AGATHIS MICROSTACHYEA OLEORESIN*

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Agathic acid (I), the major constituent present in the oleoresin of the New Zealand kauri (Agathis australis), is not present in the resin of the South Queensland kauri (A. robusta). Consequently we have examined the oleoresin of one of the North Queensland kauris, A. microstachya, and have found that agathic acid is the major constituent of this resin also.

Agathic acid was readily obtained from the A. microstachya resin by chromatography of the crude acid fraction through a charcoal–kieselguhr column. The losses due to oxidation on the column are not known, but at least 50% of the acid fraction, which in itself comprised 90% of the oleoresin, was agathic acid. The compound was identified by comparison with an authentic sample and by reduction to agathadiol (II).

**Experimental**

The hard, brittle, semi-transparent oleoresin was collected on the Atherton Tableland, North Queensland. The resin (200 g) was warmed in a mixture of aqueous 5% Na₂CO₃ and methanol (70:30) until all had dissolved. Heating at 50° under reduced pressure was continued to remove the methanol. The cooled aqueous solution was filtered and extracted with ether to give ether-soluble neutrals (20 g). Acidification (dil. H₂SO₄) of the aqueous solution gave the free acids as a gummy precipitate which was collected by filtration, washed as well as possible with water, and air-dried at 25° (180 g).

The acids (5 g) in methanol were filtered through a column of charcoal–kieselguhr (1:1200 g). Elution with methanol gave agathic acid (2·6 g), m.p. 203° (from aqueous methanol), showing no mixed m.p. depression with an authentic sample, [α]D +65° (c, 0·8 in 95% ethanol) (Found: C, 71·7; H, 9·1%. Calc. for C₁₉H₂₇O₄: C, 71·8; H, 9·0%). Its infrared spectrum in Nujol was identical with that of an authentic sample with peaks at 2620br, 1690s, 1680s, 1640w, 1630m, 1410m, 1325m, 1246s, 1162m, 1029m, 929s, 894s, 867s, 792s, 695s om-l. Amax. (ethanol) 218 mp (log ε = 4). Proton magnetic resonance spectrum (CDCl₃): 4.27 (broadened singlet, C(16) proton), 5.07, 5.43 (broadened singlets, C(14) protons), 7.80 (doublet, J = 1 c/s, C(15) methyl), 8.73 (C(18) methyl), 9.37 (C(20) methyl) 7.

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‡ Literature values: m.p. 203–204°, [α]D +58°, λmax 216–220 μ (log ε = 4·1–4·2).

Agathadiol.—Agathic acid in dioxan was reduced with lithium aluminium hydride in the normal manner. Chromatography of the product over 50 times its weight of alumina gave, on elution with benzene–ether (1:1), agathadiol, m.p. 106–107°* (from diisopropyl ether) (Found: C, 78·2; H, 11·1%. Calc. for C_{16}H_{34}O_{2}: C, 78·4; H, 11·2%). Its infrared spectrum (Nujol) had peaks similar to those reported in the literature at 3250br, 1645w, 1026s, 994s, 896s, 854w, 845w, 720w cm⁻¹. Proton magnetic resonance spectrum (CDCl₃): 4·62 (broadened triplet, J = 7 c/s, C(16) proton), 5·18, 5·48 (two broadened singlets, C(14) protons), 5·86 (two-proton doublet, J = 7 c/s, C(17) protons), 6·1–6·8 (unsymmetrical AB quartet, C(19) protons), 8·31 (broadened singlet, C(15) methyl), 9·02 (C(18) methyl), 9·34 (C(20) methyl) τ.

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