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Some Extractives of *Melicope octandra* (Rutaceae)

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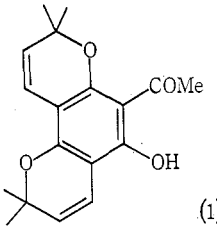
Abstract

From the leaves of *Melicope octandra* (F. Muell.) Druce were isolated multiflorenol, β-sitosterol, melisimplexin, meliternatin and 'octandrenolone' (6-acetyl-2,2,8,8-tetramethyl-2*H*,8*H*-benzo[1,2-*b*:3,4-*b*']dipyran-5-ol), each in small yield. The main constituents of the bark were multiflorenol and meliternatin; small amounts of β-sitosterol, glutinol, globulol, melisimplexin and octandrenolone were also isolated. The wood gave a small yield of β-sitosterol.

In continuation of our studies[1] on the phytochemistry of members of the Rutaceae we have examined *Melicope octandra* (F. Muell.) Druce. This is a small tree up to 20 m high and 20 cm stem diameter which occurs in eastern Australia from the Clarence River in New South Wales to northern Queensland.

Webb[2] obtained a weakly positive spot test for alkaloids in the leaves and bark, but no other chemical examination of the species appears to have been made. In the present work the leaves, bark and wood were each extracted with light petroleum, ether and methanol and the extracts worked up systematically. No alkaloids could be detected but both the bark and the leaves yielded the flavonoids, melisimplexin and meliternatin. Since flavonoids may display distinctly basic properties (cf. Briggs and Locker[3]), the apparent discrepancy in the two sets of results is explicable. In addition to the flavonoids, the leaves yielded the triterpenoids multiflorenol and β-sitosterol and a substance, 'octandrenolone', all in small amounts. As well as the two flavonoids the bark gave multiflorenol as a major component, and smaller amounts of β-sitosterol and glutinol, the sesquiterpene, globulol, and octandrenolone. The wood gave a small yield of β-sitosterol.



(1)

[1] Croft, J. A., Ritchie, E., and Taylor, W. C., *Aust. J. Chem.*, 1975, **28**, 2019, 2093.
[2] Webb, L. J., CSIRO (Aust.) Bull., No. 268, p. 85 (1952).
[3] Briggs, L. H., and Locker, R. H., *J. Chem. Soc.*, 1949, 2157.

The structure of octandrenolone, $C_{18}H_{20}O_4$, was deduced as 6-acetyl-2,2,8,8-tetramethyl-2*H*,8*H*-benzo[1,2-*b*:3,4-*b*']dipyran-5-ol (1) from its spectroscopic properties and confirmed by direct comparison with a synthetic specimen.[4] So far as we are aware its natural occurrence has not been previously reported.

Experimental

General directions are as in Corrie *et al.*[5] The plant material (CSIRO SN9041) was collected at Mt Nardi, northern New South Wales. Substances isolated were identified by comparison (mixed m.p., i.r., and n.m.r. spectroscopy) with authentic specimens.

Extraction of the Leaves

The air-dried milled leaves (18·2 kg) were extracted at room temperature successively with light petroleum, ether and methanol.

The light petroleum extract was concentrated to a small bulk and refrigerated. The amorphous material (3·75 g) that separated appeared from its i.r. and n.m.r. spectra to consist of esters of long chain alcohols and was not further examined. The filtrate was freed of solvent, then dissolved in ether and the solution extracted with 1N hydrochloric acid, 2% sodium carbonate and 2% sodium hydroxide. The basic fraction was negligible. The acidic fractions (69 g and 10·5 g) consisted of fatty acids (i.r. and n.m.r. spectroscopy) and were not examined further. The neutral fraction (215 g) was separated into 'non-oxygenated' and 'oxygenated' fractions by partitioning between light petroleum–benzene (1 : 1) and methanol–water (9 : 1). The non-oxygenated fraction (200 g) was chromatographed on alumina; a mixture of alkanes (30·6 g), multiflorenol (1·1 g), m.p. 188–190°, β-sitosterol (1·5 g), m.p. 135°, and meliternatin (0·07 g), m.p. 203°, were eluted in turn. The oxygenated fraction (15 g) similarly yielded meliternatin (0·08 g).

