Aust. J. Chem., 1975, **28**, 1393–5

The Chemical Constituents of Australian *Flindersia* Species. XX* An Examination of *F. pimenteliana*

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Abstract

The bark of *F. pimenteliana* F. Muell. yielded seselin, xanthyletin, betulin, sitosterol and traces of dictamnine and skimmianine. The leaves gave rutin, skimmianine, betulin and sitosterol. From the wood only sitosterol could be isolated and a trace of alkaloid detected.

In continuation of studies[1] of the extractives of members of the genus *Flindersia* (for a recent taxonomic review of the genus see[2]) the bark, leaves and wood of *F. pimenteliana* F. Muell. have been examined. This species is a large rain forest tree found in northern Queensland and New Guinea. The timber is used commercially under the names 'rose silkwood', 'red beech' and 'maple silkwood'.

Extraction of the bark with light petroleum, ether and methanol and workup of the extracts by conventional procedures gave seselin as the major extractive with smaller amounts of xanthyletin, betulin and sitosterol, and traces of dictamnine and skimmianine. The small amount of psoromic acid isolated probably originated from lichens growing on the bark. In contrast, the leaves yielded skimmianine and rutin as major products with smaller amounts of betulin and sitosterol. The wood afforded only sitosterol in a small amount and only a trace of alkaloid could be detected.

Furoquinoline alkaloids, coumarin derivatives, triterpenes and flavonoids have been found in other *Flindersia* species,[3] and thus *F. pimenteliana* is not chemically unusual.

Experimental

General directions are as in Corrie *et al.*[4] Known substances were identified by comparison with authentic specimens (mixed m.p. and comparison of i.r. and n.m.r. spectra).

Extraction of the Bark

(i) The dried milled bark (16 kg) (CSIRO SN TGH 10,493; collected in New Guinea) was exhaustively extracted at room temperature in turn with light petroleum, ether and methanol and the extracts concentrated. Any material which separated was removed by filtration. The methanol extract was shaken with ether and a large volume of water and the aqueous layer discarded.

* Part XIX, *Aust. J. Chem.*, 1966, **19**, 455.

[1] Breen, C. J. W., Ritchie, E., Sidwell, W. T. L., and Taylor, W. C., *Aust. J. Chem.*, 1966, **19**, 455.
[2] Hartley, T. G., *J. Arnold Arbor. Harv. Univ.*, 1969, **50**, 481.
[3] Ritchie, E., *Rev. Pure Appl. Chem.*, 1964, **14**, 47.
[4] Corrie, J. E. T., Green, G. H., Ritchie, E., and Taylor, W. C., *Aust. J. Chem.*, 1970, **23**, 133.

The three extracts after dilution with ether were washed successively with 2% hydrochloric acid, 5% sodium bicarbonate, 2% sodium carbonate and 2% sodium hydroxide. The remaining neutral fraction was partitioned in the usual manner between benzene–light petroleum (1 : 1) and methanol–water (9 : 1) to yield 'non-oxygenated' and 'oxygenated' neutral fractions.

(ii) Material (8·0 g) deposited from the light petroleum extract was essentially seselin, m.p. 119–120°. A second crop was a mixture; washing with acetone removed a small amount of seselin and left a product which crystallized from chloroform–acetone as a colourless solid, m.p. 83–84°, identified by i.r. and n.m.r. spectroscopy as a long chain ester; it was not examined further.

(iii) Amorphous material deposited from the ether extract was intractable and was discarded.

(iv) The light petroleum bicarbonate-soluble fraction (0·5 g) and the corresponding fraction of the methanol extract (2·0 g) yielded no pure substance on chromatography on silica gel. The fraction (5·0 g) from the ether extract however gave a solid on elution with benzene–ether (9 : 1), which on recrystallization from ethanol afforded psoromic acid (0·047 g; 0·003% yield), m.p. 275–276° (dec.).

(v) The three carbonate-soluble extracts (total 24 g) on chromatography gave only fatty acids which were not further examined.

(vi) The three 'phenolic' fractions (total 15 g) yielded no crystalline substances and were discarded.

(vii) The combined basic fractions (2·1 g) were chromatographed on alumina. Dictamnine (0·0015 g; 0·00001% yield), m.p. 130°, was eluted by benzene–ether (3 : 1), and skimmianine (0·012 g; 0·00075% yield), m.p. 179°, by benzene–ether (1 : 1).

(viii) The light petroleum 'oxygenated' neutral fraction (129 g) was chromatographed on alumina. Seselin (20 g) was eluted by benzene, xanthyletin, m.p. 128–130° (2·1 g), by benzene–ether (98 : 2) and sitosterol (0·3 g), m.p. 136–138°, by benzene–ether (1 : 1).

