

A DICTIONARY
OF
APPLIED CHEMISTRY

BY

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ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

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| <i>Amer. Chem. J.</i> . . . | American Chemical Journal. |
| <i>Amer. J. Pharm.</i> . . . | American Journal of Pharmacy. |
| <i>Amer. J. Sci.</i> . . . | American Journal of Science. |
| <i>Anal. Fis. Quim.</i> . . . | Anales de la Sociedad Española Física y Quimica. |
| <i>Analyst</i> . . . | The Analyst. |
| <i>Annalen</i> . . . | Annalen der Chemie (Justus Liebig). |
| <i>Ann. Chim. anal.</i> . . . | Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie. |
| <i>Ann. Chim.</i> . . . | Annales de Chimie. |
| <i>Ann. Falsif.</i> . . . | Annales des Falsifications. |
| <i>Ann. Inst. Pasteur.</i> . . . | Annales de l'Institut Pasteur. |
| <i>Ann. Physik.</i> . . . | Annalen der Physik. |
| <i>Ann. Physique</i> . . . | Annales de Physique. |
| <i>Annali Chim. Appl.</i> . . . | Annali di Chimica Applicata. |
| <i>Apoth. Zeit.</i> . . . | Apotheker-Zeitung. |
| <i>Arch. Pharm.</i> . . . | Archiv der Pharmazie. |
| <i>Atti R. Accad. Lincei</i> . . . | Atti della Reale Accademia dei Lincei. |
| <i>Bentl. a. Trim.</i> . . . | Bentley and Trimen. Medicinal Plants. |
| <i>Ber.</i> . . . | Berichte der Deutschen chemischen Gesellschaft. |
| <i>Ber. Deut. pharm. Ges.</i> . . . | Berichte der Deutschen pharmazeutischen Gesellschaft. |
| <i>Bied. Zentr.</i> . . . | Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb. |
| <i>Bio-Chem. J.</i> . . . | The Bio-Chemical Journal. |
| <i>Biochem. Zeitsch.</i> . . . | Biochemische Zeitschrift. |
| <i>Brewers J.</i> . . . | Brewer's Journal. |
| <i>Bull. Imp. Inst.</i> . . . | Bulletin of the Imperial Institute. |
| <i>Bull. Soc. chim.</i> . . . | Bulletin de la Société chimique de France. |
| <i>Chem. Ind.</i> . . . | Chemische Industrie. |
| <i>Chem. News</i> . . . | Chemical News. |
| <i>Chem. Soc. Proc.</i> . . . | Journal of the Chemical Society of London. Proceedings. |
| <i>Chem. Soc. Trans.</i> . . . | Journal of the Chemical Society of London. Transactions. |
| <i>Chem. Weekblad</i> . . . | Chemisch Weekblad. |
| <i>Chem. Zeit.</i> . . . | Chemiker Zeitung. |
| <i>Chem. Zentr.</i> . . . | Chemisches Zentralblatt. |
| <i>Compt. rend.</i> . . . | Comptes rendus hebdomadaires des Séances de l'Académie des Sciences. |
| <i>Dingl. poly. J.</i> . . . | Dingler's polytechnisches Journal. |
| <i>Färber-Zeit.</i> . . . | Färber-Zeitung. |
| <i>Flück. a. Hanb.</i> . . . | Flückiger and Hanbury. Pharmacographia. |
| <i>Frdl.</i> . . . | Friedländer's Fortschritte der Teerfarbenfabrikation. |
| <i>Gazz. chim. ital.</i> . . . | Gazzetta chimica italiana. |
| <i>Helv. Chim. Acta</i> . . . | Helvetica Chimica Acta. |
| <i>Jahrb. Min.</i> . . . | Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. |
| <i>J. Amer. Chem. Soc.</i> . . . | Journal of the American Chemical Society. |
| <i>J. Bd. Agric.</i> . . . | Journal of the Board of Agriculture. |
| <i>J. Franklin Inst.</i> . . . | Journal of the Franklin Institute. |
| <i>J. Ind. Eng. Chem.</i> . . . | Journal of Industrial and Engineering Chemistry. |
| <i>J. Inst. Brewing</i> . . . | Journal of the Institute of Brewing. |
| <i>J. Pharm. Chim.</i> . . . | Journal de Pharmacie et de Chimie. |
| <i>J. Phys. Chem.</i> . . . | Journal of Physical Chemistry. |
| <i>J. pr. Chem.</i> . . . | Journal für praktische Chemie. |
| <i>J. Russ. Phys. Chem. Soc.</i> . . . | Journal of the Physical and Chemical Society of Russia. |
| <i>J. Soc. Chem. Ind.</i> . . . | Journal of the Society of Chemical Industry. |
| <i>J. Soc. Dyers.</i> . . . | Journal of the Society of Dyers and Colourists. |
| <i>J. Tokyo Chem. Soc.</i> . . . | Journal of the Tokyo Chemical Society. |
| <i>J. Washington Acad. Sci.</i> . . . | Journal of the Washington Academy of Sciences. |
| <i>Kolloid Zeitsch.</i> . . . | Kolloid-Zeitschrift. |
| <i>Met. & Chem. Eng.</i> . . . | Metallurgical and Chemical Engineering. |
| <i>Min. Mag.</i> . . . | Mineralogical Magazine and Journal of the Mineralogical Society. |
| <i>Monatsh.</i> . . . | Monatshefte für Chemie und verwandte Theile anderer Wissenschaften. |
| <i>Pharm. J.</i> . . . | Pharmaceutical Journal. |
| <i>Pharm. Zeit.</i> . . . | Pharmaceutische Zeitung. |

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| <i>Phil. Mag.</i> | Philosophical Magazine (The London, Edinburgh and Dublin). |
| <i>Phil. Trans.</i> | Philosophical Transactions of the Royal Society. |
| <i>Phot. J.</i> | Photographic Journal. |
| <i>Proc. Roy. Soc.</i> . . | Proceedings of the Royal Society. |
| <i>Proc. Roy. Soc. Edin.</i> | Proceedings of the Royal Society of Edinburgh. |
| <i>Rec. trav. chim.</i> . . | Receuil des travaux chimiques des Pays-Bas et de la Belgique. |
| <i>Trans. Faraday Soc.</i> | Transactions of the Faraday Society. |
| <i>Zeitsch. anal. Chem.</i> | Zeitschrift für analytische Chemie. |
| <i>Zeitsch. angew. Chem.</i> | Zeitschrift für angewandte Chemie. |
| <i>Zeitsch. anorg. Chem.</i> | Zeitschrift für anorganische Chemie. |
| <i>Zeitsch. Nahr.</i> | |
| <i>Genussm</i> | Zeitschrift für Untersuchung der Nahrungs- und Genussmittel. |
| <i>Zeitsch. öffentl.</i> | |
| <i>Chem.</i> | Zeitschrift für öffentliche Chemie. |
| <i>Zeitsch. physikal.</i> | |
| <i>Chem.</i> | Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre. |
| <i>Zeitsch. physiol.</i> | |
| <i>Chem.</i> | Hoppe-Seyler's Zeitschrift für physiologische Chemie. |

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A

DICTIONARY

OF

APPLIED CHEMISTRY.

L

L-ACID. 1-Naphthol-5-sulphonic acid.

LABDANUM or **LADANUM** *v.* OLEO-RESINS.

LABEL VARNISH *v.* VARNISH.

LABRADORITE *v.* FELSPAR.

LACCASE *v.* Japanese *Lacquer*, art.

RESINS.

LAC DYE. Lac dye is produced by an insect, the *Coccus lacca* or *ficus*, living on the twigs of various kinds of trees, particularly the *Ficus religiosa* (Linn.), the *Zizyphus jujuba* (Lam.), and the *Butea frondosa* (Roxb.). These insects appear usually in November, and subsequently fasten themselves to the fleshy portions of the young branches. Gradually the abdomen of the insects becomes covered by a viscous fluid, which slowly forms a cellule surrounding the animal. The substance composing this cellule is the *stick lac*. The cellule attains its full size in March, and the insect then exhibits the appearance of a red oval-shaped, smoothly polished lifeless sac entirely filled with a beautiful red liquid; its size is then the same as that of the fully grown cochineal (Crookes, *Dyeing and Calico Printing*, 354). Commercial stick lac is chiefly gathered on the hilly banks of the Ganges in India, that for dyeing purposes possessing a deep red colour, whereas the pale perforated kind in which no insects exist is employed for varnish-making, and constitutes the material for *shellac*.

Of *lac*, the following varieties occur: *stick lac*, the crude product together with the twigs upon which it is formed; *grained lac*, the material removed from the twigs; and *caked lac*, the latter variety fused and cast into moulds.

Such a resinous material is not suitable for dyeing purposes, and a simple process is adopted to remove the colouring matter from the resin, or at least to obtain it in a more concentrated form. This consists in extracting the stick lac with hot dilute sodium carbonate solution, evaporating the extract, and moulding the residue into square cakes. According to Crookes the product, which is *lac dye*, contains on

an average about 50 p.c. of colouring matter, 25 p.c. of resin, and 22 p.c. of earthy impurities.

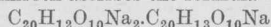
Lac dye is an extremely ancient dyestuff, and was employed in the East for many centuries before it was known in Europe. It appears to have been introduced into this country about 1790. Early in the last century, lac dye was a very important article of commerce, so much so that at one time shellac was practically a by-product of its manufacture. The position of these products has now been reversed, for whereas the dyestuff is almost no longer used, the shellac industry is of considerable importance.

According to the older writers, the colouring matter of lac dye was considered to be identical with that of cochineal, but that this is not the case has been clearly established by Schmidt (Ber. 20, 1285).

Laccaic acid.—Finely powdered lac dye, after treatment with dilute hydrochloric acid to remove mineral matter, is extracted with boiling water, and the colouring matter is precipitated from the resulting solution by means of lead acetate. The lead precipitate, suspended in water, is decomposed with sulphuretted hydrogen, and the filtrate which contains the free colouring matter is evaporated to dryness. The residue thus obtained is extracted with alcohol and ether and is then added to the solution until a precipitate no longer forms. The filtered liquid on gradual evaporation deposits crystals of laccaic acid. According to Schmidt, the amount of pure colouring matter which can be isolated by this method from a kilogram of lac dye is 20 grams.

