CHEMICAL STUDIES OF THE MYRTACEAE*

III. TRITERPENOIDS FROM THE WOOD OF TRISTANIA CONFERTA R.Br.

By E. Ritchie,† Diana Snape,† and W. C. Taylor†

Tristania conferta R.Br. is one of the most familiar trees of eastern Australia. It ranges from Port Stephens in New South Wales to Bowen in Queensland and is used very extensively in Sydney for street planting. The timber of this tree, which may reach a height of 120 ft, is close-grained, hard, and heavy. Commercially it is known as brush box and is used as decking for wharves and bridges and for flooring.

Preliminary tests by Simes *et al.* (1959) suggested that triterpenoids were present in the bark, leaves, and wood. In the present work, the wood has been systematically extracted. From the light petroleum extract a neutral fraction was obtained which after saponification yielded, in addition to the widespread sitosterol, cycloeucalenol, previously reported by Cox, King, and King (1956) from the wood of *Eucalyptus microcorys*, and 24-methylenecycloartanol recently obtained by Ohta and Shimizu (1958) from a quite unrelated source, namely Japanese rice bran oil. The ether extract of the wood yielded large quantities (3·5%) of arjunolic acid, first isolated by King, King, and Ross (1954) from the wood of *Terminalia* species; the acetone and methanol extracts gave further small quantities of the same substance.

Experimental

Melting points are uncorrected.

(*a*) *Extraction with Light Petroleum.*—The milled wood (28 kg) was exhausted with light petroleum (b.p. 60–90 °C) at room temperature and the combined extracts concentrated to a thick reddish brown gum (360 g). This was dissolved in ether and the solution washed in turn with aqueous Na_2CO_3 and NaOH. These reagents extracted only small amounts of gums which were discarded. The ether was removed and the residue saponified by refluxing with excess 10% alcoholic KOH for 8 hr. The reaction mixture was worked up as usual to yield an acidic and a neutral fraction. The former, a dark reddish brown gum, which apparently consisted of fatty acids, was discarded. The neutral fraction was dissolved in light petroleum and chromatographed systematically on alumina (7 kg). The early fractions eluted by ether–benzene consisted essentially of a mixture of cycloeucalenol and 24-methylenecycloartanol, and later fractions eluted by ether–benzene and by ether, of sitosterol. By a combination of fractional crystallization from methanol and chromatography of the appropriate fractions, eventually sitosterol (0·3%), 24-methylenecycloartanol (0·12%), and cycloeucalenol (0·004%) were separated. Cycloeucalenol was eluted more readily than the other two substances. Each substance, together with its acetate, was identified by direct comparison (mixed m.p.'s and i.r. spectra) with an authentic specimen.

* Manuscript received March 6, 1961.

† Department of Organic Chemistry, University of Sydney.

(*b*) *Isolation of Arjunolic Acid.*—Following the extraction with light petroleum, the wood was extracted with ether until almost no solid separated on concentration of the ether solution (about 8–10 times). The total extract was concentrated to a small bulk and the cream solid which separated, collected and washed with a little ether (3·5% yield).

The product could be purified either by recrystallizing its sodium salt from aqueous alcoholic NaOH followed by regeneration, or more satisfactorily, by direct crystallization as follows. The acid (10 g) was dissolved in a little methanol and ethyl acetate (700 ml) added. The filtered solution was boiled down on the steam-bath until bumping due to separation of crystals became bad. The mixture was allowed to cool, then quickly heated to boiling and the liquid decanted from the crystals which were collected with the aid of a little fresh ethyl acetate. Repetition of this procedure yielded a total of 5·6 g of crystalline acid, m.p. 320–322 °C (decomp.). Further recrystallization from ethyl acetate and then from a little methanol gave prismatic needles, m.p. 328–330 °C (decomp.), undepressed by admixture with an authentic specimen. The i.r. spectra of the two specimens were also identical, and the identification was confirmed by direct comparison of the triacetyl-lactones.

By re-working the mother liquors further quantities of arjunolic acid were obtained, but no other substance could be isolated. The acetone and methanol extracts of the wood on evaporation to a small bulk and dilution with ether also gave further small quantities of arjunolic acid.

The authors are grateful to the Forestry Commission of New South Wales for a supply of the plant material, and to Dr. T. J. King, University of Nottingham, and Dr. M. Shimizu, Daiichi Seiyaku Co. Ltd., Japan, for specimens of cycloeucalenol, arjunolic acid and its derived triacetyl-lactone, and of 24-methylenecycloartanol, respectively.

References

Cox, J. S. G., King, F. E., and King, T. J. (1956).—*J. Chem. Soc.* **1956**: 1384.

King, F. E., King, T. J., and Ross, F. M. (1954).—*J. Chem. Soc.* **1954**: 3995.

Ohta, G., and Shimizu, M. (1958).—*Chem. Pharm. Bull. Japan* **6**: 325.

Simes, J. J. H., Tracey, J. G., Webb, L. J., and Dunstan, W. J. (1959).—An Australian phytochemical survey. C.S.I.R.O. Aust. Bull. No. 281.