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THE CHEMICAL CONSTITUENTS OF AUSTRALIAN *FLINDERSIA* SPECIES

IV. THE CONSTITUENTS OF FLINDERSIA BOURJOTIANA F. MUELL.*

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Flindersia bourjotiana F. Muell. is a large tree found in the rain-forest of the Atherton Tableland, Queensland. It attains a height of about 120 ft. and a stem diameter of up to 30 in. The standard timber name is Queensland silver ash. When the bark is cut it is pinkish brown in colour becoming yellower towards the sapwood.

From a concentrated methanolic extract of the bark, a high yield of a colourless, crystalline substance, m.p. 256-257 °C. (decomp.) was obtained and identified as the well-known glycoside hesperidin from its constants and by comparison with an authentic specimen. The extract also yielded a small amount of colourless, crystalline, basic product, m.p. 182–183 °C. This melting point was unaltered on repeated crystallization from methanol, and a paper partition chromatogram gave only a single spot, but further examination revealed that the product was a mixture of skimmianine and flindersiamine (Anet *et al.* 1952).

Experimental

All melting points are uncorrected. Analyses are by Dr. Weiler and Dr. Strauss, Oxford.

(i) Extraction of the Bark and Isolation of Hesperidin.—The milled bark was boiled with methanol repeatedly, the extracts filtered hot and evaporated until crystallization commenced. The crude glycoside (yield 1.4%) was filtered off and washed with a large volume of methanol. The substance was best purified by dissolving it in a large volume of boiling methanol, then evaporating the solution until crystallization began, when it was obtained as colourless microneedles, m.p. and mixed m.p. with an authentic specimen of hesperidin 256-257 °C. (decomp.), $[\alpha]_{D}^{30^{\circ}}$ —77.5° (c 0.428 in pyridine) (lit. $[\alpha]_{D}^{20^{\circ}}$ —75.8°).

The acetate crystallized from methanol as colourless micro-needles, m.p. and mixed m.p. with hesperidin octa-acetate 175–176 °C., $[\alpha]_D^{21^\circ} - 45.8^\circ$ (c 1.038 in pyridine) (lit. $[\alpha]_D^{20^\circ} - 47.3^\circ$).

The aglycone, hesperitin crystallized from aqueous alcohol as needles, m.p. 227-229 °C. (decomp.) (lit. 226 °C.); its acetate crystallized from alcohol as colourless needles, m.p. 126-127 °C. (lit. 127-129 °C.).

(ii) Isolation of the Alkaloids.—The methanolic filtrate from the hesperidin was evaporated on the water-bath and the residue exhaustively extracted with chloroform. The chloroform solution was shaken repeatedly with 10% hydrochloric acid, the acid extracts basified with ammonia, and the crude product dissolved in benzene. This solution was run through a short

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column of alumina to remove coloured impurities, the pale yellow eluate evaporated, and the residue crystallized from methanol as colourless prisms (yield 0.03%), m.p. 182–183 °C. This product gave a single spot (with iodine) on a paper partition chromatogram using *n*-butanol-5% acetic acid, and the melting point was not raised on recrystallization from methanol or benzene. On warming with concentrated sulphuric acid the product gave a prussian blue coloured solution.

A partial separation of the component alkaloids was effected by extracting a solution of the product (2 g.) in benzene (200 ml.) with 10 ml. portions of 0.5% hydrochloric acid until practically no precipitate (A) was obtained on basifying the acid solution. The remainder of the alkaloids (B) in the benzene layer was extracted with 5% hydrochloric acid. Each of these acid extracts was treated with ammonia and the precipitated bases dissolved in the minimum volume of benzene. The solutions were then run through columns of alumina which were sufficiently long to adsorb completely all basic material, and each column was developed with benzene. Every 25 ml. of eluate was evaporated and the m.p. of each residue and the colour reaction with hot concentrated sulphuric acid was determined.

It was found that the first fractions from A gave a strongly positive colour test (prussian blue) and melted 180–185 °C. As the chromatogram was developed the colour test grew much weaker and the m.p. of the residue fell to 176-178 °C. These last fractions were combined and recrystallized from methanol when colourless prisms were obtained, m.p. and mixed m.p. with an authentic specimen of skimmianine from *Melicope fareana* F. Muell. (Crow and Price 1949) 175-176 °C. A concentrated sulphuric acid solution gave only a very pale green colour on warming, identical with the colour obtained with authentic skimmianine.

Found: N, 5.2; CH₃O, 35.6%.

Calculated for $C_{14}H_{13}O_4N$: N, 5.4; $3 \times CH_3O$, 35.9%.

The picrate formed flat, yellow needles from methanol, m.p. and mixed m.p. 192-194 °C.

The first benzene eluates from the column containing *B* had m.p. 204-208 °C. and gave a yery strong colour test. The m.p. of the later fractions gradually fell to about 190 °C. Those fractions of m.p. above 200 °C. were combined and crystallized from alcohol when colourless needles were obtained, m.p. and mixed m.p. with authentic flindersiamine from *Flindersia collina* 207-208 °C. The colourless solution in concentrated sulphuric acid became intensely prussian blue on warming.

Found : C, 61·4; H, 3·9%.

Calculated for $C_{14}H_{11}O_5N$: C, $61\cdot 5$; H, $4\cdot 1\%$.

The picrate crystallized as bright yellow laths from *n*-propanol, m.p. and mixed m.p. 200 $^{\circ}$ C. (decomp.).

Found: N, 11.1%.

Calculated for $C_{20}H_{14}O_{12}N_4$: N, 11.2%.

(iii) Separation of isoSkimmianine and isoFlindersiamine.—The product, m.p. 182–183 °C. (2 g.) in chloroform (1 ml.) was heated with methyl iodide (3 ml.) in a sealed tube at 100 °C. for 4 hours. The solution was evaporated to dryness and the residue extracted with cold benzene. The solution (C) was filtered from the insoluble residue (D) and chromatographed on alumina. Evaporation of the eluate and recrystallization of the residue from water yielded colourless needles, m.p. and mixed m.p. with *iso*skimmianine 184–185 °C. *iso*Skimmianine also gave a pale green solution on heating with concentrated sulphuric acid.

Found: C, 64.7; H, 5.3; N, 5.5%.

Calculated for $C_{14}H_{13}O_4N$: C, 64.9; H, 5.1; N, 5.4%.

Crystallization of D from benzene, then from aqueous alcohol, yielded fine colourless needles, m.p. and mixed m.p. with *iso*flindersiamine 208-209 °C. (decomp.); mixed m.p. with flindersiamine 160-170 °C. *iso*Flindersiamine gave a prussian blue coloured solution on warming with concentrated sulphuric acid.

Found : N, 5.0%.

Calculated for $C_{14}H_{11}O_5N$: N, 5.1%.

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(iv) Examination of a Synthetic Mixture of Skimmianine and Flindersiamine.—Approximately equal quantities of authentic skimmianine and flindersiamine were dissolved in hot methanol, the solution seeded with a crystal of the naturally-occurring mixture, and allowed to cool. Large, characteristic prisms were obtained, m.p. 183–184 °C., which did not depress the m.p. of the natural product.

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References

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