A simpler process has been described by Dimroth and Goldschmidt (Annalen, 1913, 399, 62), in which the stick lac is digested in water at 50°, the clear red solution, after cooling, acidified with acetic acid, separated from the resinous matter that is precipitated, and, after evaporation to small bulk, acidified with hydrochloric acid. When the crude product thus obtained is crystallised from hot 85 p.c. formic

acid, washed, dried (at 60°–70°C.), and recrystallised from hot dilute hydrochloric acid, laccic acid separates in the form of dark red microscopic rhombohedra. The acid is soluble in water yielding blood-red solutions, but is insoluble in ether; when heated it decomposes at about 180°, yielding a small quantity of a red sublimate. Only the sodium hydrogen salt has been prepared in crystalline condition, and to this Dimroth ascribes the formula



whilst he concludes that the acid has the composition $\text{C}_{20}\text{H}_{14}\text{O}_{10}$, and not $\text{C}_{16}\text{H}_{12}\text{O}_8$, as previously supposed.

Although no distinction is to be observed in the absorption spectra of the aqueous and alkaline solutions of laccic and carminic acids, it is possible when the colouring matters are dissolved in sulphuric acid to discriminate between them in this way. When fused with potassium hydroxide, laccic acid gives, in addition to a substance (a) volatile in steam, colourless needles, m.p. 142°–143°; a compound (b) $\text{C}_{10}\text{H}_8\text{O}_6$, or $\text{C}_{10}\text{H}_8\text{O}_8$, m.p. 285°, readily soluble in water; a compound (c) $\text{C}_8\text{H}_8\text{O}_8$, m.p. 169°, possibly a hydroxytoluic acid; and (d) an easily soluble substance, the aqueous solution of which gives a black coloration with ferric chloride (Schmidt).

Reduction of laccic acid with tin and hydrochloric acid, or with zinc-dust and aqueous ammonia, yields a compound $\text{C}_{20}\text{H}_{16}\text{O}_9$, which crystallises in brown-yellow rhombohedra, and which on oxidation by means of cupric chloride and hydrochloric acid, yields a substance of the composition $\text{C}_{20}\text{H}_{14}\text{O}_9$, which Dimroth considers is related to the former substance as quinone to hydroquinone.

Although laccic acid does not yield crystalline bromination products similar to α - and β -bromocarmine, compounds of this nature have been obtained by Dimroth from its oxidation product, calaic acid.

Calaic acid is produced when laccic acid is oxidised by means of hydrogen peroxide (2½–3 molecular proportions) in the presence of a catalyst (cobalt, manganous, cerous, or ferrous salts; manganous chloride is best). This acid, $\text{C}_{18}\text{H}_{14}\text{O}_{11}$, crystallises from ether in small yellow prisms, and from water in needles having the composition $\text{C}_{18}\text{H}_{14}\text{O}_{11} \cdot 2\frac{1}{2}\text{H}_2\text{O}$. It does not possess dyeing properties, contains one carbonyl and three carboxyl groups, and may be purified by means of its crystalline barium salt. A silver salt, $\text{C}_{18}\text{H}_{12}\text{O}_{11}\text{Ag}_2$, has also been prepared.

When calaic acid is brominated in glacial acetic acid, two products are formed: (i) an α -ketonic acid $\text{C}_{12}\text{H}_{10}\text{O}_4\text{Br}_2$, and (ii) β -bromolaccain $\text{C}_{12}\text{H}_8\text{O}_5\text{Br}$, these products being separated by taking advantage of the solubility of the latter in cold acetone.

The α -ketonic acid forms brown-yellow crystals, m.p. 208°–209°; it gives an impure red-violet colour reaction with ferric chloride, and when heated to 80°–90° with concentrated sulphuric acid, it loses carbon monoxide, yielding a monobasic acid $\text{C}_{11}\text{H}_{10}\text{O}_5\text{Br}_2$, which has m.p. 245°–246° (decomposition), and gives an intense violet colour reaction with ferric chloride. The keto-acid forms a phenyl-hydrazone and semicarbazone, and, by treatment with methyl alcoholic hydrobromic acid,

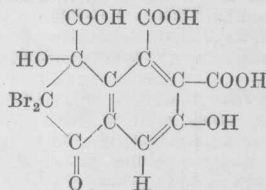
yields the hydrobromic acid compound of its methyl ester $\text{C}_{13}\text{H}_9\text{O}_5\text{Br}_2 \cdot \text{HBr}$, colourless needles, m.p. 133°–134° (decomposition).

β -Bromolaccain separates from water in crystals of the composition

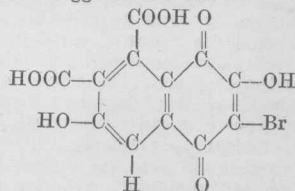


it has m.p. 234°–235° (decomposition). It dyes wool orange from an acid bath, and gives a strong red colour with ferric chloride. The potassium salt $\text{C}_{12}\text{H}_7\text{O}_5\text{BrK} \cdot \text{H}_2\text{O}$, crystallises in hexagonal plates. Concentrated sulphuric acid and acetic anhydride produce *diacetyl- β -bromolaccain anhydride* $\text{C}_{16}\text{H}_7\text{O}_9\text{Br}$, indicating that two hydroxy groups are present in the molecule, and that it also contains two carboxyl groups in the ortho position.

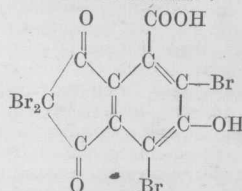
Oxidation of β -bromolaccain by means of hydrogen peroxide in warm glacial acetic acid yields two products, viz. (i) *hydroxy-tricarboxy-phenyl-glyoxylic acid*, and (ii) a compound $\text{C}_{12}\text{H}_6\text{O}_9\text{Br}_2$. The former, which is the chief product, crystallises in plates, m.p. 229°–230° (decomposition), and on treatment with concentrated sulphuric acid at 130°–140° yields a phenol-tetracarboxylic acid which melts at 212°–214° (decomposition). The second oxidation product of β -bromolaccain has m.p. 188°–190° (decomposition), and readily loses bromine; for it Dimroth tentatively proposes the formula—



For β -bromolaccain itself Dimroth and Goldschmidt suggest the structure—



and for this they find support in the fact that it resembles 2:6-dihydroxy- α -naphthoquinone in its colour reactions. Moreover, it behaves very similarly to β -bromocarmine in that it yields an indone derivative, α -bromolaccain (cf. α -bromocarmine), when its boiling solution in water is treated with bromine:—



This compound crystallises in colourless needles, and yields 2:6-dibromophenol-3:4:5-tricarboxylic acid, m.p. 257°–258°, and bromoform when treated with sodium hypobromite.

Dyeing properties.—The dyeing properties of lac dye are practically identical with those of cochineal, but the shades obtained are somewhat faster. Owing to the resinous and mineral impurities accompanying the colouring matter, it is not readily soluble in water, and before use it is therefore ground to a paste with the requisite quantity of tin spirit together with a little hydrochloric acid, and allowed to stand overnight. Cochineal and lac dye can be used together with advantage, or after the wool is dyed with lac it may be entered into a fresh bath with cochineal. Its employment at the present time is, however, extremely limited.

Fowler (Indian Textile Jour. 1917, 244) has made attempts to standardise various Indian colouring matters so that they may be marketed in uniform strengths. It would appear that 'Lac dye' is one of those with which he has been concerned. A. G. P.

LACMOID $C_{12}H_9NO_4$ (?)

Preparation.—(1) A mixture of resorcinol (20 parts), sodium nitrite (1 part), and water (1 part) is slowly heated to 110° , when a vigorous reaction sets in; the mass is then kept at 115° – 120° until it has become quite blue and no more ammonia is evolved. The product is dissolved in water and the lacmoid precipitated with hydrochloric acid (Traub and Hock, Ber. 1884, 17, 2615). (2) By fusing resorcinol (5 parts) with potassium nitrite (6 parts) (Benedict and Julius, Monatsh. 1884, 5, 534). (3) By the action of H_2O_2 on ammoniacal resorcinol solution (Wurster, Ber. 1887, 20, 2938).

To purify the substance, extract it almost completely with boiling water, cool, filter, and acidify the blue solution with hydrochloric acid. Filter off the precipitated lacmoid, wash with cold water and dry it below 100° . An alternative method is to warm gently powdered lacmoid (8 parts) with 20 p.c. alcohol (100 parts) for 15 minutes, cool and filter (Foerster, Zeitsch. angew. Chem. 1890, 3, 163).

Properties.—A glistening brown powder, easily soluble in methyl, ethyl, or amyl alcohol, acetone, acetic acid, or phenol, less easily in ether or water, insoluble in benzene or petroleum spirit. It dissolves in concentrated HCl or H_2SO_4 , yielding a blue solution. Heated below 200° it decomposes.

Lacmoid differs from the colouring matter of litmus in being soluble in strong alcohol. Its absorption spectrum resembles that of azolitmin (Hartley, Proc. Roy. Dublin Soc. 5, 159).

For the use of lacmoid as an indicator, v. Thomson (Chem. News, 1885, 52, 18, 29) and ACIDIMETRY AND ALKALIMETRY.

LACQUER (*Urushi*, *Ki-urushi*). A varnish usually obtained from the juice of *Rhus vernicifera* (DC.), a tree indigenous to China, whence in early times it was introduced into Japan (Bull. Imp. Inst. 1910, 8, 32; J. Soc. Chem. Ind. 1910, 639).

Burmese lacquer, or 'thitsi,' is obtained from the stems of *Melanorrhoea usitata* (Wall) as a grey viscous liquid of sp.gr. 1.0016 at 20° , which, on exposure to air, becomes first brown, and then, very rapidly, deep black. The drying of the lacquer is not accelerated by siccatives, and is retarded by dry heat, the presence of moisture being essential. The constituent of the lacquer soluble in alcohol is not identical

with the urushinic acid (urushiol) of Japan lacquer. It is known as *thitsiol* $C_{23}H_{36}O_2$, and is a homologue of *isohydrourushiol*. The ether extract consists of a gummy substance soluble in water, and a nitrogenous, coagulable substance which acts as an oxygen carrier in the drying of the lacquer, but loses its activity when heated above 60° (Rosenthal, Farbenzeit., 1914, 19, 1573; Majima, Ber. 1922, 55, 191).

