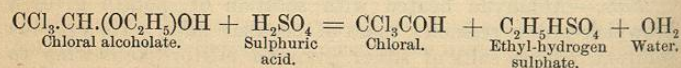
Acetal* by further chlorination yields trichloroacetal:—



Trichloroacetal when acted on by hydrochloric acid yields ethyl chloride and chloral alcoholate.

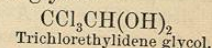
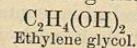


From the alcoholate, chloral is liberated by treatment with sulphuric acid:—

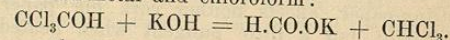


**Methylal*, $\text{CH}_2(\text{OCH}_3)_2$ the lowest term of the series, is occasionally used as a soporific.

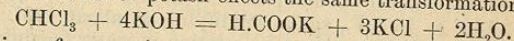
Properties.—It is a colorless liquid, of oily consistence. Sp. gr. 1.502. Boiling-point, 201.2°F . Its vapor has a penetrating smell, and is somewhat irritating to the eyes. Mixed with water, heat is disengaged and solid white, crystallizable, hydrous chloral (*Chloral*, U. S. P.), $\text{CCl}_3\text{CH}(\text{OH})_2$, or, what is more generally though irregularly termed *chloral hydrate*, or *Hydrate of Chloral* (*Chloral Hydras*, B. P.), results. Hydrous chloral is a true glycol, the water not being simply water of crystallization, but of combination, the systematic name being trichlorethylidene glycol:—



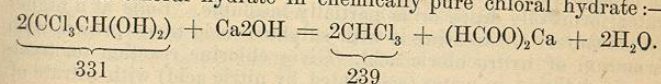
Hydrous chloral fuses when heated, solidifies at about 120°F ., boils at from 202° to 206°F . It sublimes as a white crystalline powder. Both chloral and chloral hydrate are soluble in water, alcohol, ether, and oils. Oils and fats are also soluble in chloral hydrate. The aqueous solution should be neutral and give no reaction with nitrate of silver. Chloral, especially if it contains a trace of acid, may undergo a spontaneous change into an opaque white isomeric modification, *metachloral*, insoluble in water, alcohol, or ether, but convertible by prolonged contact with water or by distillation into the ordinary condition. By action of weak alkalies chloral yields formate of the alkali-metal and chloroform:—



Chloral, or rather strong aqueous solution of chloral hydrate (3 in 4), injected beneath the skin yields nascent chloroform by action of the alkali of the blood, and produces narcotic effects (Liebreich, Personne). Chloroform itself admits of similar hypodermic use (Richardson). If administered by the stomach, thirty to eighty grains of solid hydrate are required. The final products of the reaction of the chloroform and blood are formate and chloride of sodium. A strong spirituous solution of potash effects the same transformation:—



Solution of ammonia and moist hydrate of calcium, as well as weak solutions of fixed alkalies, convert hydrate of chloral into formate of the metal and chloroform. The reaction with the slaked lime being especially definite and complete (Wood), it may be employed in ascertaining the richness of a sample of commercial chloral hydrate in chemically pure chloral hydrate:—



From the foregoing equation and molecular weights it is obvious that 100 grains of hydrate of chloral, if quite dry, will yield by distillation with 30 grains of slaked lime and an ounce of distilled water (in a small flask and long bent tube kept cool by moistened paper) 72.2 grains of chloroform by weight or (the sp. gr. of chloroform being taken at 1.497) 47.56 grains by measure, or about 52 minims. 100 grains

of the official hydrate of chloral "should yield not less than 70 grains of chloroform." (Any such definite quantity of chloroform, on account of its volatile nature, is perhaps best measured, the weight being obtained by multiplying the volume by 1.5.)

