# TRITERPENOIDS FROM THE BARK OF *AVICENNIA MARINA**

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*Avicennia marina*, commonly known as the grey mangrove, is distributed widely along the coast of New South Wales. It is used as a source of tannin in some countries and the very hard timber is used occasionally in boat-building. The bark has now been examined for neutral and acid constituents and was found to contain betulic acid (0·3%), taraxerol (0·06%), and taraxerone (0·05%). A minute amount of a hydrocarbon, probably triacontane, was also isolated.

## *Experimental*

Melting points are uncorrected and were determined in evacuated capillaries. Analyses were carried out by the C.S.I.R.O. Microanalytical Laboratory. Light petroleum refers to the fraction, b.p. 60–80 °C.

Chopped, dried bark (3 kg; collected along the Hunter River, Newcastle, N.S.W.) was extracted continuously with ether for 2 days. The extract (5 l.) was reduced to 1 l. and shaken with N NaOH. The precipitated sodium salt was filtered off and, without drying, purified by treatment of a solution in 50% alcohol (200 ml) with charcoal followed by acidification. The crude acid was dissolved in a 5% solution of KOH in 50% alcohol (200 ml), the solution treated with charcoal and then acidified. Recrystallization from methanol gave 8·5 g of betulic acid, m.p. 308–310 °C, $[\alpha]_D^{20}$ 10° (*c*, 0·4 in methanol) (Found: C, 78·4; H, 10·3%. Calc. for $C_{30}H_{48}O_3$: C, 78·9; H, 10·6%). The methyl ester, prepared by reaction with diazomethane and purified by chromatography over alumina, had m.p. 221–222 °C, $[\alpha]_D^{20}$ 4·8° (*c*, 1·1 in chloroform) (Found: C, 78·9; H, 10·7%. Calc. for $C_{31}H_{50}O_3$: C, 79·1; H, 10·7%). White (1956) records for betulic acid, m.p. 320–321 °C, $[\alpha]_D$ 12° and its methyl ester, m.p. 224–225 °C, $[\alpha]_D$ 5°. The infrared spectrum of the methyl ester (Nujol mull) was identical with that of an authentic specimen of methyl betulate (kindly supplied by Professor D. E. White).

The ethereal solution remaining after the sodium hydroxide extraction was washed with dilute hydrochloric acid, then with water and evaporated to dryness. The sticky residue was extracted with boiling light petroleum and on cooling a pale yellow solid (*A*) was precipitated. A further crop of this solid (*A*) was obtained on concentration of the filtrate, giving a total of 4·1 g. Evaporation of the filtrate to dryness yielded a trace of sticky, green residue (*B*).

Solid *A* (4 g) was dissolved in benzene–light petroleum (1 : 1; 50 ml) and carefully chromatographed over alumina (500 g). Elution with benzene–light petroleum (1 : 1) gave 1·5 g of taraxerone, m.p. 236–237 °C, $[\alpha]_D^{20}$ 14° (*c*, 1·2 in chloroform) (small plates from ethyl acetate) (Found: C, 84·8; H, 11·3%. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%). Elution with benzene–ether (9 : 1) gave 1·8 g of taraxerol, m.p. 273–275 °C (small needles from acetone), $[\alpha]_D^{20}$ 0° (*c*, 1·1 in chloroform) (Found: C, 84·8; H, 11·7%. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). The infrared spectrum of this substance was identical with a published spectrum of taraxerol (Chapon 1955). White (1956) gives for taraxerone, m.p. 245–249 °C, $[\alpha]_D$ 12° and taraxerol, m.p. 282–285 °C, $[\alpha]_D$ ±0°.

Residue *B* was dissolved in light petroleum (1 ml) and chromatographed over alumina (5 g). Elution with light petroleum gave 11 mg of triacontane, m.p. 66 °C (lit. gives 66 °C) (Found:

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C, 84·8; H, 14·5%. Calc. for $C_{30}H_{62}$: C, 85·2; H, 14·8%). The infrared spectrum showed absorption peaks at 720 $cm^{-1}$ (carbon disulphide solution) and at 720 and 730 $cm^{-1}$ (solid film) characteristic of a long chain of the type $-(CH_2)_n-$, where $n>4$ (Bellamy 1954).

## *References*

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