Chinese lacquer. The tree is abundant in Central China, growing wild or under cultivation at altitudes of 3000 to 7500 feet. It is tapped in June or early July; shallow incisions are made in the bark of the stem and the greyish-white, milky juice collected in shells, bamboos, &c., and covered with oiled paper to prevent oxidation. The tapping is repeated seven times at intervals of 7 days, and the tree is then left for 5–7 years to recover. Much of the varnish is sent to Japan. The lacquer is frequently adulterated with tung oil.

Japanese lacquer. The lacquer tree grows abundantly all over Japan, and is cultivated largely in the district north of Tokyo. Tapping takes place when the tree is 10 years old and is continued from June to October, each tree yielding from 27 to 54 grams of lacquer. Usually the tree is left to recover, but sometimes it is cut down. In the latter case, a further yield of lacquer is obtained from the branches by steeping them in water for 10–20 days, and then making incisions and heating the water to cause the sap to exude. The varnish thus obtained, called *sesshime-urushi*, is harder and of poorer quality, and is used only for groundwork and for cheap articles. The best quality is obtained from between the inner and outer bark of trees from 14 to 15 years old. It is called *ki-urushi* (Pudor, Zeitsch. öffentl. Chem. 1910, 16, 315). A very inferior quality, known as *Moku-yshi*, is used mixed with the better kinds in varying proportions. Both Chinese and Japanese lacquer contain urushiol (*q.v.*).

Yunan lacquer is derived from *R. succedanea* (L. fil.), Formosan lacquer from *Semecarpus vernicifera*, and ivy lacquer from *R. toxicodendron*. These contain *laccol* $C_{23}H_{36}O_2$, a homologue of urushiol. Siam lacquer is probably a mixture of Yunan and Burmese lacquers. Korean lacquer is probably identical with Japanese lacquer (Riko Majima, J. Tokyo Chem. Soc. 1919, 40, 91).

The raw varnish is packed in wooden tubs and covered with oiled paper to prevent oxidation. It is prepared for use by various processes, the quality and value of the varnish and of the lacquered ware produced depending upon the time and care spent upon the purification.

The juice is strained from particles of bark, &c., and is allowed to stand in wooden vessels until it separates into various layers, when the lighter and finer qualities are decanted from the heavier and inferior varnish. The product is finally filtered through hempen or cotton cloth and exposed in shallow wooden pans to the heat of the sun or to artificial warmth. It thus becomes syrupy and of a dark brown colour, the change being due principally to loss of water. It is thinned with camphor or oil of turpentine or other suitable solvent.

Coloured lacquers are prepared from *ki-urushi* during the exposure to the sun (*v.s.*) by

mixing in appropriate pigments, those most commonly employed being as follows (Miyama, J. Coll. Engineering, Imp. Univ. Tokyo, 1908, 4, 201; J. Soc. Chem. Ind. 1909, 318):—

White.—Barium sulphate; bismuth oxy-chloride.

Red.—Cinnabar; rouge.

Blue.—Prussian blue; ultramarine.

Yellow.—Cadmium sulphide; lead chromate; orpiment.

Green.—Chromic oxide (or by the addition of indigo from *Polygonum tinctorum* (Ait.) to the yellow lacquer).

Black.—Lampblack; iron powder or compounds of iron.

Brown.—Mixture of red and black.

The so-called 'pear-ground' lacquer, used with gold-dust, is prepared with gamboge.

Use of the lacquer.—The prepared surface of the article to be lacquered first receives several coats of the poorer quality mixed with a special clay called *ching-chu*, or in some cases with an inferior clay or with pottery dust. After each coat, the article is kept for several days in a moist atmosphere until the lacquer has set, and it is then rubbed down with pumice to a dull, smooth surface before another coat is given. The final coat is of the better quality lacquer, and the article may be further decorated with a pattern in coloured lacquer. Any joint in the wood is scraped down below the general level of the surface and then filled up with alternate layers of silk and lacquer.

Lacquering is applied to small articles, e.g. card-cases, vases, images, &c., either for ornamental purposes or for practical use. Hollow articles of lacquer are made by building up a layer of lacquer and silk on a clay model which is afterwards washed out with water through a hole left for that purpose. (For full details of the manufacture of lacquered ware, see Nightingale, J. Indust. and Engineering Chem. 1911, 3, 59; also Workshop Receipts, 3rd series, 306.)

The drying of lacquer at ordinary temperatures is caused by an enzyme (an oxydase) called *laccase*, contained in the sap (Tschirch and Stevens, Arch. Pharm. 1905, 243, 504; J. Soc. Chem. Ind. 1906, 81). During the drying it absorbs 5.75 p.c. of oxygen.

It may also be dried by heat, this process being specially applicable to lacquered articles of glass, porcelain, and papier-mache (Miyama, J. Soc. Chem. Ind. 1909, 318). At 100° it dries in 4–5 hours, at 150° in 30 minutes, and at 180° in 10 minutes. The drying by heat is attended by absorption of oxygen and some decomposition, giving a dark-coloured coating which is harder and more durable than the cold-dried lacquer. Coloured lacquers cannot usually be dried by heat because of the darkening of the lacquer. For a similar reason it is not the practice to use 'driers' in lacquers.

Composition of lacquer.—The main constituent of most lacquers to which their peculiar properties are due, is an unsaturated polyhydric phenol, *urushiol*, having the formula $C_{26}H_{30}O_2$ (Majima, Ber. 1909, 42, 3664; 1912, 45, 2727).

Miyama gives the following analyses of typical specimens of the juice (J. Coll. Eng. Tokyo, 1908, 4, 89; J. Soc. Chem. Ind. 1908, 456):—

| | Japanese | Chinese | Indian |
|--------------------|------------------|------------|------------|
| Moisture | 17.81–26.72 p.c. | — | — |
| Urushiol | 64.14–77.63 „ | 36.88 p.c. | 26.39 p.c. |
| Gum | 2.62–7.57 „ | 23.5 „ | 37.78 „ |
| Nitrogenous matter | 1.78–2.47 „ | — | — |

Sun-dried Japanese lacquer contains 94.5 p.c. urushiol.

Urushiol forms a compound with barium hydroxide, and is estimated by titrating with a solution of that base, using phenolphthalein as indicator.

Urushiol may be obtained from lacquer by repeated extraction with alcohol, and is purified by treatment with petroleum spirit. It is a light brown, viscous fluid, sp.gr. 0.9687 at 21.5°/4°, and is readily soluble in most organic solvents. It forms a dimethyl ether and an easily hydrolysable acetyl derivative. On dry distillation it yields various hydrocarbons and polyhydric phenols, but no simple alicyclic hydrocarbon or ordinary terpene (Majima and Cho, Ber. 1907, 40, 4390; Majima, *ibid.* 1909, 42, 1418, 3664; 1912, 45, 2727; Majima and Nakamura, *ibid.* 1913, 46, 4080; *ibid.* 1915, 48, 1597; Majima and Tahara, *ibid.* 1915, 48, 1606). Tschirch and Stevens (*l.c.*) found in the lac an irritant poison, named by them *verniciferol*. This substance may be identical with the compound $C_{15}H_{22} \cdot C_6H_3(OH)_2$ found in lacquer, which, according to Toyama and Kayaba (Chem. Soc. Abst. 1918, 114, ii, 143), is poisonous. Lacquer also contains a hydrated and a methylated urushiol which are toxic, and a dimethylated and a hydro-dimethylated urushiol which are non-toxic.

Lacquer poisoning may be produced in susceptible individuals by passing near a lacquer tree or through a store containing lacquered articles.

LAC RESIN v. RESINS.

LACTANIN v. SYNTHETIC DRUGS.

LACTARIC ACID $C_4H_4O_6$ is obtained by extracting the fungus *Agaricus integer* with alcohol (Chuit, Bull. Soc. chim. [iii.] 2, 153); m.p. 69.5°–70°.

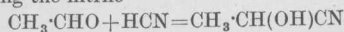
LACTASE is the enzyme decomposing lactose (milk sugar) to dextrose and galactose. The distribution in animals is limited, being confined entirely to the intestine and generally of young animals only. Lactase has not been found in the mammary gland or milk of animals; this fact is regarded as opposed to the theory that it plays any part in the synthesis of lactose in these tissues (Bradley, J. Biol. Chem. 1913, 13, 431). Plimmer (J. physiol. 1906, 35, 20) found lactase in the cat and the pig during the whole of their lives, but only in the young guinea pig. The gastro-intestinal sac of snails contains a lactase (Bierry, Compt. rend. 1909, 148, 949). It is present in a few torula (*S. fragilis*, *S. kayser*, *S. adametz*, &c.) and in kephir. Lactose is also hydrolysed by the emulsin derived from almonds, which accordingly contains a lactase. There is apparently a difference between kephir and almond lactase, since the hydrolytic activity of the former is restricted mainly by galactose, that of the latter mainly by glucose (Armstrong, Proc. Roy. Soc. 1908, B, 80, 321). According to Stephenson (Bio-Chem. J. 1912, 6, 250), the lactase in the intestines of animals is inhibited only by glucose,

and is therefore similar to almond lactase. Lactase also hydrolyses β -methylgalactoside and melibiose. The optimum activity is about 37° . Lactase is precipitated by alcohol, and behaves very similarly to emulsin; its rate of action is governed by the same laws. It has not been fully investigated. E. F. A.

LACTIC ACID or α -HYDROXYPROPIONIC ACID (Ger. *Milchsäure*), $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, was first obtained by Scheele in 1780 from sour milk. Its exact constitution was, however, first ascertained by Liebig and Mitscherlich (Annalen, 7, 47) and by Gay-Lussac and Pelouze (*ibid.* 7, 40). It is widely distributed in nature, occurring in the lesser centaury (*Erythraea Centaurium* [Pers.]) (Habermann, Chem. Zeit. 30, 40); in the sap of the vine; and in most fermented liquids of vegetable origin, especially in sour milk; it is not, however, present in fresh milk. It is found in beet molasses, and owes its origin to the boiling of the sucrose solution with lime in the process of defecation (Schöne and Tollens, J. Soc. Chem. Ind. 1901, 54; Weisberg, *ibid.* 375; Beythien, Parcus and Tollens, Annalen, 255, 228). It has also been found in small quantities in saliva; in the brain and under certain conditions in the gastric juice; in the blood and in urine. The acid obtained by Braconnot, and termed *nanceic acid*, as well as the *thebolactic acid* obtained from opium, have been proved to be identical with common lactic acid. On the other hand, the acid obtained by Berzelius from flesh, and further investigated by Liebig, differs from the ordinary lactic acid in certain of its properties, and is therefore distinguished as *paralactic acid*. This will be described later on.