Small quantities of chloral hydrate in dilute solutions may be estimated by converting its chlorine into hydrochloric acid by nascent hydrogen, and titrating with volumetric solution of nitrate of silver (Short). A quantity of solution containing not more than .05 gram is placed in a small flask with granulated zinc and acetic acid, and allowed to stand twenty-four hours; the solution is then poured off and the zinc washed two or three times with distilled water; a little red chromate of potassium is added, and it is then titrated with decinormal nitrate of silver solution in the usual way, the acetic acid and acetate of zinc not interfering with the indications. 1000 c.c. of the silver solution indicate 5.52, nearly, of chloral hydrate.

Pure Chloral Hydrate.—Liebreich, who first proposed the use of chloral hydrate, gives the following as the characteristics of a pure article: Colorless, transparent crystals. Does not decompose by the action of the atmosphere, does not leave oily spots when pressed between blotting-paper, affects neither cork nor paper. Smells agreeably aromatic, but a little pungent when heated. Tastes bitter astringent, slightly caustic. Seems to melt on rubbing between the fingers. Dissolves in water like candy without first forming oily drops, and the solution is neutral or faintly acid to test-paper. Dissolves in bisulphide of carbon, petroleum, ether, water, alcohol, oil of turpentine, etc. Its solution in chloroform gives no color when shaken with sulphuric acid. Boiling-point, 203° to 205° F. It volatilizes without residue. Distilled with sulphuric acid, the chloral should pass over at 205° to 207° F. Melting-point, 133° to 136° F., again solidifying at about 120°. Gives no chlorine reaction on treating the solution in water (acidulated by nitric acid) with nitrate of silver.

Impure Chloral Hydrate.—Yellowish, cloudy. Decomposes; leaves spots by pressing between blotting-paper; decomposes corks and paper of the packing. Smells pungent and irritating; on opening the bottle is sticky, and often emits fumes. Taste strongly caustic. With water forms oily drops or is partially insoluble. Boils at a higher temperature. On treating it with sulphuric acid turns brown, with formation of hydrochloric acid. Gives chlorine reaction on treating the solution in water (acidulated by nitric acid) with nitrate of silver.

Alcoholates of chloral are obtained on combining alcohols with chloral. Chloral alcoholate or trichlorethylidene ethyl ether, $\text{CCl}_3\text{CH} < \begin{smallmatrix} \text{OH} \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$, is obtained by mixing alcohol with chloral; it is, in fact, "chloral hydrate," with one hydroxyl group replaced by (OC_2H_5) .

Bromal, CBr_3COH , *hydrate of bromal*, $\text{CBr}_3\text{CH}(\text{OH})_2$, and *alco-*

holates of bromal, are produced when bromine instead of chlorine attacks alcohol. *Iodal*, CI_3COH , also exists.

BUTYL CHLORAL, $\text{C}_4\text{H}_7\text{Cl}_3\text{COH}$, originally, but erroneously, termed *croton chloral*, is a product of the action of dry chlorine on cold aldehyde. Its name expresses its constitution; it is *chlorinated butyric aldehyde*—ordinary chloral being chlorinated acet-aldehyde. *Butyl-chloral hydrate*, *croton-chloral hydrate*, wrongly so called *hydrate of butyl-chloral* (*Butyl-chloral Hydrate*, B. P.), *hydrous butyl-chloral*, $\text{C}_4\text{H}_7\text{Cl}_3\text{CH}(\text{OH})_2$ (*trichlorobutylidene glycol*), occurs "in purely white crystalline scales, having a pungent but not acid odor, resembling that of hydrous chloral, and an acrid, nauseous taste. It fuses at about 172° F. (77.8° C.) to a transparent liquid, which in cooling commences to solidify at about 160° F. (71.1° C.). Soluble in about fifty parts of water, in its own weight of glycerin and of rectified spirit, and nearly insoluble in chloroform. The aqueous solution is neutral or but slightly acid to litmus-paper. It does not yield chloroform when heated with solutions of potash or with milk of lime."

The Acetic Series of Acids—continued.

