## THE CHEMICAL CONSTITUENTS OF AUSTRALIAN FLINDERSIA SPECIES\*

XIII. THE CONSTITUENTS OF FLINDERSIA BENNETTIANA F. MUELL.

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Flindersia Bennettiana F. Muell. is a large tree found in the rain-forests of eastern Australia, ranging from the Clarence River to Maryborough. The wood finds some use in cabinet-making and is known commercially as "Bennett's ash".

The bark, leaves, and wood have now been systematically extracted and some of the constituents isolated and identified, the results being presented in Table 1. As with several other members of the genus, some of the extracts yielded sizable "acidic" and "phenolic" fractions from which pure substances

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could not be isolated. It may also be noted that the *iso*pimpinellin isolated had the pale yellow colour, described originally by Wessely and Kallab (1931), which extensive purification did not eliminate.

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Substance	Bark (%)	Leaves (%)	Wood (%)
Osthol	0.14	0.016	0.0032
Seselin	0.039	0.0066	0.0013
isoPimpinellin	0.014		_
Flindersiamine	0.0020	0.00052	
Skiammianine	0.00025		_
Maculine		_	0.00065
Sitosterol	0.010	0.0028	0.0059

Table 1
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## Experimental

Melting points are uncorrected. Light petroleum refers to the fraction of b.p. 60–90 °C. The ultraviolet spectrum was measured in purified ethanol with a Hilger Uvispek and infra-red spectra in paraffin mulls with a Perkin–Elmer Infracord 137. The general procedure for extraction and isolation that was followed has been outlined in Part XII of this series (Ritchie, Taylor, and Willcocks 1960). Substances isolated were identified by direct comparison (mixed m.p.'s and infra-red spectra) with authentic specimens.

(a) Extraction of the Bark.—The bark  $(26 \cdot 0 \text{ kg})$  had been collected at Imbil, Queensland (C.S.I.R.O. SN 6033).

The light petroleum extract gave a crude alkaloid fraction which, after being combined with a similar fraction from the ether extract, yielded on chromatography on alumina, flindersiamine (0.37 g) and skiammianine (0.045 g). After removal of acidic and phenolic fractions, the residual dark oil was dissolved in light petroleum (2 volumes) and the solution refrigerated for several days, when crude osthol (24·3 g) separated. The material in the filtrate on cold saponification yielded a neutral fraction, which on chromatography on alumina, afforded sitosterol (0.93 g), and a lactone fraction, which crystallized on scratching. Two recrystallizations from methanol gave osthol (1.82 g). The combined mother liquors were evaporated and the residue chromatographed on alumina. The light petroleum, benzene, and ether eluates yielded colourless crystalline material melting over the range 65-75 °C. Attempts to separate the constituents of this mixture by chromatography, fractional crystallization, or by fractional sublimation or distillation, were unsuccessful. However, when a dilute solution in light petroleum was allowed to evaporate at room temperature a mixture of needles and large prisms formed which it was possible to separate manually. On recrystallization from light petroleum, the needles afforded osthol (2.84 g), and the prisms, seselin (7.68 g). The chloroform eluates contained isopimpinellin which separated from methanol in pale yellow needles (0.21 g) (light absorption: ultraviolet,  $\lambda_{\text{max}}$ , 223,240–250 (plateau), 270, and 312 m $\mu$ ; log  $\epsilon$  4·25, 3·98, 4·11, and 3·93 respectively).

The ether extract gave an alkaloid fraction which was combined with that from the light petroleum extract (see above). After removal of the acid and phenolic fractions, the neutral fraction was dissolved in benzene-ether (4 volumes, 5:1) and refrigerated for several weeks, when isopimpinellin  $(1\cdot52~\mathrm{g})$  crystallized out. The remainder of the material after cold saponification yielded osthol  $(2\cdot23~\mathrm{g})$ , seselin  $(0\cdot93~\mathrm{g})$ , and sitosterol  $(1\cdot43~\mathrm{g})$ .

The acetone extract was concentrated and the residue shaken with ether and water. The ethereal solution on working up in the usual manner gave flindersiamine (0.156 g), skimmianine (0.02 g), osthol (1.72 g), seselin (1.5 g), isopimpinellin (1.87 g), and sitosterol (0.19 g).

The methanol extract was treated in the same way as the acetone extract and afforded osthol (0.54 g), seselin (0.093 g), isopimpinellin (0.07 g), and sitosterol (0.15 g).

- (b) Extraction of the Leaves.—The leaves  $(16\cdot1 \text{ kg})$  were extracted successively with light petroleum, ether, and methanol. The light petroleum extract yielded osthol  $(1\cdot08\text{ g})$  and seselin  $(0\cdot46\text{ g})$ , the ether extract, osthol  $(0\cdot83\text{ g})$ , seselin  $(0\cdot31\text{ g})$ , and sitosterol  $(0\cdot37\text{ g})$ , and the methanol extract, flindersiamine  $(0\cdot083\text{ g})$ , osthol  $(0\cdot73\text{ g})$ , seselin  $(0\cdot29\text{ g})$ , and sitosterol  $(0\cdot08\text{ g})$ .
- (c) Extraction of the Wood.—The wood  $(14\cdot5\,\mathrm{kg})$  was treated as in (b) above. The light petroleum extract afforded maculine  $(0\cdot033\,\mathrm{g})$ , osthol  $(0\cdot35\,\mathrm{g})$ , seselin  $(0\cdot11\,\mathrm{g})$ , and sitosterol  $(0\cdot28\,\mathrm{g})$ , the ether extract, maculine  $(0\cdot058\,\mathrm{g})$ , osthol  $(0\cdot11\,\mathrm{g})$ , seselin  $(0\cdot082\,\mathrm{g})$ , and sitosterol  $(0\cdot57\,\mathrm{g})$ , and the methanol extract, maculine  $(0\cdot004\,\mathrm{g})$ .

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## References

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