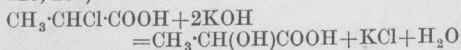
Lactic acid is formed in the fermentation of various sugars, of mannitol, and of dextrin (*v. FERMENTATION*), and also by the action of caustic alkalis on the sugars. It has also been obtained synthetically in a number of ways, the three most important of which are the following:—

(1) Aldehyde unites with hydrogen cyanide, forming the nitrile

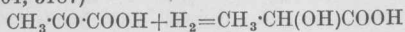


and this on treatment with acids is converted into lactic acid (Wislicenus, Annalen, 128, 13, 22).

(2) By the action of alkalis on α -chloropropionic acid (Friedel and Machuca, Annalen, 120, 285)



(3) By the reduction of pyruvic acid with sodium amalgam, hydriodic acid (Wislicenus, Annalen, 126, 227), zinc (Debus, *ibid.* 127, 332), or electrolytically (Tafel and Friedrichs, Ber. 1904, 3187)



These syntheses clearly show that the acid is α -hydroxypropionic acid.

In order to distinguish lactic acid from the allied acids it is frequently called *ethylidene-lactic* or *fermentation lactic acid*.

Preparation.—Lactic acid is usually prepared by the fermentation of sugar. McLauchan (J. Soc. Chem. Ind. 1909, 734) recommends the following method: 400 grams of commercial glucose are dissolved in 1200 c.c. of hot water, and to this is added 170 grams of whitening or well-powdered calcium carbonate and 20 grams

of malt, previously boiled for a few minutes with 100 c.c. of water. The solution is kept simmering for 30 minutes, then cooled to 60° – 70° , and after stirring is poured into a narrow-necked bottle, of 2½ litres capacity. The calcium carbonate is rinsed out with water and the solution made up to 1800 c.c. The bottle is placed in an air-bath at 45° , a small quantity of sour milk or casein added to start fermentation, and a wad of cotton used to stopper the bottle. The bottle is shaken every few hours for 6 days and when the unfermented sugar is less than 0.4 p.c. the solution is filtered. The final filtrate after concentration should be one litre of 25 p.c. acid. Kassner (Chem. Zentr. 1897, ii. 20) dissolves 300 grams of cane sugar and 15 grams of tartaric acid in 1700 grams of boiling water and allows the solution to stand for several days, the temperature being maintained at 60° ; 100 grams of old cheese and a little more than the calculated quantity of finely powdered chalk are then added and fermentation is allowed to proceed with daily stirring for about 3 weeks. Brensch (Annalen, 61, 177) proceeds in a similar manner, but during fermentation keeps the temperature at 30° – 35° . Lautemann (*ibid.* 113, 142) replaces the chalk in the original mixture by 2 kilos. zinc white. After about 10 days a magma of zinc lactate together with some mannitol is formed, which may be recrystallised from water. The purified salt obtained by any of these methods is dissolved in boiling water, and precipitated with H_2S , the filtrate evaporated to a syrup, cooled, and separated from mannitol and any undecomposed salt by extraction with ether. The syrup which remains after evaporation of the ether is then warmed on the water-bath.

A large number of micro-organisms are capable of causing lactic fermentation of sugar; these are classified according to their morphological properties, their growth on media, and chiefly their fermentative power (*cf.* Lore and Brooke, U.S. Dept. Agric. Bull. 154, 1). *Bac. acidilacti*, types i. and ii., and *Bac. lactis aerogenes* are those most commonly occurring, and of these the first named is by far the most plentiful. The solution must be kept neutral, and access of air must be allowed, as well as the necessary nitrogenous food. Its form in a highly nitrogenous saccharine solution, is a double truncated cone, and it has the tendency of all lactic bacteria to link itself together in pairs or short chains (Clafin, J. Soc. Chem. Ind. 1897, 516). Where potato or other starch saccharified by malt is used for the mash, *Bac. Delbreickii*, which ferments maltose, is used as the fermenting organism. (For further particulars of the micro-organisms, *v.* Andreasch, J. Soc. Chem. Ind. 1897, 53; Leichmann and Bazarewski, *ibid.* 1900, 698; Harden, Chem. Soc. Trans. 1901, 624; J. Soc. Chem. Ind. 1901, 921; Hashimoto, *ibid.* 1902, 506; Beijerinck, *ibid.* 1903, 106; Henneberg, *ibid.* 1904, 332; Buchner and Meisenheimer, Annalen, 349, 125; Wehmer, Chem. Zeit. 30, 1033; Heinemann, J. Biol. Chem. 1907, 2, 603.) Lactolase is an enzyme which causes the formation of lactic acid in plant cells (Stoklasa, Chem. Zentr. 1905, i. 265; 1907, i. 828). Malic, succinic, tartaric, and citric acids are all readily converted into lactic acid by certain moulds such as *Penicillium*

glaucum, *Aspergillus niger*, and *Botrytis cinerea* (Bied. Zentr. 1908, 37, 215).

For the preparation of the acid from sugar by the action of caustic alkalis, Kiliani (Ber. 1882, 699) recommends the following method: 500 grams cane sugar are mixed with 250 c.c. water, and 10 c.c. of the sulphuric acid employed later on, and warmed in a flask of 2 litres capacity to 50° for 2 hours. To the well-cooled solution 400 c.c. of caustic soda solution (1 part of caustic to 1 part water) are gradually added, the mixture being constantly cooled. The exact quantity of sulphuric acid necessary is then allowed to flow in; the acid is prepared by adding 3 parts H_2SO_4 to 4 parts water, and previously directly compared with the caustic soda solution by titration. A crystal of Glauber's salt is added to facilitate crystallisation, the whole being cooled and well shaken, and allowed to stand 24 hours. The mass is then extracted with 93 p.c. alcohol, filtered on the pump, and half the filtrate neutralised with $ZnCO_3$ on the water-bath, then mixed with the other portion, and the whole allowed to stand 36 hours. The separated zinc salt is filtered off, well pressed, recrystallised from water, and converted into the acid as before.

Just as lactic acid may be obtained by boiling hexoses and hexobioses with caustic alkalis, so it may be obtained from pentoses such as arabinose and xylose (Katsuyama, Ber. 1902, 669; Araki, Zeitsch. physiol. Chem. 19, 463) and from cane sugar and raffinose (Beythien, Pareus, and Tollens, Annalen, 255, 222). Meisenheimer (Ber. 1908, 1009) states that lactic acid is formed in small quantities when glucose, fructose, or galactose are allowed to stand in dilute sodium hydroxide for many months in the dark.

Manufacture.—There are three stages in the manufacture of lactic acid, the preparation of the saccharine solution, the fermentation process, and the conversion of the fermented liquid into commercial lactic acid. The saccharine solution, which should have a sp.gr. of about 1.075, i.e. a saccharine content of $7\frac{1}{2}$ –11 p.c., and which should be faintly alkaline or neutral but not acid, is sterilised either by boiling for an hour, or by blowing live steam into the solution for one hour at 95°. It is advantageous to have about 10–15 p.c. of the saccharine matter in the form of cane sugar and the remainder as glucose. After sterilisation, the liquid is conveyed to the fermentation tank, cooled to between 45° and 55°, and impregnated. Where continuous manufacture of lactic acid is carried on, impregnation takes place from a previously fermented liquor where a lively fermentation is in progress; for an original fermentation, milk, which has been kept until it is slightly sour, is used. For efficient working, the lactic acid ferment must be well nourished with nitrogenous matter, the most convenient sources being vegetable matter, e.g. as extracted from bran by the action of boiling water and dilute acid. If mineral food is employed, ammonium salts should be in excess of nitrates. Pollak claims that the amount of lactic acid is increased by the repeated addition of ammonium salts in preparing the mash for fermentation (Eng. Pat. 13193, 1913). As the fermentation proceeds, the temperature is allowed to decrease and

the solution is neutralised with milk of lime or chalk in suspension, as the lactic acid bacteria are only healthy in solutions containing between 0.02 and 0.5 p.c. of acid; the fermentation is best completed in from 3 to 6 days. The fermented liquid, which contains calcium lactate with a layer of dead bacteria floating on it, is evaporated and filtered. For a commercial acid, decomposition of the syrupy solution of calcium lactate with sulphuric acid gives an acid of sufficient purity, which may be concentrated *in vacuo*. Iron may be removed by stirring the cooled liquor from the vacuum pans and leaving it to stand for some days, or the addition of a little potassium ferrocyanide has been used. It is important that the lactic acid used by the dyer should be iron-free. The concentrated acid for commercial purposes is about 80 p.c. If a pure acid is required, the solution of calcium lactate is set to crystallise; the solid crystals are pressed to remove mother liquor, and may be recrystallised if required (Clafin, J. Soc. Chem. Ind. 1897, 516; Dreher, *ibid.* 1898, 1070; McLauchan, *ibid.* 1907, 734; cf. Just, U.S. Pat. 868444; J. Soc. Chem. Ind. 1907, 1211; D. R. P. 203306; Chem. Zentr. 1908, ii. 1843). Various methods have been patented for the manufacture of lactic acid, differing mainly as to the source of the saccharine solution. Mislin and Lewin (Eng. Pat. 10436; Fr. Pat. 355520; J. Soc. Chem. Ind. 1905, 1248) place alternate layers of malt and rye in a suitable apparatus until saccharification of the starch is complete. The must is removed by pressure and fermented as in above method (cf. Brookes, Eng. Pat. 5780; J. Soc. Chem. Ind. 1885, 116; Avery, Pharm. J. Aug. 5, 1882). Jean and Bougard obtain lactic acid from powdered grain or oil-free cake (Fr. Pats. 315325, 315326, 321374; J. Soc. Chem. Ind. 1903, 225), and Clafin uses as the starting material a wort containing about 10 p.c. of fermentable material (U.S. Pat. 861163; J. Soc. Chem. Ind. 1907, 985). Boullanger acts on starch or sugar containing substances with a mould such as *Rumex acetosella*, and then proceeds as above (D. R. P. 118083; Chem. Zentr. 1901, i. 650).