Propylic or *Propionic Acid* (ethyl-formic acid), $\text{C}_2\text{H}_5\text{COOH}$, is produced by oxidation of propylic alcohol.

Butyric or *Tetrylic Acid* (propyl-formic acid), $\text{C}_3\text{H}_7\text{COOH}$, is formed by general methods; also during the fermentation of cheese. It is found as a glyceric salt in butter (whence its name).

Pentyllic, *Valerianic*, or *Valeric Acid*, $\text{C}_4\text{H}_9\text{COOH}$.—There are several varieties of this acid, the valerianic acid from valerian and angelica root, and that artificially formed from amylic alcohol (*vide p. 450*), being the iso-primary valerianic acid or iso-propylacetic acid, $\text{CH}(\text{CH}_3)_2\text{CH}_2\text{COOH}$, the primary having the constitution of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$.

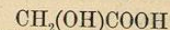
Palmitic Acid, $\text{C}_{15}\text{H}_{31}\text{COOH}$, from fats; *stearic acid*, $\text{C}_{17}\text{H}_{33}\text{COOH}$, from suet; *cerotic acid*, $\text{C}_{26}\text{H}_{53}\text{COOH}$, from beeswax; and *melissic acid*, $\text{C}_{29}\text{H}_{59}\text{COOH}$, derivable from beeswax and from canauba wax (from the leaves of *Copernicia cerifera*, a Brazilian palm), all belonging to the acetic series.

The Lactic Series.

Acids of the Lactic Series, $\text{C}_n\text{H}_{2n}(\text{OH})\text{COOH}$.—This series is formed of hydroxyderivatives of the acetic series, one atom of hydrogen in the latter being replaced by the hydroxyl group:—



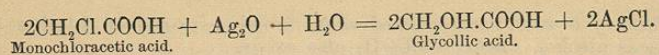
Acetic acid.



Hydroxyacetic or glycollic acid.

Though they possess only one carboxyl (COOH) group, yet, having an alcoholic hydroxyl group, they form di-substitution-derivatives with the metals.

They may be formed by partial oxidation of glycols by diluted nitric acid, and by acting on monochloro-derivatives of the acids of the acetic series by moist silver oxide.



Carbonic Acid or *Hydroxyformic Acid*, OH.COOH , the first of this series, has been studied already. *Carbamide* or *Urea*, $\text{NH}_2\text{CO.NH}_2$, the normal amide of carbonic acid, is interesting historically as being the first organic body synthetically produced from inorganic sources. (See Index, "Urea, artificial production of.") The acid amide of carbonic acid, *carbamic acid*, $\text{NH}_2\text{CO.OH}$, occurs as an ammonium salt, $\text{NH}_2\text{CO.ONH}_4$, in the carbonate of ammonium of pharmacy. The carbamate of ethyl, or urethane, $\text{NH}_2\text{CO.OC}_2\text{H}_5$, is a mild hypnotic.

Glycollic Acid (Hydroxyacetic acid), $\text{CH}_2\text{OH.COOH}$, is found in the leaves of the Virginia Creeper; artificially it may be obtained by carefully oxidizing glycol and by the action of silver oxide on dextrose and lævulose.

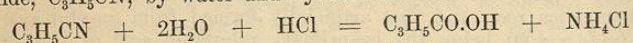
Lactic Acid (Hydroxypropionic acid), $\text{C}_2\text{H}_4(\text{OH})\text{COOH}$.—Three isomeric lactic acids are known; the fermentative lactic acid (ethylidene * lactic acid), $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ (see p. 344), and sarcosolactic acid, from flesh, being those of importance.

The Acrylic Series.

Acids of the Acrylic Series, $\text{C}_n\text{H}_{2n-1}\text{COOH}$.

Acrylic Acid, $\text{C}_2\text{H}_3\text{COOH}$, or $\text{CH}(\text{CH}_2)\text{COOH}$, is formed by oxidizing acrolein (acrylic aldehyde; see Glycerin) by oxide of silver.

