

CHIOS TURPENTINE RESIN. The name Chios turpentine is, properly, restricted to the oleo-resin from species of *Pistacia*, although turpentine from some of the larches is often termed Chios turpentine. It is similar in character to ordinary turpentine oleo-resin. Emmanuel (Pharm. Acta Helv. 1935, 10, 12) isolated from the resin of *Pistacia Terebinthus*, terminthic acid, $C_{14}H_{20}O_2$, m.p. 136°–137°; terminthinic acid, $C_{16}H_{24}O_4$, m.p. 124°; and termintholic acid, $C_{13}H_{20}O_4$, m.p. 102°; and termintholinic acid, $C_{22}H_{34}O_3$, m.p. 128°. These acids have not yet been characterised by the preparation of crystalline derivatives.

Chios turpentine is variable in composition, and its characters depend entirely on the relative proportions of essential oil and resin.

E. J. P.

CHIRETTA. *Chirata*, B.P. Is the plant *Swertia Chirata* Buch.—Ham. collected when in flower and dried. Japanese chiretta is *Swertia chinensis* Franchet. Höhn (Arch. Pharm. 1869, 215) found two bitter constituents in Indian chiretta, viz. chiratin and ophelic acid.

CHITENINE, QUITENINE. An oxidation product of quinine, found in the urine after the administration of quinine. Crystallises from dilute alcohol in prisms, m.p. 281°–282°, $[\alpha]_D^{17} -122.6^\circ$.

CHITIN. $[\alpha]_D -14.7^\circ$ (in conc. HCl). Is a polysaccharide containing nitrogen which forms part of the skeletal substance of insects and crustacea; it is also an important skeletal element in the fungi. It is not possible to distinguish between animal and vegetable chitin by total nitrogen or by X-ray analysis; their chemical identity has been shown by Zechmeister and Tóth (Z. physiol. Chem. 1934, 223, 53).

Chitin is extremely resistant to hydrolysis, but on boiling with concentrated hydrochloric acid it is converted into 1 mol. of glucosamine (2-aminoglucose) together with 1 mol. of acetic acid.

It is considered by Meyer and Mark (Ber. 1928, 61, [B], 1936) to be built up of *N*-acetylglucosamine units in β -glucosidic linkages exactly as in cellulose.

Karrer and Hoffman state that an enzyme from the vineyard snail is able to hydrolyse chitin (Helv. Chim. Acta, 1929, 12, 616, 986), the end product being acetylglucosamine.

By acetolysis of chitin with acetic acid in sulphuric acid, Bergmann *et al.* (Ber. 1931, 64, [B], 2436) obtained the octa-acetate of a disaccharide chitobiose.

Zechmeister and Tóth (Ber. 1931, 64, [B], 2028; 1932, 65, [B], 161, 1706) obtained in addition a chitotriose and an amorphous water soluble chitodextrin.

The Röntgen diagram (Meyer, Helv. Chim. Acta, 1935, 18, 589) also confirms the structure as being of the long chain cellulose type. It is not known whether the glycoside linkage is α or β .

E. F. A.

CHITINASE, the enzyme which hydrolyses chitin, was discovered by Karrer and Hoffmann (Helv. Chim. Acta, 1929, 12, 616) in the digestive juices of *Helix*. It attacks genuine chitin

only slowly, but after solution in concentrated hydrochloric acid, and separation by pouring into water, the chitin is easily hydrolysed. *N*-Acetylglucosamine is the final product alike from chitin of animal and fungal origin; chitodextrins are intermediate products. Chitinase is not the same as emulsin; it has, however, been obtained from the outer part of almonds free from β -glucosidase (Grassmann, Ber. 1934, 67, [B], 1; Helferich, Z. Physiol. Chem. 1933, 221, 253).

It has also been obtained from *Aspergillus oryzae* and is obviously widely distributed. The optimal p_H is 5.2; it is destroyed at 70°. Perhaps it is a mixture of two enzymes acting in succession.