Boehringer states that calcium lactate and sulphuric acid form a paste which is very difficult to work up. The method recommended is to take 300 litres of calcium lactate solution (10°Bé.), obtained from fermentation process, and evaporated to 50 litres; 50 kilos. of a 50 p.c. solution of lactic acid is added and then the calcium lactate is decomposed by sulphuric acid. The solution of lactic acid thus obtained is 50 p.c. (Eng. Pat. 7094; Fr. Pat. 401395; D. R. P. 221112; J. Soc. Chem. Ind. 1909, 674).

Patents have been granted for processes to recover lactic acid from brewers' and distillers' slop and from the waste water of jam factories. One such method consists in neutralising the liquid with milk of lime, partly evaporating and causing the albuminoid substances to coagulate, filtering and allowing the calcium lactate to separate out from the filtrate (Beckers, D. R. P. 104281; Chem. Zentr. 1899, ii. 926; v. also Beckers, D. R. P. 113383; Chem. Zentr. 1900, ii. 702; Roehr, U.S. Pat. 823366; J. Soc. Chem. Ind. 1906, 901).

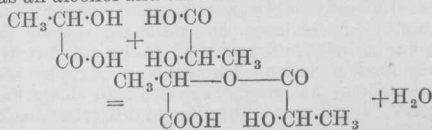
Several processes have been patented for

the purification of the acid thus obtained. Waite (Eng. Pat. 13403; D. R. P. 140319; J. Soc. Chem. Ind. 1901, 931) washes the crude acid with amyl alcohol and distils off the solvent from the alcoholic solution of the acid, or washes this solution with water and concentrates the aqueous solution. Blumenthal and Chain (D. R. P. 169992; J. Soc. Chem. Ind. 1907, 279) mix the crude acid with aniline (150 parts 60 p.c. acid with 93 of aniline) and cool to -5° ; the precipitate is recrystallised from a small quantity of water, decomposed with steam, and the acid concentrated *in vacuo*. Noerdlinger (Eng. Pat. 26415; Fr. Pat. 364468; D. R. P. 221786; U.S. Pat. 924494; J. Soc. Chem. Ind. 1908, 245) distils the crude acid in a current of inert gas. The water is first expelled and then pure lactic acid passes over. Laudau (Eng. Pat. 7998, 1915) boils the commercial acid with charcoal while a current of inert gas is passed through. It is concentrated *in vacuo* to 90–95 p.c., and the dextrins present precipitated by alcohol. After standing 24 hours, the liquid is filtered and the alcohol distilled off. Blaise recommends boiling the technical acid for 12 hours with an equal weight of water, and concentrating quickly *in vacuo* at a temperature not above 60° (Bull. Soc. chim. [4] 15, 666). In another process the mixture of calcium sulphate and lactic acid is dried at 130° when lactide and lactic anhydride are formed. After removal of the soluble impurities, pure lactic acid is obtained by hydrolysis in steam (U.S. Pat. 1240766, 1917). Erdmann (D. R. P. 217846; Chem. Zentr. 1910, i. 701) obtains pure lactic acid from copper lactate and water, heated at 150° – 250° .

Properties.—The acid thus obtained forms a syrup of sp. gr. 1.21–1.24, and is soluble in all proportions in water and alcohol, less readily in ether. It is hygroscopic, colourless, and inodorous, but has a very sharp acid taste. The syrup is, however, not the pure acid, but a mixture of the latter with small quantities of water and the anhydride. The pure acid cannot be obtained by evaporation of the aqueous solution, as formation of the anhydride commences before all the water is driven off. Krafft and Dyès (Ber. 1895, 2589; Chem. Zentr. 1896, i. 742) have obtained lactic acid in the form of very hygroscopic white crystals, m.p. 18° , by the distillation of the commercial acid under reduced pressure. Lactic acid is slightly volatile at the ordinary temperatures, lactide is less volatile, and lactic anhydride practically non-volatile (Müller, Bull. Soc. chim. 1896, 15, 1206); lactic acid is volatile in steam, but not sufficiently volatile to be quantitatively separated from aqueous solutions by this means (Utz, Chem. Zeit. 1905, 29, 363). Lactic acid contains an asymmetric carbon atom, and hence can exist in two optically active modifications (*v. infra*). The fermentation lactic acid is optically inactive, but the acid obtained from the works is sometimes optically active. According to McKenzie (Chem. Soc. Trans. 1905, 1377), this is due to the fact that the action of the pure culture on sugar is to produce equal amounts of *d*- and *l*-isomerides. On converting these into the calcium salts and recrystallising, the crop of crystals which separate is mostly calcium *r*-salt, the active salt remaining in solution. If crystallisation takes place from a concentrated

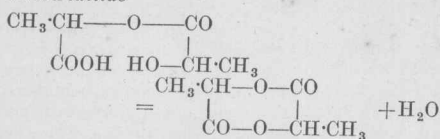
solution and the precipitate is not washed free from mother liquor, the acid obtained will be optically active. This would also be the case if the bacterial action had been such as to produce an excess of one isomeride (*cf.* Pottevin, J. Soc. Chem. Ind. 1899, 700). Wehmer recommends the use of *Oidium lactis* and two mycoderma to decompose lactic acid in liquids where its presence is not desirable (Chem. Zentr. 1903, i. 891). An aqueous solution of lactic acid is stated to decompose in sunlight into acetaldehyde, pyruvic acid, carbon dioxide, and water (Ganassini, Boll. Chim. Farm. 48, 785; Giorn. Farm. Chim. 61, 540), but this is denied by Neuberg (Biochem. Zeitsch. 39, 158). Oxidation of lactic acid with hydrogen peroxide yields pyruvic acid (Fenton and Jones, Chem. Soc. Trans. 1900, 71); with bromine water, pyruvic acid (Ciusa and Piergallini, Atti R. Accad. Lincei, 1914, 821); oxidation by bacteria yields pyruvic acid and ketonic substances (Mazé, Compt. rend. 1918, 81, 1150); with potassium permanganate, pyruvic acid (Aristoff, J. Russ. Phys. Chem. Soc. 1884, 2, 249), acetaldehyde and malic acid (Schoorl, Zeitsch. angew. Chem. 1900, 15, 367); with dilute sulphuric acid at 130° , or by heating alone at 440° – 460° , acetaldehyde and formic acid (Nef, Annalen, 335, 296); with chromic acid, acetic acid, and carbon dioxide (Dossios, Zeitsch. Chem. 1866, 451; Chapman and Smith, *ibid.* 1867, 477). Photochemical oxidation in the presence of uranyl or ferric salts yields acetaldehyde and carbon dioxide (Bolin, Zeitsch. physikal. Chem. 87, 490). Oxidation of the ammonium salt with hydrogen peroxide yields acetaldehyde, acetic acid, and carbon dioxide (Dakin, J. Biol. Chem. 4, 91). Reduction with hydriodic acid yields propionic acid. Electrolysis of the sodium salt results in the production of acetaldehyde and carbon dioxide (Walker, Chem. Soc. Trans. 1896, 1278; Ber. 1894, 467; Kolbe, Annalen, 113, 244). Phosphorus pentachloride converts lactic acid into α -chloropropionic acid (Walden, Ber. 1895, 1293; Le Bel, *ibid.* 1895, 1923); bleaching powder converts it into chloroform and formic acid (Eberhard, Chem. Soc. Abstr. 1901, i. 357). Lactic acid reduces the nitrates of the heavy metals, *e.g.* bismuth, silver, mercury, cadmium, &c.; cobalt and nickel yield strongly magnetic powders (Vanino and Hauser, Zeitsch. anal. Chem. 1900, 29, 506). When the silver salt is treated with alkyl iodides, the hydrogen of the hydroxyl and carboxyl groups are both attacked (Purdie and Lander, Chem. Soc. Trans. 1898, 296, 300). For thermo-chemical data, *v.* Berthelot and Delépine, Compt. rend. 1899, 129, 920; dielectric constant, electrical conductivity, Drude, Zeitsch. physikal. Chem. 23, 349; Walden, *ibid.* 46, 103; 54, 129.

Lactic anhydride, which has been mentioned above, is formed by the elimination of a molecule of water from two molecules of the acid in the following manner, the one molecule acting as an alcohol and the other as an acid:—



This compound, *lactic anhydride* or *lactolactic acid*, is at the same time an alcohol, an acid, and an ethereal salt. It is a light yellow amorphous mass, easily soluble in alcohol and ether, insoluble in water, and is decomposed by alkalis, forming salts of lactic acid.

On further heating, another molecule of water is driven off, forming a second anhydride called *lactide*



This substance, which is a double ethereal salt, is very slightly soluble in water, and forms white needles melting at 124.5° (Bischoff and Walden, *Annalen*, 279, 71; Nef, *ibid.* 335, 296; Raper, *J. Physiol.* 32, 216).