Crotonic Acid, or methacrylic acid, $\text{C}_3\text{H}_5\text{COOH}$, or $\text{CH}(\text{CHCH}_3)\text{COOH}$, formerly supposed to be a constituent of croton oil, may be formed by oxidizing crotonic aldehyde, and by acting on allyl cyanide, $\text{C}_3\text{H}_5\text{CN}$, by water and hydrochloric acid:—



Oleic Acid, $\text{C}_{18}\text{H}_{34}\text{O}_2$, or $\text{CH}(\text{C}_{16}\text{H}_{32})\text{COOH}$, is found as a glyceric salt in many fats and oils.

Preparation.—Olive oil is saponified with caustic potash, and the resulting soap decomposed by tartaric acid, which liberates oleic and stearic acids. The oleic and stearic acids are heated with lead oxide, forming lead oleate and stearate, the former being dissolved out from the latter by ether. The ether is evaporated and the lead oleate treated with hydrochloric acid, which liberates the oleic acid.

Elaidic Acid (isomeric with oleic acid) is formed by passing nitrogen peroxide into oleic acid; it is more stable than oleic acid, distilling unchanged.

The Benzoic or Aromatic Series.

Acids of Benzoic or Aromatic Series, $\text{C}_n\text{H}_{2n-7}\text{COOH}$.—The acids of this series are formed by oxidizing hydrocarbons, by oxidation

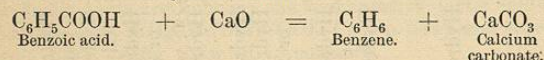
* Bodies having the CH_3CH group are called ethylidene compounds. Compare chloral hydrate, trichlorethylidene glycol, $\text{Ca}_3\text{CH.C}(\text{HO})_2$.

TABLE SHOWING THE RELATIONS OF THE ACIDS OF THE ACETIC, LACTIC, AND GLYCOLLIC SERIES.

Acids of the Acetic Series, $\text{C}_n\text{H}_{2n+1}\text{CO.OH}$.	Acids of the Hydroxyacetic or Lactic Series, $\text{C}_n\text{H}_{2n}(\text{OH})\text{CO.OH}$.	Acids of the Dihydroxyacetic or Glyoxylic Series, $\text{C}_n\text{H}_{2n-1}(\text{OH})_2\text{COOH}$.
Methylic or Formic	Hydroxyformic or Carbonic	Dihydroxyacetic or Glyoxylic
Ethylic or Acetic	Hydroxyacetic or Glycollic	Dihydroxypropionic or Glyceric
Propylic or Propionic	Hydroxypropionic or Lactic	Dihydroxybutyric
Butylic or Butyric	Hydroxybutylic	
Pentylic or Valeric	Hydroxybutylic	
Hexylic or Caproic	Hydroxybutylic	
Heptylic or Caproic	Hydroxybutylic	
Octylic or Chanthylic	Hydroxybutylic	
Caprylic or Nonylic or Pelargonic	Hydroxybutylic	
Capric	Hydroxybutylic	
Lauric	Hydroxybutylic	
Myristic	Hydroxybutylic	
Palmitic	Hydroxybutylic	
Stearic	Hydroxybutylic	
Arachidic	Hydroxybutylic	
Behenic	Hydroxybutylic	
Cerotic	Hydroxybutylic	
Melissic	Hydroxybutylic	

of alcohols of the benzylic series, and by acting on the cyanides of the members of the benzene series. All the acids of this series, with the exception of benzoic acid, possess many isomers.

