

# TRITERPENOID CONSTITUENTS OF *BACKHOUSIA ANGUSTIFOLIA* F. MUELL.\*

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The triterpene acids obtained from an extract of leaves and twigs of *Backhousia angustifolia* F. Muell. (Myrtaceae) have been separated by repeated chromatography of their methyl esters on alumina. The acids have now been identified as ursolic acid, oleanolic acid, and crataegolic acid.

The occurrence of crataegolic acid in *Backhousia angustifolia* is of some interest. This substance [which had been isolated previously from *Crataegus oxyacantha* L. (Rosaceae)<sup>1</sup> and *Psidium guajava* L. (Myrtaceae)<sup>2</sup>] has recently been shown to be identical with maslinic acid<sup>3</sup> from *Olea europaea* (Oleaceae) and to have the structure 2- $\alpha$ -hydroxyoleanolic acid.<sup>3,4</sup>

## Experimental

Infrared spectra were determined in chloroform solution or in KBr disks on a Perkin-Elmer 421 spectrophotometer. Rotations were determined in chloroform solution at 25°. Melting points were determined in capillaries, and are uncorrected. Woelm neutral alumina was used for chromatography. Voucher specimens (numbered LJW, JGT3401-3406) of the plant material investigated are lodged in the National Herbarium, Division of Plant Industry, CSIRO, Canberra.

### (a) Extraction and Preliminary Separation of the Crude Triterpene Acids

(i) Leaves and twigs were collected from several trees growing at Good Night Scrub, Queensland, in February 1958. The combined, air-dried material (5.4 kg) was milled, extracted with methanol (Soxhlet), the extract evaporated, and volatile oil removed by steam distillation. Isolation of the crude triterpene acids (which was incidental to another investigation<sup>5</sup>) was achieved by shaking an ethereal extract of the non-volatile residue with aqueous NaOH. The crude acids (43 g) were obtained as an amorphous solid.

(ii) The crude acids (20.0 g) were esterified with diazomethane (6.0 g) in methanol and the crude methyl esters chromatographed in benzene on alumina (activity I, 85 g) and eluted successively with benzene, chloroform, and methanol. An initial fraction of waxy material was obtained and the main bulk of material appeared in the benzene eluate as a brown oil. It was rechromatographed in a similar way. Elution with benzene gave a yellow, oily, solid A (5.0 g) and elution with chloroform yielded a deep brown oil. The combined residues from the chloroform eluates of two consecutive columns were rechromatographed in benzene on alumina (activity IV, 50 g). The benzene eluate gave a yellow-brown, semi-solid residue (3.5 g), but elution with

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<sup>1</sup> Tschesche, R., and Fugmann, R., *Chem. Ber.*, 1951, **84**, 810; Tschesche, R., Heesch, A., and Fugmann, R., *Chem. Ber.*, 1953, **86**, 626; Tschesche, R., and Poppel, G., *Chem. Ber.*, 1959, **92**, 320.

<sup>2</sup> Arthur, H. R., and Hui, W. H., *J. Chem. Soc.*, 1954, 1403.

<sup>3</sup> Caglioti, L., and Cainelli, G., *Tetrahedron*, 1962, **18**, 1061.

<sup>4</sup> Tschesche, R., Henckel, E., and Snatzke, G., *Liebigs Ann.*, 1964, **676**, 175.

<sup>5</sup> Cannon, J. R., and Corbett, N. H., *Aust. J. Chem.*, 1962, **15**, 168; Cannon, J. R., Corbett, N. H., Haydock, K. P., Tracey, J. G., and Webb, L. J., *Aust. J. Bot.*, 1962, **10**, 119.

benzene/chloroform (1 : 1), and chloroform, gave only brown, gummy residues. The semi-solid residue eluted with benzene was extracted with light petroleum (b.p. 60–80°) and this extract, on concentration, gave a yellow solid B (2.5 g). The insoluble residue was mixed with the gummy material from the later eluates of the chromatogram and rechromatographed in benzene on alumina (activity IV, 50 g) and eluted with benzene; a gummy residue was obtained. Upon trituration with ether, it gave a yellow solid C (0.4 g), m.p. 150–162°.

(b) *Methyl Crataegolate*

The yellow solid C was twice rechromatographed in benzene on alumina (activity IV). It crystallized from an ether/light petroleum mixture as colourless needles (0.14 g), m.p. 214–216°,  $[\alpha]_D^{25} +54 \pm 1^\circ$  (c, 0.6) (Found: C, 76.85; H, 10.5. Calc. for  $C_{31}H_{50}O_4$ : C, 76.5; H, 10.4%). Its identity with methyl crataegolate (lit.<sup>1</sup> m.p. 217–219°) was established by its mixed m.p. with an authentic sample kindly provided by Dr. R. Tschesche. The infrared spectra of the two samples were also identical.

(c) *Methyl Acetylursolate and Methyl Acetyloleanate*

(i) The combined solids A and B were chromatographed in benzene on alumina (activity II, 100 g). Elution with light petroleum and benzene/light petroleum (1 : 1) gave a yellow solid which crystallized from light petroleum as colourless needles (2.5 g), m.p. 104–105°. A portion (1.0 g) of this solid was acetylated with acetic anhydride and pyridine. The colourless, crystalline acetate (1.0 g) upon fractional crystallization from ethanol gave two products: D, m.p. 242–243°, obtained by combining the most soluble and least soluble fractions, and E, m.p. 216–218°, which comprised the middle fraction.

(ii) Product D (0.53 g) was recrystallized from methanol, whence it separated as colourless needles, m.p. 245–246°,  $[\alpha]_D^{25} +63 \pm 1^\circ$  (c, 1.1) (Found: C, 77.3; H, 10.1. Calc. for  $C_{33}H_{52}O_4$ : C, 77.3; H, 10.2%). The mixed m.p. with an authentic sample of methyl acetylursolate was undepressed and the infrared spectra of the two samples were identical. Hydrolysis of the acetate with alcoholic alkali gave methyl ursolate, m.p. 169–170°, undepressed by an authentic sample with which it also had an identical infrared spectrum.

(iii) Product E (0.11 g) crystallized from an acetone/methanol mixture as colourless needles, m.p. 220–221°,  $[\alpha]_D^{25} +72 \pm 1^\circ$  (c, 0.8) (Found: C, 77.2; H, 10.1. Calc. for  $C_{33}H_{52}O_4$ : C, 77.3; H, 10.2%). The substance did not depress the m.p. of authentic methyl acetyloleanate, and the infrared spectra of the two samples were identical.

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