Chitinase is able to hydrolyse synthetic glycosides of *N*-acetylglucosamine, for example, phenyl *N*-acetylglucosaminide. It is quite without action on the non-acetylated compound; chitosan is only hydrolysed as far as the polyglucosamine stage, whereas acetylchitosan is totally hydrolysed by the enzyme. The acetyl group is thus essential for the enzyme to be active; it cannot be replaced by formyl or benzoyl.

E. F. A.

CHITOSAMINE is glucosamine (2-aminoglucose) (*v.* CHITIN).

CHIVES. *Allium Schoenoprasum*, L. A perennial plant occurring naturally in many parts of Europe and cultivated for the round onion-like leaves which are used for flavouring. The percentage composition of the leaves is given as:

Water.	Protein.	Fat.	N-free extract.	Fibre.	Ash.
91.2	2.6	0.33	3.09	1.48	1.28

Churg and Ripperton (Hawaii Agric. Exp. Stat. Bull. 1929, No. 60). The mineral constituents include Ca 0.048, Fe 0.0084, and P 0.057%.

A. G. P.

CHLOANTHITE. Native nickel arsenide, $NiAs_2$, isomorphous with smaltite ($CoAs_2$), there being no sharp line of demarcation between the two species. Found as cubic crystals and compact masses at Schneeberg in Saxony and Riechelsdorf in Hesse, where it was formerly mined as an ore of nickel. It occurs in considerable amount with silver ores at Cobalt and South Lorrain in Ontario.

L. J. P.

CHLORAL, TRICHLORACETALDEHYDE, $CCl_3 \cdot CH(OH)_2$. Chloral was first obtained by Liebig (Annalen, 1832, 1, 189) by chlorination of absolute alcohol. Its composition was established by Dumas (Ann. Chim. 1834, [ii], 56, 120) and by Städeler (Annalen, 1847, 61, 101).

Chloral is manufactured by chlorination of absolute alcohol. Chlorination is carried out in lead or lead-lined vessels provided with a reflux condenser and a chlorine distributor taken to the bottom of the vessel, and so arranged that a maximum distribution of chlorine passes through the alcohol. The vessels, of from 400 to 1,000 gallons capacity, are about two-thirds filled with alcohol, three such vessels being arranged in series so that any excess chlorine from the first vessel passes into the second and from the

second to the third in order to ensure complete absorption of the gas. The hydrogen chloride evolved during the reaction is absorbed in water. The initial reaction is vigorous and during the first stage the temperature is kept as low as possible by efficient cooling. Chlorine is passed at a rate which results in a liquid of approximately 24°Bé. at the end of the first day's run. During the next twenty-four hours the temperature is raised gradually, heat being applied if necessary, to about 50°C., and the density of the liquid at the end of this period should be from 35°–40°Bé. The reaction is completed on the third day by increasing the temperature to 95° and continuing the chlorination until the density reaches 49°Bé. A sample of the product at this stage distilled with an equal volume of concentrated sulphuric acid should indicate a yield of about 75% of chloral. The crude chloral alcoholate is allowed to cool, when it solidifies. It is then gradually mixed with an equal volume of sulphuric acid 66°Bé, the mixture being kept cool. The temperature is then gradually raised. Hydrogen chloride is evolved, together with some ethyl chloride. Between 70° and 90° alcohol is recovered, and the crude chloral passes over between 90° and 98°. The crude chloral is purified by redistillation over calcium carbonate, the portion distilling over above 94° being pure chloral.

Other processes which have been suggested include the chlorination of alcohol in the vapour phase (G.P. 133021), the chlorination of a mixture of acetaldehyde and alcohol (F.P. 12306), and the chlorination of acetal (Reichert, Bailey, and Nieuwland, J. Amer. Chem. Soc. 1933, 55, 1552).

