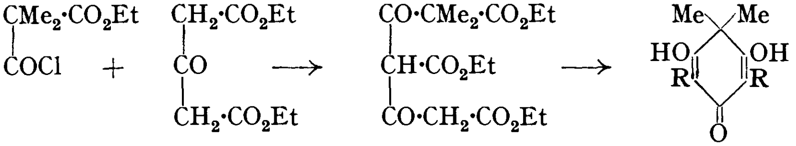
380. *Constituents of* Filix Mas. *Part II. The Synthesis of Filicinic Acid.*

By Alexander Robertson and (the late) William F. Sandrock.

By the hydrolytic decomposition of filicin, aspidin, albaspidin, and flavaspidic acid with aqueous sodium hydroxide and zinc dust Boehm isolated a compound, filicinic acid, which he concluded to be 1 : 1-dimethyl*cyclo*hexane-2 : 4 : 6-trione (*gem*-dimethylphloroglucinol) (*Annalen*, 1898, **302**, 171; 1899, **307**, 249; 1901, **318**, 230, 253; 1903, **329**, 289, 321). This important degradation product has now been synthesised by the general method used by Curd and Robertson for the synthesis of *C*-methylphloroglucinol (this vol., p. 437).



(I.) (II.) (III.) (IV.)

The interaction of (I) and the sodio-derivative of (II) gave rise to the *pentanedione* (III), which on ring closure with sodium ethoxide yielded the *ester* (IV, R = CO_2Et). Simultaneous hydrolysis and decarboxylation of this ester yielded filicinic acid (IV, R = H) identical in every way with a specimen prepared from flavaspidic acid according to the directions of Boehm (*loc. cit.*).

Experimental.

Dimethylmalonyl Chloride Monoethyl Ester.—Alcohol (80 c.c.) containing potassium hydroxide (2·8 g.) was added in 6 portions to ethyl dimethylmalonate (9·7 g.) in alcohol (40 c.c.); after each addition the mixture was warmed until neutral (about 5 minutes). The solution was finally refluxed for 10 minutes, kept for 24 hours, filtered, and concentrated in a vacuum. Ether (400 c.c.) was added to the residual liquor (30 c.c.) and the gelatinous precipitate of the monopotassium salt was collected and dissolved in a little water, the solution acidified with hydrochloric acid, and *ethyl hydrogen dimethylmalonate* isolated with ether. Distilled in a vacuum, it was obtained as a colourless oil (5 g.), b. p. 135—136°/19 mm.; 114—116°/6 mm. [Found: C, 52·5; H, 7·8; CO_2H, 29·3. $C_6H_{11}O_2(CO_2H)$ requires C, 52·5; H, 7·5; CO_2H, 28·1%].

The acid (29 g.) was treated with phosphorus pentachloride (42 g., added in portions in the course of 45 minutes), and the reaction controlled by occasional cooling in tap-water. After removal of the phosphorus oxychloride in a vacuum the residue was fractionally distilled, yielding a main fraction, b. p. 75—85°/25 mm. Redistilled several times, the *chloride* was obtained as a mobile liquid (27 g.), b. p. 74—78°/19 mm. (Found: Cl, 20·0. $C_7H_{11}O_3Cl$ requires Cl, 19·9%). Careful treatment of the chloride (1 c.c.) with aniline (2 c.c.) at 0° gave the *anilide*, which separated from light petroleum (b. p. 40—50°) in colourless flat prisms, m. p. 47—48° (Found: C, 66·5; H, 7·2. $C_{13}H_{17}O_3N$ requires C, 66·4; H, 7·2%).

The chloride was also prepared by means of an excess of thionyl chloride at room temperature and then at 90° for 1 hour, and subsequent fractionation of the mixture.

Ethyl 1 : 1-*Dimethyl*cyclo*hexane*-2 : 4 : 6-*trione*-3 : 5-*dicarboxylate* (IV, R = CO_2Et).—The foregoing chloride (20 g.) in ether (40 c.c.) was added to a solution of ethyl sodioacetonedicarboxylate (prepared at 0° from 22·8 g. of the ester and 2·6 g. of powdered sodium) in ether (400 c.c.) and the mixture was kept for 1 hour and then refluxed for 15 hours. Sufficient water was added to dissolve the sodium chloride, the ethereal layer was separated, washed, dried, and evaporated, and the residue distilled in a vacuum, yielding a main fraction (14·3 g.), b. p. 165—180°/3 mm., which consisted chiefly of *ethyl* 1 : 1-*dimethylpentane*-2 : 4-*dione*-1 : 3 : 5-*tricarboxylate* (III). This ester after repeated distillation was obtained as a yellow viscous oil, b. p. 175—180°/5 mm. [Found : OEt, 37·2. $C_{10}H_9O_5(OEt)_3$ requires OEt, 39·2%].

When the mild reaction between alcohol-free sodium ethoxide (from 1 g. of sodium) and the ester (III) (5 g.) in ether (50 c.c.) had subsided (the mixture became orange-coloured), the solvent was distilled and the residue was kept at 100° for 1·5 hours, cooled, and dissolved in water (50 c.c.). The addition of dilute sulphuric acid threw down the *ester* (IV, R = CO_2Et), which was well washed with water and crystallised from light petroleum (b. p. 80—100°), forming colourless needles, m. p. 147—148° after slight sintering at 143°, readily soluble in benzene or acetone [Found : C, 56·3; H, 6·0; OEt, 28·5. $C_{10}H_8O_5(OEt)_2$ requires C, 56·4; H, 6·0; OEt, 30·2%]. The compound rapidly dissolves in aqueous sodium bicarbonate, and gives with alcoholic ferric chloride a dark red coloration which becomes red-brown on dilution with water.

Filicinic Acid (IV, R = H).—A solution of the foregoing ester (2 g.) in 15% aqueous sodium hydroxide containing zinc dust (1 g.) was refluxed for 10 hours, and the resulting filicinic acid precipitated at 0° with cold 40% sulphuric acid. Crystallised from water, it formed colourless, irregular, octahedral prisms, m. p. 215° after sintering at 210° when slowly heated; m. p. 220° (decomp.) when placed in a bath at 210° and rapidly heated (Found : C, 62·1; H, 6·5. Calc. for $C_8H_{10}O_3$: C, 62·3; H, 6·5%). The synthetical compound was identical with the natural compound, m. p. 215° or 220°, having the same red-brown ferric chloride reaction in water and giving the characteristic colorations on warming with aniline (red-violet) and with aniline and acetic acid (green).

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