The remaining ethereal solution was concentrated to a dark brown oil (40 g), which was mixed with methanol (100 ml). After several days the crystalline material (5 g) which had separated was collected and identified after purification as sitosterol.

The methanol filtrate was evaporated and the residue saponified by keeping its solution in 10% aqueous alcoholic potassium hydroxide for 2 days at room temperature. The reaction mixture on working up yielded no crystalline acidic fractions but a further amount of sitosterol (1 g) was obtained by chromatography.

The ether extract was separated into basic, acidic, and neutral fractions as above. The combined light petroleum and ether basic fraction was dissolved in chloroform and the solution passed through a short column of alumina to remove dark impurities. The material (2 g) in the eluate on chromatography on alumina (60 g) yielded maculine (0.31 g) and flindersiamine (0.94 g).

No crystalline material could be obtained from the small acidic and phenolic fractions, but the neutral fraction after saponification gave sitosterol (1.0 g).

The acetone extract deposited a dark brown solid which, after washing with warm ethanol and recrystallization from a large volume of methanol, afforded hesperidin (14 g).

The acetone filtrate was concentrated and the residue shaken with ether and water. The ethereal extract on working up as above yielded maculine (0.18 g) and flindersiamine (0.8 g).

The methanol extract was treated by the same procedure as that used for the acetone extract. Hesperidin (20 g) and maculine (0.46 g) were isolated.

(b) Extraction of the Leaves.—The leaves (17 kg) were processed by the above methods. The acetone extract gave hesperidin (6 g).

(c) Extraction of the Wood.—The finely milled yellow wood (6.9 kg) yielded hesperidin (1.2 and 2.3 g) in the acetone and methanol extracts respectively.

The authors are indebted to Mr. W. T. Jones, C.S.I.R.O., Brisbane, for supplying the plant material.

THE CHEMICAL CONSTITUENTS OF AUSTRALIAN FLINDERSIA SPECIES*

XIII. THE CONSTITUENTS OF FLINDERSIA BENNETTIANA F. MUELL.

By M. N. GALBRAITH,† E. RITCHIE,† and W. C. TAYLOR†

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 isopimpinellin isolated had the pale yellow colour, described originally by Wessely and Kallab (1931), which extensive purification did not eliminate.

TABLE 1

THE CONSTITUENTS OF F. BENNETTIANA

<table>
<thead>
<tr>
<th>Substance</th>
<th>Bark (%)</th>
<th>Leaves (%)</th>
<th>Wood (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osthol</td>
<td>0.14</td>
<td>0.016</td>
<td>0.0082</td>
</tr>
<tr>
<td>Seselin</td>
<td>0.039</td>
<td>0.0066</td>
<td>0.0013</td>
</tr>
<tr>
<td>isopimpinellin</td>
<td>0.014</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Flindersiamine</td>
<td>0.0020</td>
<td>0.00052</td>
<td>—</td>
</tr>
<tr>
<td>Skimmianine</td>
<td>0.00025</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Maculine</td>
<td>—</td>
<td>—</td>
<td>0.0065</td>
</tr>
<tr>
<td>Sitosterol</td>
<td>0.010</td>
<td>0.0028</td>
<td>0.0050</td>
</tr>
</tbody>
</table>

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 Willoccks 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 (26.0 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 skimmianine (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, λmax 223,240–250 (plateau), 270, and 312 μμμμ; log ε 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 (1.52 g) crystallized out. The remainder of the material after cold saponification yielded osthol (2.23 g), seselin (0.93 g), and sitosterol (1.43 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 (16.1 kg) were extracted successively with light petroleum, ether, and methanol. The light petroleum extract yielded osthol (1.08 g) and seselin (0.46 g), the ether extract, osthol (0.83 g), seselin (0.31 g), and sitosterol (0.37 g), and the methanol extract, flindersiamine (0.083 g), osthol (0.73 g), seselin (0.29 g), and sitosterol (0.08 g).

(c) Extraction of the Wood.—The wood (14.5 kg) was treated as in (b) above. The light petroleum extract afforded maculine (0.033 g), osthol (0.35 g), seselin (0.11 g), and sitosterol (0.28 g), the ether extract, maculine (0.058 g), osthol (0.11 g), seselin (0.082 g), and sitosterol (0.57 g), and the methanol extract, maculine (0.004 g).

The authors are indebted to Professor F. Galinovsky and Professor F. Wessely, University of Vienna, for authentic specimens of seselin and iso-pimpinellin respectively, and to Mr. W. T. Jones, C.S.I.R.O., Brisbane, for supplying the plant material.

References

Corrigenda

VOLUME 13, NUMBER 1

Page 9, caption to Figure 7: For \( x \) read \( w \).
Page 17, equation (A25): For \( (1-m)/m \) read \( m/(1-m) \).

VOLUME 13, NUMBER 2

Page 232, Table 2, opposite Acetone: For item 3227 read 3277.