176. *Morellin, a Constituent of the Seeds of* Garcinia Morella.

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Garcinia morella belongs to a large genus of evergreen trees of the tropics which yield the gamboge of commerce. From the seeds a semi-solid edible oil is obtained, and the pericarp contains a yellow colouring matter. Extraction of the pericarp with hot alcohol yields, in addition to amorphous substances, a yellow crystalline lævorotatory phenol, m. p. 154°, for which the name *morellin* is suggested. Morellin has the composition $C_{30}H_{34}O_6$, and it contains apparently four hydroxy-groups, since it yields a *tetra-acetate*, m. p. 178—179°. Two of the hydroxy-groups are readily methylated by methyl iodide in acetone solu-

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* All m. p.'s are corrected.

tion in the presence of potassium carbonate; the *dimethyl* ether has m. p. 156°, and a *trimethyl* ether, m. p. 172°, can be prepared from its sodio-derivative. Two ethylenic linkages are also present since morellin yields a *dihydrochloride*, m. p. 131°, and a *tetrabromide*, m. p. 138—139°. On treatment with hydroxylamine an amorphous *dioxime* is obtained, which suggests two carbonyl groups, the presence of one of them being confirmed by the preparation of a crystalline *mononitroguanylhydrazone*, m. p. 205·5°.

Morellin is a somewhat unstable substance; it is resinified by prolonged digestion with alcohol or when kept at 100° for some hours. It is also converted into an amorphous substance by solution in alcoholic potassium hydroxide. A crystalline isomeride, iso*morellin*, m. p. 116°, is obtained when an ethereal solution of the phenol is shaken with aqueous potassium hydroxide or when it is digested with acetyl chloride in benzene solution in the presence of potassium carbonate.

On fusion with alkali morellin gives a variety of products, of which the following have been identified: *dl*-methylheptenol, phloroglucinol, acetic, *iso*valeric, methylsuccinic and homophthalic acids. A liquid ditertiary *glycol*, $C_{16}H_{22}O_2$, probably containing two ethylenic linkages and having a strong odour reminiscent of amyl alcohol, is also formed.

Whilst the evidence at present available is insufficient to warrant the assignment of any structure to morellin, it would appear probable that it is related to mangostin, the yellow colouring matter present in the pericarp of the seeds of *Garcinia mangostana*, which has formed the subject of a detailed investigation by Murakami (*Annalen*, 1932, **496**, 122). This phenol, like morellin, is a derivative of phloroglucinol and gives on potash fusion, amongst other products, *dl*-methylheptenol, acetic and *iso*valeric acids.

EXPERIMENTAL.

The dry powdered pericarp of the seeds (100 g.) was digested with alcohol (300 c.c.); the hot filtered solution on standing for some hours depositing morellin (7 g.), m. p. 148—150°. A further quantity (3 g.) of the colouring matter can be obtained by extraction with fresh alcohol (300 c.c.). Addition of water to the filtrate precipitated an amorphous yellow solid (11 g.), which was not further investigated. *Morellin* crystallised from methyl or ethyl alcohol in golden-yellow needles or rhombic prisms, m. p. 154°, $[\alpha]_D$ − 594° (in chloroform, *c* 4·5) [Found: C, 73·3; H, 7·3; *M* (in benzene) 485. $C_{30}H_{34}O_6$ requires C, 73·5; H, 7·0%; *M*, 490]. Morellin is insoluble in water, but readily soluble in most of the ordinary organic solvents with the exception of the alcohols and ligroin. Its alcoholic solution gives with ferric chloride a brownish-green coloration. It is insoluble in sodium carbonate solution, but dissolves in alcoholic potassium hydroxide to give a red potassium salt, which on acidification deposits an amorphous solid, m. p. 73° (Found: C, 62·5; H, 6·7%). iso*Morellin* was obtained when a mixture of morellin (2 g.), acetyl chloride (4 g.), and potassium carbonate (4 g.) in benzene was heated for 4 hours. It crystallised from ethyl alcohol in golden-yellow prisms, m. p. 116°, $[\alpha]_D$ − 561° (in chloroform, *c* 3·9) (Found: C, 73·5; H, 7·5%). Its alcoholic solution gave a dark brown ferric chloride coloration.

