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The Triterpenes of *Faradaya splendida* (Verbenaceae)

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Abstract

Extraction of the roots of *Faradaya splendida* F. Muell. has yielded 3-*O*-acetyloleanolic aldehyde, 3-*O*-acetylerythrodiol and a very small amount of the potassium salt of a new polyhydroxy triterpene diacid, $C_{30}H_{46}O_{11}$, named faradoic acid.

Faradaya splendida (Verbenaceae) is a native of Queensland, Australia, and is a reputed aboriginal fish poison. The active principle is reported to be a saponin, and extracts have shown strong hemolytic activity.[1]

Extraction of the dried roots of *F. splendida* with light petroleum gave a mixture of free triterpenes which could be separated chromatographically into two major components, identified as 3-*O*-acetyloleanolic aldehyde and 3-*O*-acetylerythrodiol. The isolation of these two triterpenes from another plant, *Machaerium incorruptibile*, has been previously reported and the biogenetic significance of their co-occurrence discussed.[2]

The plant was next extracted with ether and finally with methanol. The ether extraction gave only intractable material, but during the extraction with methanol a small amount of amorphous material (*c.* 0·05%) separated out. This substance was insoluble in organic solvents but dissolved readily in water, giving a solution which formed a large, stable froth on shaking, suggesting that it is this compound which gives *F. splendida* the reputation of containing saponins. Acidification (H_2SO_4) of the aqueous solution gave potassium sulphate and an organic acid, 'faradoic acid', which crystallized from methanol and formed a crystalline methyl ester. Faradoic acid and its methyl ester were insoluble in water and only very sparingly soluble in organic solvents. Elementary analyses corresponded to the formula $C_{30}H_{46}O_{11}$ for faradoic acid and to $C_{32}H_{50}O_{11}$ for methyl faradoate. No accurate estimation of molecular weight could be obtained: mass spectrum analysis of methyl faradoate gave no definite peaks above *m/e* 442, and molecular weight determinations by other conventional means could not be effected satisfactorily because of the poor solubility of the acid and its ester. Nevertheless, Zeisel methoxyl analyses of methyl faradoate were in excellent agreement with the formulation of faradoic acid as a dicarboxylic acid with

[1] Webb, L. J., 'Guide to the Medicinal and Poisonous Plants of Queensland' CSIRO Bull. No. 232, p. 168 (CSIRO: Melbourne 1948).
[2] Alves, H. M., Arndt, V. H., Ollis, W. D., Eyton, W. B., Gottlieb, O. R., and Magalhães, M. T., *Phytochemistry*, 1966, **5**, 1327.

the above molecular formula. Faradoic acid and methyl faradoate gave positive Liebermann–Burchard tests and the n.m.r. spectra (deuterated dimethyl sulphoxide) of faradoic acid and of methyl faradoate showed the characteristic pattern of tertiary methyl signals of triterpenes in the region of δ 0·8–1·4 p.p.m. A multiplet at δ 5·5 indicated the presence of at least one vinyl proton. The infrared spectrum (Nujol) of methyl faradoate showed absorption at 1737sh, 1720 (carbonyl) and at 3590 and 3450 cm^{-1} (hydroxyl). Attempts to acetylate faradoic acid or methyl faradoate under a variety of conditions gave complex mixtures.

Experimental

General experimental procedures which have been described previously[3] apply to the work described below.

Extraction of F. splendida *with Light Petroleum*; *3-O-Acetyloleanolic Aldehyde and 3-O-Acetylerythrodiol*

The milled dried roots (1·2 kg) of *F. splendida* were extracted (Soxhlet) with light petroleum for 48 h. The extract was concentrated to 150 ml and allowed to stand to give crystals (2·6 g). The crystals were chromatographed on Peter Spence grade H alumina (100 g); elution with light petroleum–benzene (2 : 1, 1·5 l.; 1 : 1, 500 ml) and benzene (0·5 l.) gave 3-*O*-acetyloleanolic aldehyde (1·56 g) which was recrystallized from light petroleum–benzene. It had m.p. 236–239°, $[\alpha]_D$ +61·5° (lit.[2] 225–226°, +57°); it had the expected i.r. and n.m.r. spectra which were also in agreement with the details of the published spectra.[2] Reduction by lithium aluminium hydride gave erythrodiol which was identical (m.p., mixed m.p., $[\alpha]_D$, i.r. and n.m.r. spectra) with an authentic specimen.

Elution of the column with benzene–chloroform (4 : 1, 1 l.) gave traces of material only, and further elution with benzene–chloroform (1 : 1, 750 ml; 1 : 3·5, 1 l.) gave 3-*O*-acetylerythrodiol which was recrystallized from methanol; it had m.p. 239–241°, $[\alpha]_D$ +72° (lit.[2] 237–239°, +71°) and the expected i.r. and n.m.r. spectra which were in agreement with the details of the published spectra.[2]

Extraction of F. splendida *with Methanol*; *Faradoic Acid*

Extraction of the roots with ether gave only very small amounts of intractable material. The roots were then continuously extracted with methanol whereupon an amorphous solid separated out; this was removed by filtration, dissolved in water and precipitated by addition of methanol to give a white, amorphous powder (0·7 g), m.p. >360°, insoluble in all common organic solvents; ν_{max} (Nujol) 3300, 1710, 1700 and 1610 cm^{-1}.

The compound (0·7 g) was dissolved in water (50 ml) and acidified with 2N H_2SO_4. After being allowed to stand for 45 min the precipitated material was collected (the filtrate contained K_2SO_4) and recrystallized three times from methanol to give *faradoic acid* (0·28 g) as needles, m.p. 330–333°, $[\alpha]_D$ (pyridine) +22°; ν_{max} (Nujol) 3540, 3300, 3000–2700, 1737, 1710, 1250, 1040, 910 and 860 cm^{-1} (Found: C, 61·2; H, 7·9; O, 29·9. $C_{30}H_{46}O_{11}$,0·5H_2O requires C, 60·9; H, 8·0; O, 31·1%). Faradoic acid (0·1 g) was methylated with an excess of ethereal diazomethane to give *methyl faradoate* which was recrystallized from methanol to give needles (0·08 g), m.p. 229–231°, $[\alpha]_D$ (methanol) +23°; ν_{max} (Nujol) 3590, 3450, 3010, 1735sh, 1720, 1605, 1255, 1212 and 1030 cm^{-1} (Found: C: 62·0, 62·5; H, 8·1, 8·2; OMe, 10·1, 10·2. $C_{32}H_{50}O_{11}$ requires C, 62·9; H, 8·3; 2×OMe, 10·2%).

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[3] Eade, R. A., McDonald, F. J., and Simes, J. J. H., *Aust. J. Chem.*, 1973, **26**, 839.