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SHORT COMMUNICATION

FURTHER DITERPENES FROM *XYLOPIA AETHIOPICA* (ANONACEAE)*

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THE DRIED fruits of *Xylopia aethiopica* A. Rich (Anonaceae) are a common ingredient of many African traditional cough medicines. Recently we reported the isolation from the dried fruits and the structural elucidation of a new kaurane diterpene, xylopic acid.[1] In addition a high yield (2·1 per cent) of a fragrant essential oil was obtained, the gas chromatograph–mass spectrum[2] of which showed it to consist of mainly monoterpenes of molecular weight 136. We now report the isolation of five further kaurane diterpenes: (−)-kauran-16α-ol, (−)-kaur-16-en-19-oic acid (−)-kaur-16-en-15-hydroxy-19-oic acid, (−)-kauran-16α,19-diol and 15-oxo-(−)-kaur-16-en-19-oic acid. The last two compounds are being reported for the first time as natural products.

After removal of xylopic acid[1] the petroleum ether soluble extract was steam-distilled and the non-volatile material was separated into acidic and neutral fractions with NaOH. The acidic fraction was chromatographed on silica gel (Merck; 0·05–0·2 mm). 5% ether in petroleum ether eluted (−)kaur-16-en-19-oic acid, m.p. 169–173° $[\alpha]_D$ −112° (*c*, 0·23) [Lit.[3] m.p. 169–171° and 179–181°; $[\alpha]_D$ −110° (*c*, 3·0)], τ 9·05, 8·77 (2 tert. CH_3), 5·27, 2H, broad ($C{=}CH_2$). 20% ether in petroleum ether eluted (*a*) 15-oxo-(−)kaur-16-en-19-oic acid, m.p. 197–201° identical (m.p., mixed m.p., i.r. and NMR) with that prepared as previously reported[1] from xylopic acid; (*b*) (−)kaur-16-en-15-hydroxy-19-oic acid, m.p. 204–206°, identical (m.p., mixed m.p., i.r. and NMR) with deacetyl xylopic acid.[1]

The neutral fraction was chromatographed on activated alumina (Spence type H). Petroleum ether removed fatty oils. Ether:petroleum ether (1:1) eluted further oils from which a solid m.p. 56–58° separated. Elution with ether gave an oil from which (−)kauran-16α-ol crystallized on leaving in methanol. M.p. 216–219° $[\alpha]_D$ −49° (*c*, 0·242) [Lit.[4] m.p. 216–217° $[\alpha]_D$ −41° (*c*, 0·2)]. ν_{max} (nujol) 3226 cm^{-1} (OH). τ 9·2, 9·17, 8·99 and 8·65 (4 tert. CH_3). Ether/ethyl acetate (1:1) eluted gums. These were left in methanol and eventually gave a solid, m.p. 64°. Further elution with the same mixture gave more gums which on trituration with benzene deposited (−)kauran-16α,19-diol as crystals m.p. 200–203°, $[\alpha]_D$ −42° [Lit.[3] m.p. 200–201° $[\alpha]_D$ −43° (*c*, 2·6 in EtOH)]. ν_{max} (nujol) 3180–3340 cm^{-1} (OH). τ 9·05, 9·0 and 8·65 (3 tert. CH_3); 6·43, 2H, doublet of a doublet (hindered C—CH_2OH).

* Part III of the Series "Chemistry of Medicinal Plants"; D. E. U. EKONG and O. G. IDEMUDIA, *J. Chem. Soc.* (C) 863 (1967), and ref. 1 are regarded as Parts I and II.

[1] D. E. U. EKONG and A. U. OGAN, *J. Chem. Soc.* (C) 311 (1968).
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[3] C. A. HENRICK and P. R. JEFFERIES, *Australian J. Chem.* **17**, 915 (1964).
[4] L. H. BRIGGS, R. C. CAMBIE and P. S. RUTLEDGE, *J. Chem. Soc.* 5374 (1963).