Chloral is a colourless, pungent liquid, b.p. 97.7°. When pure it is stable, but in the presence of traces of impurities such as sulphuric acid it polymerises with production of metachloral, a white amorphous solid. The same product is obtained by the action of aluminium chloride on chloral (G.P. 139392). Metachloral is insoluble in water, alcohol, ether and acids, but soluble in sodium carbonate solution. On distillation at 180°–185° it is reconverted into chloral (Kolbe, Annalen, 1845, 54, 183). A water soluble polymeride is obtained by treating chloral with pyridine or an amine in the cold and then acidifying. Alcohol and water convert it into chloral alcoholate and chloral hydrate respectively. Alkalis decompose it, giving chloroform and formic acid.

CHLORAL HYDRATE, $CCl_3 \cdot CH(OH)_2$, is by far the most important derivative of chloral. It is prepared by the cautious addition of the requisite amount of water to chloral, overheating of the mixture being avoided. It is purified by crystallisation from benzene, chloroform or light petroleum. To obtain the hydrate in the form of cubes or plates rather more water is added than is theoretically necessary, the mixture thoroughly shaken until cold and the mass of crystals poured on to porcelain dishes and dried over sulphuric acid *in vacuo*.

Chloral hydrate occurs in colourless crystals, m.p. 50°–58°, with a pungent odour and bitter taste, and is readily soluble in water, alcohol, chloroform, ether and oils.

Chloral hydrate is very largely employed in medicine as a hypnotic and is official in most pharmacopoeias. It is of special value in simple nervous insomnia, delirium tremens, and certain forms of insanity. It is also a powerful deodorising and antiseptic agent. By itself, or in concentrated solution, it may be used as a vesicant. The toxic effects produced by overdoses of chloral hydrate are a fall of temperature and slow and enfeebled respiration.

CHLORAL FORMAMIDE, CHLORALAMIDE, $C_3H_4O_2NCl_3$, is prepared by gently heating chloral and formamide in equimolecular proportions. On cooling the melt sets to a solid mass which is recrystallised from water or 30% alcohol. It forms colourless crystals, m.p. 114°–115°. It is soluble in water (1:20) and very soluble in alcohol, ether and acetone. It is not decomposed by acids, but when warmed with dilute alkalis is decomposed, yielding chloroform, ammonia, and formic acid.

Chloral formamide is a somewhat slower acting hypnotic than chloral hydrate and is especially useful in the insomnia of cardiac disease, since it has not the depressant action of chloral on the heart. It is also used in combination with potassium bromide as a remedy for sea sickness.

GLUCOCHLORAL, CHLORALOSE, $C_8H_{11}O_6Cl_3$, obtained by heating chloral and glucose in equal parts on the water bath, forms crystals, m.p. 185°, is a hypnotic and sedative. An isomeric product, parachloralose, produced at the same time is devoid of hypnotic properties.

BUTYL CHLORAL, TRICHLORBUTYRIC ALDEHYDE, $CH_3 \cdot CHCl \cdot CCl_2 \cdot CHO$, is prepared by passing dry chlorine into aldehyde or paraldehyde at about -10° until the aldehyde is saturated. The temperature is then gradually raised to 100°, chlorine being continually passed in until chlorination is complete. The resulting liquid is diluted with water and then distilled in a current of steam, when the hydrate passes over. The hydrate is recrystallised from water and on distillation in a stream of hydrogen chloride the pure chloral is obtained (Pinner, Annalen, 1875, 179, 26). It is a colourless oil with a characteristic odour, b.p. 164°–165°/750 mm. sp.gr 1.3956 at 20°/4°; fuming nitric acid converts it into trichlorobutyric acid. It readily combines with water forming the hydrate.

BUTYL CHLORAL HYDRATE,



is prepared by mixing butyl chloral with about one-ninth its weight of water and recrystallising the solid mass so formed from boiling water. It forms white trimetric plates with a pungent but not acrid odour and a nauseous, bitter taste. It melts at about 78° and resolidifies at about 71°. It is soluble in about 40 parts of water, very readily soluble in alcohol, ether and glycerine, less readily in chloroform and olive oil. Butyl chloral hydrate resembles chloral hydrate in its action, but is a weaker hypnotic and has a more pronounced depressant action on the heart. It is chiefly employed in combination with camphor, phenazone or gelsemium as an analgesic in cases of neuralgia and migraine.

A. J. E.