(ix) The light petroleum 'non-oxygenated' neutral fraction (35 g) was chromatographed on alumina. A paraffin mixture (5 g) was eluted by light petroleum, seselin (0·5 g) by light petroleum–benzene (1 : 1) and sitosterol (0·5 g) by benzene–ether (3 : 1). All other fractions were combined and saponified with hot 10% ethanolic potassium hydroxide. The neutral material (12 g) was chromatographed on alumina to yield betulin, m.p. 248–250° (4·0 g), eluted by benzene–ether (1 : 1) and sitosterol (2·0 g) eluted by ether.

(x) The ether 'oxygenated' neutral fraction (15 g) after extensive chromatography on alumina afforded seselin (2·1 g), xanthyletin (0·5 g) and betulin (0·035 g).

(xi) The ether 'non-oxygenated' neutral fraction similarly gave seselin (0·5 g), sitosterol (0·5 g) and betulin (1·1 g).

(xii) Chromatography of the methanol 'oxygenated' neutral fraction (10·0 g) yielded seselin (4·1 g) and xanthyletin (0·5 g).

(xiii) The methanol 'non-oxygenated' neutral fraction (16 g) was chromatographed to yield seselin (0·5 g) and betulin (1·0 g).

Final yields were: seselin (35·7 g; 0·22%), xanthyletin (3·1 g; 0·019%), sitosterol (3·3 g; 0·02%) and betulin (6·1 g; 0·038%).

Extraction of the Leaves

(i) The dried milled leaves (20 kg) from the same source as the bark were extracted and the extracts worked up as for the bark. The crude extracts were large (700, 250 and 5000 g respectively) but each yielded only relatively small amounts of crystalline substances.

(ii) One fifth of the concentrated methanol extract was shaken with water and ether. On keeping, crude rutin (60 g; yield 1·5%) separated. Crystallization from water gave light yellow needles, m.p. 188–190°.

(iii) The concentrated ether extract deposited crude skimmianine (12 g), colourless needles from benzene, m.p. 178–179°. The combined crude basic fractions (about 20 g) on chromatography yielded more skimmianine (8 g; total yield, 0·1%).

(iv) The acidic fractions (40, 24 and 15 g respectively) in the bicarbonate and carbonate extracts gave only fatty acids which were not further examined.

(v) The phenolic fractions (3, 36 and 15 g respectively) were intractable and were discarded.

(vi) The 'oxygenated' neutral fractions (39 and 26 g) of the light petroleum and ether extracts respectively on chromatography gave sitosterol (0·2 g; total yield, 0·001%) and betulin (1·5 g). Saponification of other fractions followed by chromatography of the neutral portion gave no useful result.

(vii) The total neutral fraction of the methanol extract (75 g) was intractable and was discarded.

(viii) A portion (40 g) of the 'non-oxygenated' neutral fraction of the light petroleum extract (about 600 g) on chromatography gave only a solid mixture (3·1 g), m.p. 64–68°, of alkanes, not examined further. Further small amounts of the same mixture were obtained after saponification.

(ix) A portion (25 g) of the 'non-oxygenated' neutral fraction (about 120 g) of the ether extract on chromatography afforded betulin (0·5 g; total yield, 0·02%). No further material could be isolated by saponification followed by chromatography.

Extraction of the Wood

(i) The milled wood (8·86 kg) (SN 8818, collected near Atherton) was extracted with light petroleum, ether and methanol and the extracts worked up as above.

(ii) The combined basic fractions after chromatography on alumina gave only a trace of alkaloid which was too small for further examination and identification.

(iii) The combined acidic fractions (10·2 g) yielded only fatty acids which were not further examined.

(iv) The phenolic fraction (total 2·4 g) was intractable.

(v) By chromatography, sitosterol (1·3 g) was isolated from the neutral light petroleum fractions (52 g). No substance could be isolated from the neutral ether extract (9·0 g) but a further amount of sitosterol (0·2 g) was obtained from the neutral methanol extract (6·5 g). Saponification of other fractions followed by chromatography failed to yield additional substances. The total yield of sitosterol was 0·017%.

Acknowledgments

The authors are grateful to the Australian Government for the award of fellowship to one of them (P.K.N.), and to Dr T. G. Hartley and Mr V. K. Moriarty, CSIRO, for the collection and identification of the plant material. This work was supported by a grant from the Australian Research Grants Committee.

Manuscript received 28 February 1975

Corrigendum

Volume 28, Number 3

p. 547, second last line; *for* furanose (200 g) *read* furanose (300 g)