Benzoic Acid, C_6H_5COOH , occurs naturally in gum benzoin (Gum Benjamin), which contains from 12 to 15 per cent., the rest being mainly composed of two resins having the formulæ $C_{40}H_{46}O_9$ and $C_{30}H_{40}O_5$. Benzoic acid may be obtained by oxidizing benzoic aldehyde, C_6H_5COH , which may be prepared from trichloromethylbenzene (see Toluene, p. 427). Benzène (toluene), $C_6H_5CH_3$, may be directly oxidized into benzoic aldehyde, the methane group (CH_3) being resolved into $COOH$ —evidence that benzoic acid is really a benzène derivative, not a phenène derivative. (For other modes of obtaining benzoic acid artificially see p. 335.) It may also be produced from hippuric acid (benzamidacetic acid, p. 338). Benzoic acid heated with lime yields benzene:—

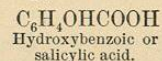
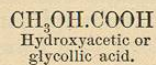


Benzoic Aldehyde or benzaldehyde, C_6H_5COOH , forms the greater part of oil of bitter almonds (see Amygdalin, p. 504). It is a colorless liquid, soluble in 30 parts of water and in all proportions in ether and alcohol. With acid-sulphite of potassium it forms a crystalline compound, $C_6H_5COH.NaHSO_3$. *Benzoyl chloride*, C_7H_5OCl , results from the action of chlorine on benzaldehyde (formerly termed benzoyl hydride, C_7H_5OH), or from the action of pentachloride of phosphorus on benzoic acid (*benzoyl hydrate*, C_7H_5OOH). Benzaldehyde also results from the oxidation of the *benzyl alcohol*, C_7H_7OH , of balsam of Peru.

The other acids of this series are unimportant.

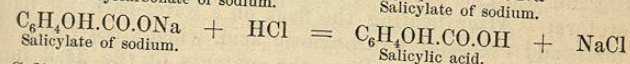
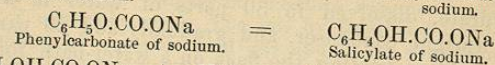
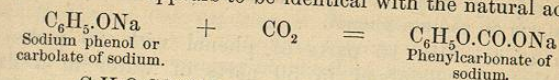
The Hydroxybenzoic Series.

Acids of the Hydroxybenzoic Series, $C_nH_{2n-8}OH.COOH$.—Just as the acids of the lactic series are related to the acetic series, so are the acids of the hydroxybenzoic (or salicylic) series related to the benzoic series.



Salicylic or Hydroxybenzoic Acid, $C_6H_4O_3$ or $C_6H_4OH.COOH$ (*Acidum Salicylicum*, U. S. P.).—Natural salicylate of methyl is described on p. 404. It also occurs in several species of violet (Mandelin). Salicylic acid may be made by the oxidation of salicylic aldehyde (*vide infra*), or by the action of carbonic acid on phenol or carbolic acid (Kolbe). To accomplish this, the phenol is mixed with caustic soda, forming sodium phenol or carbolate of sodium, C_6H_5ONa . The sodium phenol is then saturated with carbonic acid at the ordinary temperature, by which phenylcarbonate of sodium is produced.

The latter on being heated in closed vessels is transformed into salicylate of sodium, from which salicylic acid may be obtained by the action of hydrochloric acid, and purification by recrystallization from alcohol. It appears to be identical with the natural acid.



Salicylate of Phenyl, $C_6H_4OH.CO.OCH_5$, or *salicylic phenol*—or, shortened, *salol*—is a new antiseptic, antipyretic, antirheumatic remedy. It is white, crystalline, soluble in alcohol, insoluble in water, and of an aromatic odor.

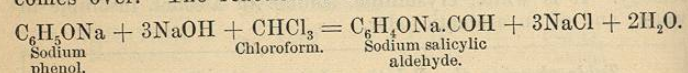
Table showing the Relations between the Benzoic and Hydroxybenzoic Acids.

Benzoic acid	$C_6H_5.CO.OH$.
Hydroxybenzoic or salicylic acid . . .	$C_6H_4OH.CO.OH$.
Dihydroxybenzoic acid	$C_6H_3(OH)_2.CO.OH$.
Trihydroxybenzoic or gallic acid . . .	$C_6H_2(OH)_3.CO.OH$.