Detection and estimation.—On heating lactic acid with potassium chromate and sulphuric acid it is decomposed into formic acid and acetaldehyde. The mixture is distilled and vapours collected in Nessler's solution, giving a yellow precipitate or opalescence (Lassar-Cohn, *Annalen*, 284, 226; Windisch, *J. Soc. Chem. Ind.* 1887, 262). Thoms (Apoth. Zeit. 1907, 22, 206) recommends treating a few c.c. of the liquid with 3 or 4 drops of 30 p.c. solution of chromic acid sufficient to impart a bright yellow tint. In the presence of free lactic acid a reddish-brown coloration is produced on warming the solution on the water-bath for 10 minutes. Denigès (Ann. Chim. 18, [viii.] 191) treats the solution with bromine water, and then after the addition of acetic acid a red-violet colour is produced on adding sodium nitroprusside. Lactic acid gives a red coloration with alcoholic guaiacol solution and may thus be distinguished from acetic, malic, benzoic and salicylic acids (Hartwig and Saar, *Chem. Ztg.* 1921, 45, 322). Other methods, *v. Denigès*, *Bull. Soc. chim.* 1909, 5, 647; Croner and Cronheim, *J. Soc. Chem. Ind.* 1905, 1258; Herzog, *Annalen*, 1907, 351, 263. The following process has been recommended by Jean (Ann. Chim. Anal. Appl. 1900, 5, 285) for estimating the commercial acid. (i.) Total acidity is determined as H_2SO_4 ; (ii.) free acids by evaporating three times to dryness on the water-bath; (iii.) lactic acid by evaporating 10 c.c. to dryness several times, and dissolving the residue in water. The solution is heated to boiling, neutralised with barium carbonate, and then filtered and evaporated to dryness in a platinum dish. The residue is incinerated to carbonate, extracted with boiling water, collected on a filter, well washed, and dissolved in a known volume of decinormal hydrochloric acid. The solution is heated to remove the carbon dioxide, titrated with decinormal alkali, and the volume of N/10-hydrochloric acid neutralised by the carbonate formed by subtraction. This number of c.c. $\times 0.009$ gives weight of lactic acid originally present. To estimate the amount of lactic acid and lactic anhydride present in a sample of lactic acid, the following process is used: (i.) dilute sample with water and titrate with normal sodium hydroxide, using phenolphthalein as an indicator; (ii.) add a known excess of sodium hydroxide and titrate back

with acid; (i.) gives actual amount of acid and (ii.) of anhydride (Philip, *Collegium*, 1906, 88; Kunz, *Chem. Zentr.* 1901, i. 791; Bellet, *Bull. Soc. chim.* 1913, 13, 565). Other methods, *v. Ulzer and Seidel*, *Monatsh.* 18, 138; Paessler, *Collegium*, 1907, 388, 396; Phelps and Palmer, *J. Amer. Chem. Soc.* 1917, 136. Estimation in wines, *v. Kunz*, *Chem. Soc. Abstr.* 1901, ii. 700; 1903, ii. 701; Sostegni and Prandi, *Chem. Zentr.* 1903, ii. 469; Müller, *Bull. Soc. chim.* 1896, 15, [iii.] 1203; Parthiel, *Chem. Soc. Abstr.* 1903, ii. 189; Arch. Pharm. 241, 401; Paris, *Chem. Zentr.* 1908, i. 773; Trummer, *Chem. Zentr.* 1908, ii. 101; Heiduschka and Quincke, *Arch. Pharm.* 245, 458. In milk, *v. Thörner*, *Chem. Zeit.* 16, 1469, 1519. In urine, *v. Proc. Physiol. Soc.* 1909, v.-vii.; *J. Physiol.* 39; *Biochem. Zeitsch.* 68, 175. In gastric juice, *v. De Jong*, *Chem. Zentr.* 1896, ii. 806. In the presence of pyruvic acid, Czapski, *Biochem. Zeitsch.* 71, 167. For the extraction of lactic acid from the tissues, amyl alcohol is recommended as the most suitable solvent, Ohlsson, *Chem. Soc. Abstr.* 1916, ii. 542.

Technical uses.—Lactic acid is used by the woollen dyer as an assistant in mordanting with potassium dichromate and its advantages over tartaric and oxalic acids are its greater reducing power, the greater solubility of itself and its salts, and the fact that it is less corrosive. It gives the wool a very fine, soft 'handle' and a beautiful lustre. *Lactolin*, which consists of equal parts of lactic acid and potassium lactate, is stated to be superior to lactic acid, which is in itself superior to tartar (Claffin, *l.c.*; Norton and Tuttle, *J. Soc. Chem. Ind.* 1891, 263; Hoffmann, *ibid.* 1896, 196, 540; Dreher, *ibid.* 1896, 448; 1898, 1070; 1899, 491; Kiehmeyer, *ibid.* 1899, 368; Kapff, *ibid.* 1900, 659; Fuchs, *Chem. Zentr.* 1897, i. 1183; Archer, *J. Soc. Chem. Ind.* 1897, 140; Düring, *Bull. Soc. Ind. Mulhouse*, 1902, [v.] 3; Paessler and Appellius, *Collegium*, 1903, 152, 153, 164, 169). Aniline lactate is used in producing aniline black on cotton (Goldey, *Bull. Soc. Ind. Mulhouse*, Jan. 9, 1900; Schener and Schoellkopf, *ibid.* 1901, 102; Düring, *Chem. Zentr.* 1905, i. 1515; D. R. P. 96600; *J. Soc. Chem. Ind.* 1899, 1119). The double lactate of calcium and antimony is used in mordanting cotton, and as a substitute for glycerin and tartaric acid in printing fabrics (Dreher, *J. Soc. Chem. Ind.* 1898, 919, 921). For methods of obtaining double lactates of antimony and calcium or of antimony and alkalis or alkaline earths, *v. Moritz*, *Zeitsch. angew. Chem.* 17, 1143; Akt. Ges. Reavler *Chem. Fab. R. Mayer*, D. R. P. 136135; *Chem. Zentr.* 1902, ii. 1286; Ch. Fab. von Heyden, D. R. P. 184202; *Chem. Soc. Abstr.* 1907, i. 888; Boehringer, D. R. P. 98939; *Chem. Zentr.* 1898, ii. 1231; Ch. Werke Schuster and Wilhelmj, D. R. PP. 216158, 217806; *Chem. Zentr.* 1909, ii. 1908; 1910, i. 701.

A solution containing the lactates of aluminium, calcium, and tin has been used instead of the above (Oswald, *Bull. Soc. Ind. Mulhouse*, 1900, 343), whilst Boehringer (D. R. P. 91230; *Chem. Zentr.* 1897, i. 1189) employs zinc lactate for the same purpose. *Lactolin* and sulphuric acid are used in hat dyeing (Düring, *J. Soc. Chem. Ind.* 1900, 660; 1901, 470) and lactic acid, free from traces of iron, is used as a discharge for

Turkey red (Düring, *ibid.* 1900, 1013). It has also been used as a solvent for dyestuffs insoluble in water (Dreher, *ibid.* 1897, 1014; 1898, 919, 921).

Lactic acid is used in tanning for colouring, bating, and plumping. In preparing the skins it completely removes the lime, ensures a fine even grain, and does not dissolve the hide substance. It is easier to control than the bran drench, which is also used for this purpose, and which owes its efficiency to the lactic acid produced during the fermentation of the bran (Clafin, J. Soc. Chem. Ind. 1901, 210, 596, 730, 913; Paessler and Appellius, *ibid.* 1902, 1461, 57; 1903, 1201). It is also used in the preparation of yeast (Büchler, *ibid.* 1901, 376) and in the distillery, e.g. to check the bacterial development in the 'Hefengut' mash (Moritz, *ibid.* 1899, 778).

Lactic acid is also used for medicinal purposes in cases of laryngeal tuberculosis and of infantile diarrhoea. It dissolves false membrane and a solution of 1 part of acid in 6 parts of water is employed in the local treatment of diphtheria and croup. Local applications are used in stopping the growth of venereal warts and in treatment of tuberculous ulcers, lupus, and epithelioma. Calcium lactate is used in the treatment of rheumatism. For pharmaceutical purposes, the acid must be colourless and inodorous, and have a sp.gr. of at least 1.21, and should leave scarcely any residue on ignition. It should be unaffected by NH_3 and $(\text{NH}_4)_2\text{S}$, should give, at most, only a faint opalescence with BaCl_2 , AgNO_3 , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and should give no precipitate on boiling with Barreswil's (Fehling's) solution. For its influence in human dietary, v. J. Soc. Chem. Ind. 1920, 236.

Esters. The esters of lactic acid may be prepared by treating a salt of lactic acid with sulphuric acid or gaseous hydrogen chloride and the corresponding alcohol; or the anhydride (lactide) may be treated with alcohol in the presence of aluminium sulphate or titanic acid anhydride as catalyst, D. R. P. 278,487. The product is distilled *in vacuo*, whereby the pure ester is obtained. By treating the pure ester with steam, distilling off the alcohol and concentrating, the pure acid is obtained (Ch. Fab. Güstrow, Hillringhaus and Heilmann, D. R. P. 171835; Chem. Zentr. 1906, ii. 470).

Methyl ester. Colourless liquid, b.p. 144.8°; sp.gr. 1.0898 at 19° (Schreiner, Annalen, 197, 12).

Ethyl ester. Colourless liquid, b.p. 154.5°; sp.gr. 1.0308 at 19° (Schreiner, l.c.; Friedel and Wurz, Ann. Chim. [iii.] 63, 102; Brüggén, Annalen, 148, 227).

Ethylidene ester. Prepared by heating acetaldehyde and lactic acid at 120°–170° for some hours: colourless liquid, b.p. 150°–151.5° (Leipen. Monatsh. 9, 45).

Glyceryl mono- and di-lactates (v. Kalle & Co. D. R. P. 216917; Chem. Zentr. 1910, i. 214).

Salts. The salts of lactic acid are all soluble in water, many so readily that they are very difficult to obtain crystalline. They are obtained by direct neutralisation of the free acid, or by double decomposition from the calcium salt.

The K, Na salts are very hygroscopic, and only the latter has been obtained crystalline

(Wislicenus, Annalen, 125, 49; Engelhardt and Maddrell, *ibid.* 63, 88; Brüning, *ibid.* 104, 192).

Ammonium lactate is crystalline and very hygroscopic. On distilling it *in vacuo*, acid ammonium lactate, a syrup (b.p. 140° at 10 mm.) passes over (D. R. P. 247,240; J. pr. Chem. [2] 87, 258).

Calcium lactate $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Ca} \cdot 5\text{H}_2\text{O}$ is usually obtained direct from sugar in the preparations of lactic acid (v. *supra*). In small quantities it is sometimes prepared by neutralising lactic acid with chalk. It forms cauliflower-like aggregates of microscopic rhombic needles, which are soluble in 9.5 parts of cold, much more readily in hot water, and also soluble in alcohol. It loses its water of crystallisation at 100°, and at 250°–275° loses another molecule of water, forming *calcium dilactate* $(\text{CH}_3\text{CH})_2\text{O}(\text{CO}_2)_2\text{Ca}$. The product is a vesicular mass, from which alcohol extracts some unaltered calcium lactate, and leaves the new compound behind as a very slightly soluble substance (Friedel and Würtz Ann. Chim. Phys. [iii.] 63, 114).

Barium lactate $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Ba} \cdot 4\text{H}_2\text{O}$ crystallises with great difficulty, forming cauliflower-like aggregates. It does not lose all its water of crystallisation at 100° (Meyer, Ber. 1886, 2454).

