

EXTRACTIVES FROM THE NEW ZEALAND MYRTACEAE*

VI. ARJUNOLIC ACID FROM THE HEARTWOOD OF METROSIDEROS UMBELLATA

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Triterpene acids have been reported from the bark and heartwood of a number of members of the family Myrtaceae (White and Ralph 1949; White and Zampatti 1952; Arthur and Hui 1954; Corbett and McDowell 1958; Ritchie, Snape, and Taylor 1961). The genus *Metrosideros* is represented in New Zealand by 10 species, of which *M. umbellata* (ironwood) is the most abundant in the South Island.

Extraction of the finely powered heartwood with ether yielded crude arjunolic acid (2.5%). Purification was effected by crystallization from methanol. This acid had previously been reported by Ritchie, Snape, and Taylor (1961), and by King, King, and Ross (1954).

Acetone extraction of the ether exhausted powder gave amorphous condensed tannins (5.8%). Tests for ellagic acid in this extract were negative. This is unusual, as the family Myrtaceae belongs to the group Myrtiflora in which ellagic acid is widespread (Bate-Smith 1956). An analysis of the tannin is included in the following section.

Experimental

Melting points are corrected. Infrared spectra were determined on a Perkin-Elmer spectrometer model 21, in Nujol.

Extraction.—The finely milled heartwood (6.07 kg; 31% passed a 60 mesh sieve, 96% passed a 30 mesh sieve) of *M. umbellata* was extracted (Soxhlet) with ether (20 l.) for 24 hr. A pale pink amorphous solid (72 g) which separated from the ether was filtered and combined with further quantities of solid (80 g) obtained by evaporation of the ether. A portion (20 g) of the solid was dissolved in methanol (325 c.c.) by hot extraction, diluted to 1500 c.c. with ether, and kept for 48 hr. The brown amorphous solid (1 g) which had separated was filtered, the filtrate concentrated to 300 c.c. and decolourized with charcoal. The clarified solution, concentrated to incipient crystallization, gave arjunolic acid (12 g), which after two further crystallizations from methanol had m.p. and mixed m.p. 337–339°C, $[\alpha]_D^{20} + 70.0^\circ$ (c, 0.51 in dioxan) (Found: C, 73.8; H, 9.7%. Calc. for $C_{30}H_{48}O_5$: C, 73.7; H, 9.9%). With diazomethane it formed methyl arjunolate, m.p. and mixed m.p. 248–249°C. The infrared spectra of the acid and its derivatives were identical with those of authentic specimens. No other substances could be isolated from the ether mother liquors.

Tannins.—Extraction of the ether exhausted sawdust with acetone gave, after removal of the solvent, condensed tannins (352 g). A tannin assay gave the following percentage composition; the percentages in brackets are the corresponding values for mimosa tannin: Tans, 69.2 (65.4); nontans, 8.8 (20.3); total solubles, 78.0 (85.7); ratio tans/nontans, 7.9 (3.2); insolubles, 9.5 (1.3); moisture, 12.5 (13.0); pH at 50°C bk, 3.4 (4.6).

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