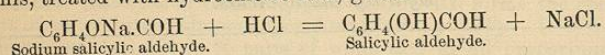
Salicylic acid, like carbolic acid, is a powerful antiseptic, but is free from the taste and smell of carbolic acid. It is only slightly soluble in cold water, but readily soluble in hot water, alcohol, ether, and in aqueous solutions of such alkali-metal salts as borax, phosphate of sodium, or citrate of potassium, which it converts into acid salts, with formation of a salicylate. A similar antiseptic *cresotic acid* (hydroxytoluic acid, $C_6H_3OH.CH_3.CO.OH$) is similarly obtained from cresol or cresylic acid, $C_6H_3OH.CH_3$. Ferric chloride strikes a violet coloration with both salicylic and cresotic acids. Both acids have antipyretic powers. The true salicylates of the alkali-metals, and probably therefore the cresotates, are very feeble antiseptics. Salicylate of sodium, *Sodii Salicylas*, B. P., $(NaC_6H_4O_3)_2.H_2O$, the old Salicylate of Soda, made by neutralizing salicylic acid with hydrate or carbonate of sodium, forms small, nearly colorless lamellar crystals, soluble in alcohol and readily soluble in water. Carbolic acid, often containing cresylic acid, commercial salicylic acid, may contain cresotic acid. An alcoholic solution of salicylic acid allowed to evaporate spontaneously, exposure to dust being avoided, should leave a white residue free from color even at the points of the crystals. Salicylic acid is soluble in strong sulphuric acid, yielding *sulpho-salicylic acid*, $C_6H_4(OH)CO.O.SO_3H$. Salicylic acid yields colored substances on being nitrated and etherified, etc. *Iodosalicylic acid* and *di-iodosalicylic acid*, $C_6H_3IO_3$ and $C_6H_2I_2O_3$, are used in medicine.

Salicylic Aldehyde, or hydroxybenzoic aldehyde, $C_6H_4OH.CO$ (salicylous acid, hydride of salicyl).—Found in the essential oil of meadow-sweet (*Spirea ulmaria*); also obtained by the oxidation of saligenin (see p. 496). It may be artificially formed by the action of chloroform on sodium phenol.

Preparation.—Mix 10 parts of phenol with 20 parts of sodium hydrate, dissolved in 30 parts of water in a flask having an upright condenser, and gradually add 20 parts of chloroform. After heating the flask on a water-bath for half an hour, add excess of hydrochloric acid, when a red-violet oil will rise to the surface. Pour the contents of the flask into a retort, and pass steam through it till no more aldehyde comes over. The reaction is as follows:—



This, treated with hydrochloric acid, gives:—

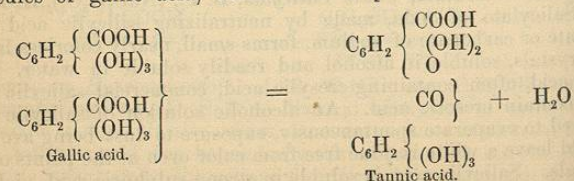


The oil which passes over (orthohydroxybenzoic aldehyde) may be purified from phenol (with which it is always contaminated) by treating with acid sulphite of sodium, which forms a compound with aldehyde, leaving the phenol, which may be removed by dissolving in ether. An isomeric salicylic aldehyde (parahydroxybenzoic aldehyde) is formed with the ortho-aldehyde, and remains dissolved in the water in the retort, from whence it is precipitated on cooling.

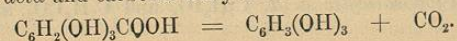
Coumarin, $C_9H_6O_2$ (the principle of the Tonka bean), may be obtained by acting on the sodium-derivative of salicylic aldehyde with acetic anhydride and sodium acetate (Perkin).

The Trihydroxybenzoic Series.

Acids of the Trihydroxybenzoic Series ($C_6H_2(OH)_3.CO$). *Gallic Acid*, or trihydroxybenzoic acid, $C_6H_2(OH)_3.CO$ (see p. 358).—By the elimination of one molecule of water from two molecules of gallic acid, tannic acid is produced.