Magnesium lactate $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Mg} \cdot 3\text{H}_2\text{O}$ is prepared by dissolving lactic acid syrup in 10 times its bulk of water, and neutralising with basic magnesium carbonate. The solution is evaporated until a skin forms, and then allowed to crystallise. It forms small light prismatic crystals, which frequently unite to form crusts. It dissolves in 28 parts of cold and 6 parts of hot water, forming a neutral very bitter solution. It loses its water of crystallisation at 100°.

Zinc lactate $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Zn} \cdot 3\text{H}_2\text{O}$ is best obtained direct from sugar by neutralising the lactic acid produced with zinc carbonate or zinc white (Lautemann, Annalen, 113, 142, Kiliani, Ber. 1882, 659). It crystallises better than any other lactate, and forms colourless, well-developed, four-sided rhombic prisms. It loses its water of crystallisation *in vacuo* or at 100°. It dissolves in 53 parts of water at 15°, and in 6 parts at 100°, forming an acid, bitter-tasting solution. It is very slightly soluble in alcohol (Strecker, Annalen, 105, 316).

Ferrous lactate $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Fe} \cdot 3\text{H}_2\text{O}$. This salt was introduced into pharmacy by Gélis and Conté in 1840, and was again recommended in 1847 by Engelhardt and Maddrell (l.c.). It is best prepared from crude calcium lactate in the following manner. The crude salt is recrystallised from water to which a little lime has been added, and if necessary the operation repeated. To the conc. aqueous solution of the purified salt the theoretical quantity of ferrous chloride is added, and the mixture allowed to stand for 3 days in a cool place. When no more crystals form the precipitated salt is filtered off, washed with a little alcohol, and dried at 50°.

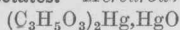
Ferrous lactate forms greenish-white crusts of needles, or a similarly coloured crystalline powder. It dissolves at the ordinary temperature in 48 parts, and at 100° in 12 parts of water, forming an acid solution with a sweetish chalybeate taste. The solution becomes yellow, and then brown, in the air, ferric lactate being formed, and also undergoes alteration on evaporation in the air, leaving a hygroscopic residue

containing ferrous and ferric lactates and some free acid. The dry salt is unaltered in the air, and loses its water of crystallisation when heated at 100° in a current of hydrogen.

Silver lactate $C_3H_5O_3Ag \cdot \frac{1}{2}H_2O$ is prepared by treating freshly prepared lactic acid, after cooling, with silver oxide, evaporating the solution in the dark *in vacuo* at the ordinary temperature. It forms colourless needles, soluble in 20 parts of cold water, insoluble in cold, but readily soluble in hot alcohol. On heating the salt in the dark for 3 hours at 80° , anhydrous silver lactate is obtained (Klimenko, J. Russ. Chem. Soc. 12, 97; Berthelot and Delépine, Compt. rend. 129, 920).

Bismuth lactate $BiC_3H_5O_3 \cdot 7H_2O$ is prepared by the slow dissolution of freshly precipitated bismuth hydroxide in lactic acid slightly diluted with water. The solution gradually deposits needles of the hydrated salt; on heating to 105° this yields the anhydrous salt, which is very sparingly soluble in water. The latter may be obtained by digesting freshly precipitated bismuth hydroxide in lactic acid at 100° . It forms rhombic tablets which decompose slightly when boiled with water for some time (Telle, Arch. Pharm. 1908, 246, 484).

Mercury lactates. *Mercurous lactate*



is prepared by dissolving freshly precipitated mercurous oxide in dilute lactic acid, which has previously been heated with water to destroy the anhydride which it contains. The solution is allowed to evaporate in a desiccator over sulphuric acid, when the salt separates in short white prismatic needles. It is not completely soluble in water, hydrolysis occurring with the formation of a basic lactate, which then decomposes into mercuric lactate and mercury.

Mercuric lactate $(C_3H_5O_3)_2Hg$, prepared in a similar manner from lactic acid and mercuric oxide, forms colourless prismatic needles, readily soluble in water. On boiling the aqueous solution, mercurous lactate, acetaldehyde, lactic acid, and carbon dioxide are produced (Guerbet, Bull. Soc. chim. 1902, 27, [iii.] 803).

Glucinium lactate (v. Tanatar and Kurowski, J. Russ. Phys. Chem. Soc. 39, 936; Glassmann, Ber. 1908, 33).

Cerous lactate (v. Morgan and Cahen, Pharm. J. 1907, 78, 428).

Optically active acids. As has already been stated, lactic acid can be resolved into two optically active components. This resolution has been effected by the fractional crystallisation of zinc ammonium lactate (Purdie and Walker, Chem. Soc. Trans. 1893, 1143; 1895, 616); of the strychnine salts (Purdie and Walker, *ibid.* 1892, 754; morphine salts (Irvine, *ibid.* 1906, 935); and of the quinine salts (Jungfleisch, Compt. rend. 1904, 139, 56, 203; 1905, 140, 719; 1906, 142, 515). Asymmetric syntheses have been made by the reduction of the *l*-menthyl (McKenzie, Chem. Soc. Trans. 1905, 1373), *l*-bornyl (McKenzie and Wren, *ibid.* 1906, 688), and *d*-amyl (McKenzie and Müller, *ibid.* 1909, 544) salts of pyruvic acid.

Paralactic acid (Sarcocollac acid, *d*-lactic acid) is present in flesh, in the blood, in muscles, in the thymus and thyroid and other animal organs (Berlinbauer, Chem. Zentr. 1888, 757; Salomon, Chem. Soc. Abstr. 1889, 64; Asker and Jackson,

Zeit. Biol. 41, 393; Moscatelli, Zeitsch. physiol. Chem. 12, 416; Griffiths, Chem. News, 91, 147; Werther, Chem. Soc. Abstr. 1890, 348; Inouye and Kondo, Zeitsch. physiol. Chem. 54, 481; Frew, *ibid.* 60, 15; Moriya, *ibid.* 43, 397). In muscle tissue, the amount increases with the degree of muscular activity. According to Embden (Zeitsch. physiol. Chem. 93, 1) a compound of phosphoric and lactic acids occurs as an intermediate metabolic product.

It is obtained from extract of meat by dissolving in 4 parts of warm water, adding 3 times the volume of 90 p.c. alcohol, and evaporating the filtrate to a syrup. This is again precipitated with alcohol, filtered, and evaporated, then acidified with H_2SO_4 , and extracted with ether (Wislicenus, Annalen, 167, 302). The crude acid may be purified by conversion into the zinc salt. If *Penicillium glaucum* is allowed to grow in the solution of the inactive ammonium lactate, the *d*-modification alone will remain (Lewkowitsch, Ber. 1883, 2720; Linossier, Bull. Soc. chim. [iii.] 6, 10). *Micrococcus acidiparalacti*, an anaerobic micrococcus formed in the preparation of the *Rauschbrand bacillus*, is found to convert sugar into paralactic acid (Nencki and Sieber, Monatsh. 10, 532).

Paralactic acid is a syrup which can only be distinguished from lactic acid by the fact that it rotates the plane of polarisation to the right, whereas lactic acid is inactive. The salts strongly resemble the lactates, but are somewhat more soluble in water. The methyl ester boils at 143° – 145° and has sp.gr. 1.1017 at $15^\circ/16^\circ$; and the ethyl ester, b.p. 152° – 154° , sp. gr. 1.0414 at $15^\circ/16^\circ$ (Frankland, Chem. Soc. Proc. 1895, 54). Further details as to rotatory power of acid and derivatives, v. Walker, Chem. Soc. Trans. 1895, 914; Purdie and Williamson, *ibid.* 1896, 827; Guye and Melikian, Compt. rend. 123, 1291; Henderson, and Prentice Chem. Soc. Trans. 1902, 658; 1903, 259; Wassmer and Guye, J. Phys. Chem. 1903, i. 257; Purdie and Irvine, Chem. Soc. Trans. 1899, 484; Walker, J. Phys. Chem. 13, 574.

***l*-Lactic acid** has not been found in nature. It is prepared by the resolution of the inactive acid (*q.v.*); by the fermentation of sugar with *Bacillus acidilavolacti* (Schardinger, Monatsh. 11, 545) or with a *l*-lactic ferment obtained from pears (Tate, Chem. Soc. Trans. 1893, 1263). It is similar in properties to *d*-lactic acid, with the exception that it rotates the plane of polarisation to the left.

Besides these acids, another isomeric acid remains to be described. *Hydracrylic acid, ethylene-lactic acid* or β -hydroxypropionic acid $CH_2(OH)CH_2CO_2H$ is prepared by the action of moist silver oxide on β -iodopropionic acid (Sokolow, Annalen, 150, 167; Wislicenus, Annalen, 166, 10); by heating the sodium salt of acrylic acid with sodium hydroxide at 100° (Linnemann, Ber. 1875, 1095); and by the action of prussic acid on ethylene chlorhydrin and saponification of the resulting nitrile (Wislicenus, Annalen, 128, 1; 167, 346; Erlenmeyer, *ibid.* 191, 268). It forms a syrup which decomposes into water and acrylic acid on heating. Chromic acid oxidises it into oxalic acid and carbon dioxide, and silver oxide converts it into glycollic acid. Wislicenus also obtained from flesh, in addition to paralactic acid, an

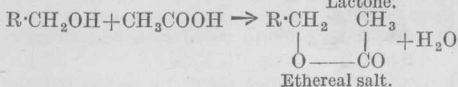
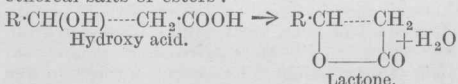
acid which he believed to be identical with this ethylene-lactic acid, but it has been shown (Siegfried, Ber. 1889, 2713) that this is in reality *acetylactic acid*.

Atrolactic acid (*α*-phenylhydroxypropionic acid) $\text{CH}_3\cdot\text{C}(\text{C}_6\text{H}_5)\text{OH}\cdot\text{CO}_2\text{H}$. Prepared by the action of fuming hydrochloric acid on acetophenone hydrocyanide (Spiegel, Ber. 1881, 14, 1353; Tiemann and Köhler, *ibid.* 1980); colourless needles, m.p. (anhydrous) $93^\circ\text{--}94^\circ$.

