CHEMICAL STUDIES OF THE MYRTACEAE*

IV. CONSTITUENTS OF THE WOOD OF ANGOPHORA SUBVELUTINA F. MUELL.

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Following the isolation of the uncommon triterpenes, cycloeucalenol, 24-methylenecycloartanol, and arjunolic acid, from the wood of *Tristania* conferta R.Br. (Ritchie, Snape, and Taylor 1961) it was decided to examine the woods of some species of related genera, and the present paper is concerned with the wood of *Angophora subvelutina* F. Muell. This medium-sized tree, commonly known as broad-leaved apple, is fairly common in the central and northern coastal regions of New South Wales, the timber often being used for fencing.

Several substances were isolated from the wood, but in small amounts only; ellagic acid (0.024%), sitosterol (0.025%), and 24-methylenecycloartanol (0.014%) were identified. In addition, fractions apparently consisting essentially of tetracosanoic acid (0.001%) and 24-hydroxytetracosanoic acid (0.021%)were obtained, but because of the small amounts available and the difficulties involved in purification (Murray and Schoenfeld 1955) their investigation was not pursued.

Experimental

Melting points are uncorrected.

(a) Light Petroleum and Ether Extracts.—The milled wood (10 kg) was extracted at room temperature with light petroleum (b.p. 60-90 °C; 4×15 l.) and then ether (3×15 l.). Evaporation of the extracts gave thick brown oils (23 and 9 g respectively) which were combined and saponified by heating under reflux with excess 10% alcoholic KOH for 6 hr. On working up in the usual manner neutral and acidic fractions were obtained together with an interfacial precipitate of insoluble potassium salts.

The neutral fraction, a thick reddish brown oil (11 g), was chromatographed on alumina (300 g). The ether-methanol (9:1) eluate crystallized from methanol, but the material $(5 \cdot 6 \text{ g})$ was obviously a mixture. On further chromatography on alumina (150 g) using benzene-ethyl acetate, 24-methylenecycloartanol $(1 \cdot 4 \text{ g})$ was first eluted, followed by sitosterol $(2 \cdot 5 \text{ g})$. The substances were identified by direct comparison (mixed m.p.'s and i.r. spectra) with authentic specimens. The acetates were also compared. No other substance could be isolated from the mother liquors.

The acidic fraction, a very dark reddish brown gum, was recycled with alkali, and then digested with light petroleum. The insoluble, dark, amorphous material was discarded and the filtrate evaporated to yield a brown gum $(2 \cdot 8 \text{ g})$ which was chromatographed in light petroleum on silica gel (100 g). The first eluates, on keeping, crystallized; repeated recrystallization from methanol, light petroleum, and ethanol gave colourless needles $(0 \cdot 1 \text{ g})$, m.p. 78-79 °C (Found : C, 78 \cdot 5; H, 13 \cdot 3%. Calc. for C₂₄H₄₈O₂: C, 78 \cdot 1; H, 13 \cdot 1%). The methyl ester crystallized from methanol in colourless plates, m.p. 56-58 °C. Tetracosanoic acid has m.p. 84 °C and its methyl ester, m.p. 59-60 °C.

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The insoluble interfacial precipitate was recycled and the acid $(2 \cdot 1 \text{ g})$ liberated from the slimy precipitate. Recrystallization from acetic acid and light petroleum gave a colourless solid, m.p. 93-94 °C (Found : C, 74 \cdot 7; H, 13 \cdot 0%. Calc. for $C_{24}H_{48}O_3$: C, 74 · 9; H, 12 · 6%). The acetate of the methyl ester had m.p. 63-65 °C. The m.p. of the acid has not been recorded, but Murray and Schoenfeld (1955) give m.p. 63 °C for the acetate of the methyl ester.

(b) Isolation of Ellagic Acid.—The wood was then extracted with acetone $(3 \times 15 l.)$ and with methanol $(7 \times 15 l.)$.

The acetone extract was concentrated to a thick reddish brown syrup which was then digested with ethyl acetate (300 ml). The insoluble solid was collected, washed with ethyl acetate, and shaken with 5% Na₂CO₃ (200 ml). The insoluble sodium salt was collected and washed with a little water. On treating with acid, ellagic acid (0.9 g) was regenerated. It was identified by the usual colour tests (Bate-Smith 1956) and by direct comparison of its acetyl derivate with authentic tetraacetylellagic acid. The ethyl acetate filtrate failed to yield any crystalline substances.

The methanol extract on concentration yielded successive crops of crystalline material and eventually a very dark reddish brown syrup. Attempts to obtain crystalline substances from the syrup either before or after hydrolyses with acid or alkali, were unsuccessful. The crystalline precipitate consisted chiefly of inorganic material, which was removed by washing with water. The residue on purification as above gave more ellagic acid $(1 \cdot 4 g)$.

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References

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