Gallotannic acid or tannin (see p. 356) by heat yields *pyrogallol* or *pyrogallic acid* and carbonic anhydride.



The Cinnamic Series.

Acids of the Cinnamic Series, $C_9H_7O_2$.—Cinnamic acid, $C_9H_7O_2$, may be obtained from the balsams of Tolu, Peru, and storax.

1. *Balsam of Peru* (*Balsamum Peruvianum*, U. S. P.), an exudation from the trunk of *Toluifera Pereira*, is a mixture of oily matter with about one-quarter or one-third resinous matter and 6 per cent. of cinnamic acid. The oil, by fractional distillation in an atmosphere of carbonic acid gas and under diminished pressure, furnishes *benzyl hydrate* or *benzylic alcohol* ($C_6H_5.CH_2OH$), *benzoate of benzyl* ($C_6H_5.CO.OC_6H_5$), and *cinnamate of benzyl* ($C_6H_5.CO.OC_6H_4$) or *cinnaméin* (Kraut). By action of alcoholic solution of potash it yields benzoate and cinnamate of potassium and benzylic alcohol; also *cinnamic alcohol* ($C_6H_5.CH_2OH$), otherwise known as *peruvine* or *styrone*; it also often holds in solution *metacinnaméin* or *styracin* ($C_{15}H_{16}O_2$), isomeric with cinnamic aldehyde (C_9H_7O). The resin of balsam of Peru seems to result from the action of moisture on the oil. Any admixture of resin, oil, storax, benzoin, or copaiva with balsam of Peru is detected by mixing six grains of slaked lime with ten drops of the balsam, when a soft product results if the specimen be pure, but hard if impure; further, the mixture, on being warmed until volatile matter is expelled and charring commences, gives no fatty odor. 2. *Balsam of Tolu* (*Balsamum Tolutanum*, U. S. P.) is an exudation from the trunk of *Toluifera balsamum*; in composition it closely resembles balsam of Peru, but is more susceptible of resinification. It contains benzoate and cinnamate of benzyl, cinnamic acid, a little benzoic acid (Busse), and about 1 per cent. of a volatile hydrocarbon, *tolene*, $C_{10}H_{16}$. The cinnamic acid crystals may be seen with a lens when a little of the balsam is pressed between two warmed pieces of glass. Old hard balsam of Tolu is a convenient source of cinnamic acid, which may be extracted by the same process as that by which benzoic acid is obtained from benzoin—namely, ebullition with alkali, filtration, and precipitation by hydrochloric acid. 3. *Storax* (*Styrax*, U. S. P.) is an oleo-resin obtained from the *Liquidambar orientale*. It contains a volatile oil termed *styrol*, *cinnamene*, or *cinnamol* (C_8H_8)—which possibly (Berthelot) is condensed acetylene, $4C_2H_2$ —cinnamic acid, styracin, or cinnamate of cinnamyl ($C_8H_7.CO.OC_8H_9$), and a soft and a hard resin. Styrol differs from similar hydrocarbons in being converted into a polymeric solid termed *metastyrol* or *draconyl* on heating to about 400 F. For medicinal use, Storax (*Styrax Præparatus*, B. P.) is purified by solution in alcohol, filtration, and removal of the alcohol by distillation. By oxidation with red chromate of potassium and sulphuric acid it yields an odor resembling that of essential oil of bitter almonds.

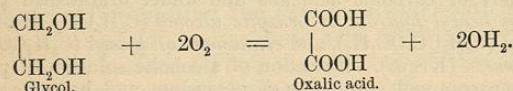
DIBASIC ACIDS.

Dibasic Acids are acids having two carboxyl ($COOH$) groups in the molecule.

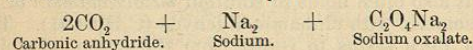
The Succinic Series.