Morellin Dihydrochloride.—Although morellin is not affected by digestion with concentrated hydrochloric acid, a *dihydrochloride* is formed when a solution of morellin (2 g.) in acetic acid (15 c.c.) is saturated with hydrogen chloride. Addition of ice precipitates an orange solid, m. p. 131° after crystallisation from methyl alcohol (Found: Cl, 12·3. $C_{30}H_{34}O_6,2HCl$ requires Cl, 12·6%).

Morellin Tetrabromide.—To a solution of morellin (2·5 g.) in chloroform (20 c.c.) a solution of bromine (1·74 g.) in chloroform was added. Removal of the solvent in a vacuum gave orange-yellow crystals which, after recrystallisation from alcohol, had m. p. 138—139°, $[\alpha]_D$ − 156° (in chloroform, *c* 4·91) (Found: Br, 39·7. $C_{30}H_{34}O_6Br_4$ requires Br, 39·5%).

Morellin dioxime, prepared by treatment of an alcoholic solution of morellin with hydroxylamine hydrochloride and sodium acetate, was an amorphous yellow powder, m. p. 148—149° (Found: C, 68·8; H, 7·1; N, 5·6. $C_{30}H_{36}O_6N_2$ requires C, 69·2; H, 6·9; N, 5·6%). *Morellin mononitroguanylhydrazone* crystallised from alcohol–ethyl acetate in thick yellow prisms, decomp. 205·5°, $[\alpha]_D$ − 748° (in chloroform, *c* 3·1) (Found: C, 62·4; H, 6·6. $C_{31}H_{37}O_7N_5$ requires C, 62·9; H, 6·3%). *Morellin tetra-acetate*, prepared by digestion of the phenol with acetic anhydride and sodium acetate, crystallised from methyl alcohol in yellow prisms, m. p. 178—179°, $[\alpha]_D$ −327° (in chloroform, *c* 4·7) (Found: C, 69·6; H, 6·4; OAc, 25·8. $C_{38}H_{42}O_{10}$ requires C, 69·3; H, 6·4; 4OAc, 26·1%).

Morellin Dimethyl Ether.—To a boiling solution of morellin (10 g.) in acetone (100 c.c.) containing potassium carbonate (10 g.) in suspension, methyl iodide (20 g.) was added during 8 hours. The filtered solution gave, on removal of the solvent, a solid which crystallised from methyl alcohol in pale yellow rosettes of rectangular prisms, m. p. 156°, $[\alpha]_D - 242°$ (in chloroform, *c* 6·2) [Found : C, 74·0; H, 7·2; OMe, 12·4. $C_{30}H_{32}O_4(OMe)_2$ requires C, 74·1; H, 7·4; OMe, 12·0%]. Its alcoholic solution gave no colour with ferric chloride. The *dioxime* separated from dilute alcohol as a white amorphous powder, m. p. 118°, $[\alpha]_D + 241°$ (in chloroform, *c* 4·0) (Found : N, 4·9. $C_{32}H_{40}O_6N_2$ requires N, 5·1%). The *diacetyl* derivative of the dimethyl ether separated from alcohol as a microcrystalline powder, m. p. 82—83° (Found : C, 69·0; H, 6·8; OAc, 14·2. $C_{36}H_{42}O_8$ requires C, 69·2; H, 6·8; 2OAc, 14·3%), and the *tetrabromide*, prepared in chloroform solution, after crystallisation from methyl alcohol, had m. p. 124° (Found : Br, 38·0. $C_{32}H_{38}O_6Br_4$ requires Br, 38·4%).

Morellin Trimethyl Ether.—The dimethyl ether (5 g.) in toluene (50 c.c.) was heated with sodium wire (0·5 g.) until evolution of hydrogen ceased. The toluene solution was decanted from unchanged sodium and, after the addition of methyl iodide (15 g.), heated for 4 hours. Removal under diminished pressure of the toluene from the filtered solution gave a solid, which separated from benzene–ligroin as a microcrystalline yellow powder, m. p. 170—172° [Found : C, 74·6; H, 7·5; OMe, 17·0. $C_{30}H_{31}O_3(OMe)_3$ requires C, 74·4; H, 7·6; OMe, 17·5%]. The use of methyl sulphate in place of methyl iodide gave a resinous product.