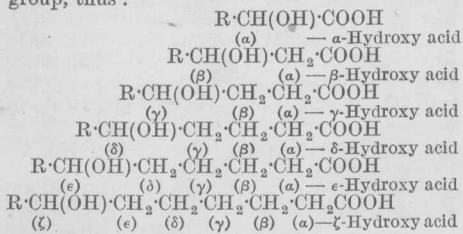
LACTIC FERMENTATION GUM v. GUMS.

LACTOLIN. Trade name for potassium di-lactate used as a mordant.

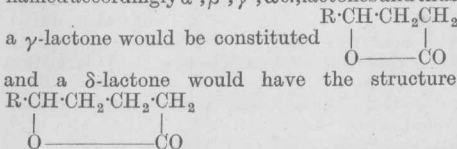
LACTONES. Generally speaking a lactone is formed by the elimination of water from a hydroxyl group and a carboxyl group present in the same molecule. They may therefore be regarded as internal salts corresponding with the external salts which are known as the ethereal salts or esters:



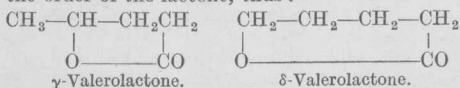
The lactones are therefore derived from that class of organic compounds known as the hydroxyacids. The hydroxy acids are divided into several series depending on the position of the hydroxyl group in respect to the carboxyl group and are named α -, β -, γ -, &c., hydroxy acids according as the hydroxyl group is in the α -, β -, γ -, &c., position in respect to the acid group, thus:



The lactones derived from these acids are named accordingly α -, β -, γ -, &c., lactones and thus

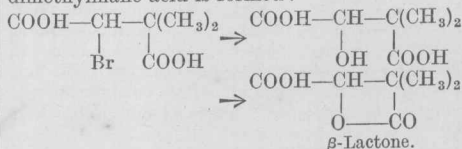


Nomenclature.—The name of the lactone is usually taken from the trivial name of the acid from which the corresponding hydroxy acid is derived, as for example, butyrolactone from γ -hydroxybutyric acid, valerolactone from γ -hydroxyvaleric acid. In those cases where the formation of two isomeric lactones is possible the prefix γ - or δ - is added to indicate the order of the lactone, thus:

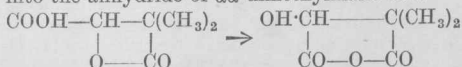


α -Lactones are not known, and in only a few exceptional cases has the formation of β -lactones

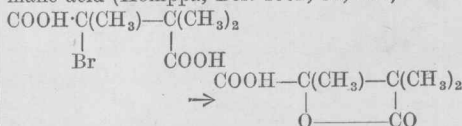
been observed. Thus Baeyer and Villiger (Ber. 1897, 30, 1954; compare also Fichter and Hirsch, *ibid.* 1900, 33, 3273) have shown that when α -bromo- α' -dimethylsuccinic acid is treated with moist silver oxide the β -lactone of dimethylmalic acid is formed:



This compound crystallises in rhombic plates containing 1 mol. of water, and melts at $54^\circ\text{--}55^\circ$; it loses this water of crystallisation at 45° in a vacuum. When distilled under diminished pressure it passes by rearrangement into the anhydride of $\alpha\alpha$ -dimethylmalic acid



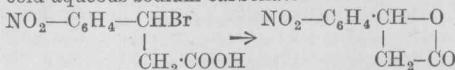
In the same way, trimethylbromosuccinic acid is converted into the β -lactone of trimethylmalic acid (Komppa, Ber. 1902, 35, 534)



The formation of a similar compound has been recorded by Meldrum (Chem. Soc. Trans. 1908, 93, 598), who finds that when acetone is condensed with malonic acid in the presence of acetic anhydride containing a little sulphuric acid, the β -lactone of β -hydroxyisopropylmalonic acid $(\text{CH}_3)_2\text{C}\text{---CH}\cdot\text{COOH}$ is formed. This substance

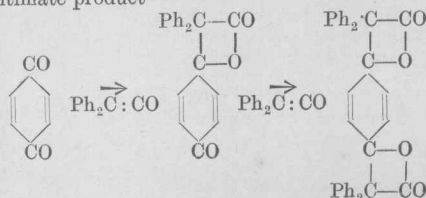
crystallises from acetone in transparent four-sided plates melting at 97° .

β -Lactone formation occurs in the aromatic series from β -hydroxy acids having a phenyl-group, in which strongly negative groups are present, attached to the β -carbon atom. Thus the lactones of *o*-, *m*-, and *p*-nitrophenyl- β -lactic acids are formed when the corresponding nitrophenyl- β -bromopropionic acids are treated with cold aqueous sodium carbonate

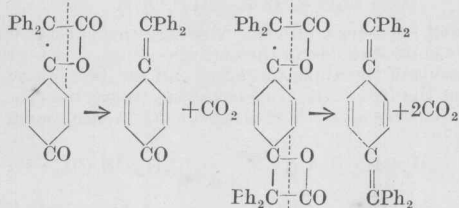


o-Nitrophenyllactic acid lactone readily passes into indigo when boiled with glacial acetic acid.

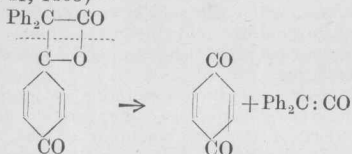
A remarkable series of aromatic β -lactones have been prepared by Staudinger by condensing diphenylketene with various quinones. When, for example, quinone itself is used the reaction proceeds in two stages, a di- β -lactone being the ultimate product—



Both lactones eliminate carbon dioxide when heated—



but in the former case a certain amount of fission takes place in the other direction (Ber. 1908, 41, 1355)—



γ -Lactones. The remarkable tendency which exists for the formation of the five-membered ring causes the γ -hydroxy acids to be, usually, unstable at the ordinary temperature and to pass, with elimination of water, into the γ -lactone

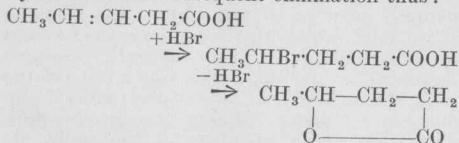
$$\begin{array}{ccc}
 \text{R}-\text{CH}-\text{CH}_2-\text{CH}_2 & & \text{R}-\text{CH}-\text{CH}_2-\text{CH}_2 \\
 | & & | \\
 \text{OH} & \rightarrow & \text{O} \\
 \gamma\text{-Hydroxy acid.} & & \gamma\text{-Lactone.}
 \end{array}$$

The tendency for the formation of the inner anhydride is so great that the change from the hydroxy acid to the lactone is usually effected by merely raising the temperature of an aqueous solution of the acid and in many cases the lactone exists in aqueous solution at the ordinary temperature. The simplest member of the class,

butyrolactone $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}$, was discovered

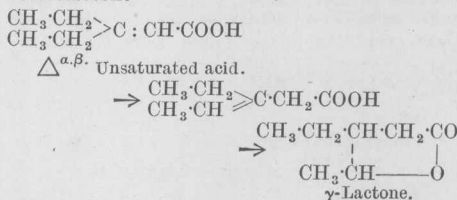
by Saithew in 1873, although certain naturally occurring lactones, such as coumarin and meconine (*q.v.*), were known before that time. (For a general description of the lactones, compare E. Hzelt, Ahrens' Samml. 1903, 8, 83.)

Formation.—The methods usually adopted for the preparation of γ -hydroxy acids, that is of the γ -lactones, may be briefly summarised as follows: (1) The transformation of the $\Delta^{\beta,\gamma}$ -unsaturated acids by the addition of halogen hydride and its subsequent elimination thus:

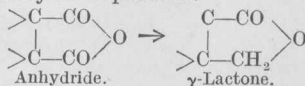


The $\Delta^{\beta,\gamma}$ -unsaturated acids are also transformed into the γ -lactones either by merely heating them alone or by warming them with a mixture of equal volumes of concentrated sulphuric acid and water at 140° (Fittig, Ber. 1894, 27, 2667; Annalen, 1894, 283, 51). In the latter instance, the same change is shown by those $\Delta^{\alpha,\beta}$ -unsaturated acids which have two alkyl groups on the β -carbon atom. Thus Fichter, Kiefer, and Bernoulli (Ber. 1909, 42,

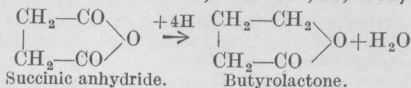
4710) find that when $\beta\beta$ -diethylacrylic acid is warmed for a short time with 60 p.c. aqueous sulphuric acid, it is converted into β -ethyl- γ -valerolactone



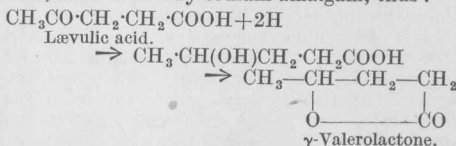
(2) The relation between the anhydrides of the dibasic acids and the γ -lactones, which is illustrated by the expression:



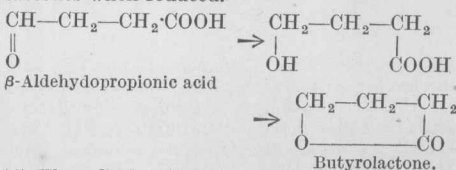
indicates that the last-named compounds can be derived from the anhydrides by reduction. Thus butyrolactone is formed when succinic anhydride is reduced by sodium amalgam (Fichter and Herbrand, Ber. 1896, 29, 1192):



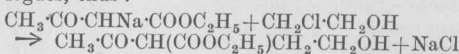
(3) The sodium salts of γ -hydroxy acids are also formed when γ -ketonic acids, such as lœvulinic acid, are reduced by sodium amalgam, thus:



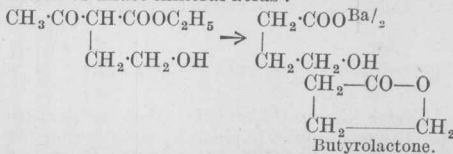
In a similar manner, β -aldehydo acids, for example, β -aldehydopropionic acid, yield γ -lactones when reduced.



(4) The alkyl salts of γ -hydroxy acids may be formed by the condensation of chlorhydrins of the type $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{OH}$ with the sodium compounds of ethyl acetoacetate and its homologues, thus:



When this ethyl salt is hydrolysed with baryta, the acetyl group is eliminated and the barium salt of the hydroxy acid, which is then formed, is converted into the γ -lactone by the action of dilute mineral acids:



(5) The formation of certain γ -lactones may