The ether extract was worked up by the same procedure. The basic fraction was again negligible. The acid fractions (846 g) apparently consisted of fatty acids. The neutral fraction (267 g) gave eventually alkanes (16·0 g), multiflorenol (0·65 g), β-sitosterol (0·6 g), meliternatin (3·1 g), melisimplexin (1·8 g), m.p. 185°, and octandrenolone (1·05 g), m.p. 91°, after purification by t.l.c.

The methanol extract was concentrated and then shaken with ether and water. The aqueous layer was discarded. The ether extract gave an acidic fraction (96 g) and a neutral fraction (310 g). The latter after working up as above yielded meliternatin (0·7 g).

Total yields were: multiflorenol, 0·006%; β-sitosterol, 0·012%; meliternatin, 0·022%, melisimplexin, 0·0099%; octandrenolone, 0·0058%.

Extraction of the Bark

The air-dried, milled bark (19·6 kg) was extracted as above with light petroleum, ether and methanol.

The light petroleum extract after concentration deposited crude meliternatin (2·2 g). The remainder of the light petroleum was removed and the residue dissolved in methanol, whereupon after standing more meliternatin (5·0 g) separated. Solvent was removed and the residue dissolved in ether. The solution was fractionated and the several fractions worked up as above. The large acidic fractions (188 g and 114 g respectively) again appeared to consist of fatty acids. The neutral fractions (305 g) deposited multiflorenol (29·0 g) from methanol, and after chromatography, saponification and further chromatography gave alkanes (10·9 g), multiflorenol (7·57 g), β-sitosterol (1·92 g), melisimplexin (1·34 g), meliternatin (1·54 g), octandrenolone (0·513 g), glutinol, m.p. 209–212°, (0·175 g) and globulol, m.p. 89–90° (0·175 g).

The ether extract was processed as above. Meliternatin (6·9 g) separated from the methanol solution. The acidic fractions were again large (310 g and 107 g respectively). The neutral fractions afforded melisimplexin (1·03 g), meliternatin (0·42 g), octandrenolone (0·48 g), multiflorenol (0·12 g) and β-sitosterol (0·32 g).

The methanol extract was concentrated, diluted with water and the mixture extracted first with ether and then with chloroform.

[4] Donnelly, W. J. G., and Shannon, P. V. R., *J. Chem. Soc., Perkin Trans. 1*, 1972, 25.
[5] Corrie, J. E. T., Green, G. H., Ritchie, E., and Taylor, W. C., *Aust. J. Chem.*, 1970, **23**, 133.

The chloroform extract was evaporated and the residue dissolved in a little methanol. Meliternatin (1·0 g) separated on standing.

The ether extract on working up as above gave acidic fractions (98 g and 21 g respectively), meliternatin (3·56 g), melisimplexin (0·45 g), multiflorenol (0·51 g), β-sitosterol (0·14 g) and globulol (0·49 g).

Total yields were: meliternatin, 0·11%; melisimplexin, 0·014%; multiflorenol, 0·19%; β-sitosterol, 0·012%; glutinol, 0·0009%; globulol, 0·0034%; octandrenolone, 0·0051%.

Extraction of the Wood

The wood shavings (18·1 kg) were extracted as above. The combined light petroleum and ether extracts gave small acidic fractions (3·3 g and 1·1 g respectively) and a neutral fraction (40 g). The latter was saponified and the neutral product chromatographed. Only β-sitosterol (0·6 g, 0·0033% yield) could be isolated. The material in the methanol extract (4·5 g) gave no crystalline material.

Acknowledgments

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Corrigendum

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P. 1142, first line of fifth new paragraph: *For* No close analogues of (4) with η^5-C_4O groups have been reported *read*

Only one close analogue of (4) has been reported (Bannister, W. D., Green, M., and Haszeldine, R. N., *J. Chem. Soc. A*, 1966, 194).