Fusion of Morellin with Potassium Hydroxide.—Morellin (20 g.) with potassium hydroxide (100 g.) and water (10 c.c.) was heated in a nickel crucible at 220° in a current of nitrogen (mechanical stirring), the volatile products of the fusion being collected in a well-cooled receiver. The distillate, which had a strong odour of amyl alcohol, was dissolved in ether, the ethereal extract dried, and the solvent removed. On distillation under diminished pressure two fractions were obtained : (a) b. p. 80—85°/15 mm., $d_{30^\circ}^{30^\circ}$ 0·852, $n_D^{30^\circ}$ 1·4450, identified as *dl*-methylheptenol by oxidation with chromic acid to *dl*-methylheptenone, semicarbazone, m. p. 129—130° (Found : N, 22·8. Calc. for $C_9H_{17}ON_3$: N, 22·9%); and (b) an *oil*, b. p. 130—140°/8 mm., $d_{30}^{30^\circ}$ 0·917, $n_D^{30^\circ}$ 1·47898, which resembled amyl alcohol in odour [Found : C, 76·1; H, 10·9; OH, 12·7; *M* (Rast), 258. $C_{16}H_{26}(OH)_2$ requires C, 76·2; H, 11·1; OH, 13·5% ; *M*, 252]. The alcohol did not react with phthalic anhydride at 140°, and titration with bromine showed the presence of two ethylenic linkages.

The fusion was dissolved in water, saturated with carbon dioxide, and extracted with ether. The residue after removal of the ether was distilled in steam, a volatile oil being obtained which resembled thymol in odour and partly crystallised on keeping, m. p. 50—55°. It gave a bluish-black coloration with alcoholic ferric chloride and formed a phenylurethane, m. p. 149—150° (Found : C, 72·8; H, 5·6%), which was not identified. The aqueous residue from the steam distillation was concentrated and extracted with ether, which left on evaporation a solid, m. p. 219°, identified as phloroglucinol by conversion into its trinitro-derivative, m. p. 165°, both alone and in admixture with trinitrophloroglucinol (Found : N, 15·8. Calc. for $C_6H_3O_9N_3$: N, 16·1%).

The sodium carbonate solution from which the phenols had been separated was acidified with sulphuric acid and distilled in steam. The acids volatile in steam were extracted with ether and distilled under diminished pressure, four fractions being obtained : (i) b. p. 85—90°/65 mm., (ii) 95°/35 mm., (iii) 96—98°/35 mm., and (iv) 140—150°/10 mm. Fraction (i) was a mixture of acetic and *iso*valeric acids, characterised by the preparation of acetanilide, m. p. 121°, and *iso*valeramide, m. p. 135—136°. Fractions (ii) and (iii) were pure *iso*valeric acid, and (iv), which was not identified, appeared to be phenolic.

The aqueous residue from the steam distillation was extracted with ether; this left on evaporation an oil, which partly solidified. The solid after crystallisation from water had m. p. 176° and was identified as homophthalic acid [Found : C, 59·6; H, 5·0; *M* (Rast), 185. Calc. for $C_9H_8O_4$: C, 60·0; H, 4·4% ; *M*, 180]. The amide had m. p. 180—181° and the *p*-nitrobenzyl ester, m. p. 135°. The liquid acids remaining after removal of the homophthalic acid were converted through their silver salts into the methyl esters. These, on fractionation, gave an oil, b. p. 88—95°/8 mm., which consisted essentially of methyl methylsuccinate, since it gave an amide, m. p. 224°, and a *diphenacyl* ester, m. p. 101° (Found : C, 69·0; H, 5·8. $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·4%). The higher-boiling fractions contained, in addition to homophthalic acid, two other acids which were not obtained pure.

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