Acids of the Succinic Series, $C_nH_{2n}(COOH)_2$.—These acids may be formed by the oxidation of glycols, or by the action of water and hydrochloric acids on the cyanides of the olefines, obtained by acting on the olefine dibromo-additive derivatives by potassium cyanide.

Oxalic Acid, $C_2O_4H_2$ or $(COOH)_2$, is the first of this series. It may be obtained by oxidizing glycol, $C_2H_4(OH)_2$:—



Also by the action of carbonic anhydride on metallic sodium :—



(For other methods, see Oxalic Acid, p. 315.)

Oxamide, $C_2O_4(NH_2)_2$, the analogue of urea (Carbamide, $CO(NH_2)_2$), is formed on mixing oxalate of ethyl with ammonia.

Succinic Acid, $C_2H_4(COOH)_2$. See p. 355.

The Malic Series.

Acids of the Malic Series, $C_nH_{2n-1}OH(COOH)_2$.—Malic or hydroxysuccinic acid, $C_2H_3(OH)(COOH)_2$, is obtained artificially by acting on bromosuccinic acid, $C_2H_3Br(COOH)_2$, with moist silver oxide, the bromine being replaced by hydroxyl. It is contained in unripe mountain-ash berries, morello cherries, etc. (See p. 348.)

Asparagine (amidosuccinamic acid), $C_2H_3NH_2 < \begin{array}{c} CONH_2 \\ COOH \end{array}$. (See p. 349.)

The Tartaric Series.

Acids of the Tartaric Series, $C_nH_{2n-2}(OH)_2(COOH)_2$.—*Tartaric Acid* (dihydroxysuccinic acid), $C_2H_2(OH)_2(COOH)_2$, may be obtained by oxidizing erythrite, $C_2H_4(OH)_2(CH_2OH)_2$. (See p. 467. For other modes of formation, see p. 315.) There are four isomeric tartaric acids, differing by their action on a ray of polarized light.

The Phthalic Series.

Acids of the Phthalic Series, $C_nH_{2n-8}(COOH)_2$.—*Phthalic Acid*, $C_6H_4(COOH)_2$, is obtained by the oxidation of naphthalene and naphthalene dichloride, or a mixture of benzene and benzoic acid. By distillation it forms phthalic anhydride, $C_8H_4O_3$, which when heated with phenol and sulphuric acid yields phenolphthalein, a light-yellow crystalline powder, which when dissolved in alcohol is used in alkalimetry for its property of turning brilliant red with the slightest excess of alkali.

TABLE SHOWING THE RELATIONS BETWEEN THE ACIDS OF THE ACETIC SERIES AND THE DIBASIC ACIDS.

Acids of the Acetic Series, $C_nH_{2n+1}COOH$	Acids of the Succinic Series, $C_nH_{2n}(COOH)_2$	Acids of the Hydroxysuccinic or Malic Series, $C_nH_{2n-1}OH(COOH)_2$	Acids of the Dihydroxysuccinic or Tartaric Series, $C_nH_{2n-2}(OH)_2(COOH)_2$
Formic, $H.CO.OH$	Oxalic, $COOH.COOH$	—	—
Acetic, $CH_3.CO.OH$	Malonic, $CH_2(CO.OH)_2$	Tartaric (oxymalonic), $CH.OH.(COOH)_2$	Mesoxalic, $C(OH)_2(COOH)_2$
Propylic, $C_2H_5.CO.OH$	Succinic, $C_2H_4(CO.OH)_2$	Malic (oxysuccinic), $C_2H_3OH.(COOH)_2$	Tartaric (or dihydroxysuccinic), $C_2H_2(OH)_2(COOH)_2$
Tetrylic, $C_3H_7.CO.OH$	Pyrotartaric, $C_3H_6(COOH)_2$	Glutaric, $C_3H_5OH.(COOH)_2$	Homotartaric, $C_3H_4(OH)_2(COOH)_2$