Phytochemistry, 1969, Vol. 8, pp. 669 to 671. Pergamon Press. Printed in England.

SHORT COMMUNICATION

TERPENOIDS OF *DACRYOIDES EDULIS*[1]

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(*Received* 19 *August* 1968, *in revised form* 1 *November* 1968)

THE TREE *Dacryoides edulis* (G. Don) H. J. Lam (syn. *Pachylobus edulis* G. Don) Burseraceae is a cultivated fruit tree common in the midwestern and eastern parts of Nigeria. It yields an edible fruit whose pulp is rich in a butter-like fat with a pleasant aroma. The bark when injured produces a gum which is used in Nigeria as a bush candle. Extraction of a sample of the wood with petrol. ether gave an oil which was chromatographed on silica gel to yield mixtures of fatty acids and their esters. These were not further investigated.

Freshly gathered gum (500 g) (collected in eastern Nigeria in August 1966) was steam distilled and yielded a peppery essential oil (45 g) shown by gas chromatographic analysis to be rich in sabinene and β-phellandrene, in addition to limonene.* From the non volatile fraction the acidic constituents were extracted with lithium carbonate and from the acidic gum in methanol canaric acid (3 g) crystallized as needles. These sublimed above 180° but in a sealed tube had m.p. 226–228°; $[\alpha]_D+46°$ (lit.[2] m.p. 215–216° $[\alpha]_D+43°$). (Found: C, 81·7; H, 10·9 per cent; Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0). ν_{max} 1690 (CO_2H), 1645, 880 and 895 (2C$=$CH$_2$) cm^{-1}. Treatment with CH_2N_2 gave a methyl ester ν_{max} 1735 cm^{-1} (CO_2Me). NMR bands at τ 5·25 (4H, multiplet, 2C$=$CH$_2$), 6·35 (3H, singlet, CO_2Me), 8·30 (6H, broad singlet, 2 vinyl CH_3), 8·93, 9·03, 9·17 and 9·20 (singlets, 4 tert. CH_3). Hydrogenation over Adam's catalyst gave tetrahydrocanaric acid m.p. 226–228° (decomp.) $[\alpha]_D-26°$ (lit.[2] m.p. 221° $[\alpha]_D-24°$). (Found: C, 81·6; H, 12·1. Calc. for $C_{30}H_{52}O_2$: C, 81·0; H, 11·8 per cent.)

The mother liquor from the crystallization of canaric acid was concentrated and the solid (18·2 g) obtained was chromatographed on silica gel (200 g) and yielded a further amount of canaric acid as well as a *keto acid* and the corresponding *hydroxy acid.* The keto acid crystallized in two forms. One form on recrystallization from methanol-ether had m.p. 179–184° $[\alpha]_D+70°$. The other form crystallized from methanol had m.p. 185–188° $[\alpha]_D+65°$. Both forms had identical NMR, i.r., u.v. and mass spectra. (Found: C, 78·8; H, 10·1 per cent; *M* (mass spectrum), 454; $C_{30}H_{46}O_3$ requires C, 79.2; H, 10·2 per cent; *M*, 454. ν_{max} (nujol) 2600–2500 and 1680 (CO_2H), 1700 (saturated ketone), 1640 and 1280 (double bond) cm^{-1}. λ_{max} 215 nm (ϵ 17,700). Treatment of the keto acid with ethereal CH_2N_2 gave a methyl ester. This crystallized from methanol and had m.p. 117–119° $[\alpha]_D+66°$, *M* (mass spectrum) 468.

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* Analysis by J. A. Rogers, Fritzsche Brothers Inc., New York, to whom we express our thanks.

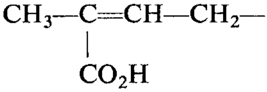
[1] Part XXIII in the series "West African Timbers"; for Part XXII, see C. W. L. BEVAN, D. E. U. EKONG and J. I. OKOGUN, *J. Chem. Soc.* (C) 1067 (1968).

[2] T. G. H. JONES and F. BERRY-SMITH, *Proc. R. Soc. Queensland* 37, 92 (1925); E. M. CARMAN and D. COWLEY, *Australian J. Chem.* 18, 213 (1965); E. M. CARMAN, *ibid.* 18, 1493 (1965).

ν_{max} (nujol) 1706 cm^{-1} (strong, CO_2Me and C=O), 1650 cm^{-1} (double bond). NMR bands at τ 8·15 (3H, broad, vinyl methyl) 6·25 (3H, singlet, CO_2Me), 3·24 (1H, triplet, $J^* = 14{\cdot}5$ c/s, $\mathrm{—CH_2—C}H\mathrm{{=}C—CO_2Me}$).

The hydroxy acid gave crystals m.p. 209–212° (from methanol). (Found: C, 75·9; H, 10·7 per cent. $C_{30}H_{48}O_3.CH_3OH$ required: C, 76·2; H, 10·7 per cent.) ν_{max} 3380 (OH), 2640, 1690 (CO_2H) 1640 (double bond) cm^{-1} λ_{max} 217 nm ($\epsilon = 13{,}600$). NMR bands at τ 9·3 (3H, singlet, tert. CH_3) 8·9–9·2 (5 CH_3), 8·16 (3H, broad singlet, vinyl CH_3), 6·58 (1H, multiplet, $W_H = 6$ c/s, equatorial *H*COH), 6·27 (3H, singlet, CO_2Me), 3·25 (1H, triplet $J^* = 14{\cdot}5$ c/s, $\mathrm{—CH_2—C}H\mathrm{{=}C—CO_2Me}$).

Jones oxidation of the methyl ester of the hydroxy acid gave a keto ester m.p. 114–115° identical with the methyl ester of the keto acid described above. (Mixed m.p. 115–119°, i.r., u.v. and NMR spectra identical.) The spectral properties of the acids thus indicate the presence of the grouping



$$\underset{\displaystyle CO_2H}{CH_3—\underset{|}{C}{=}CH—CH_2—.}$$

There being no other low field signals in the NMR spectrum the spectral properties (coupled with biogenetic considerations) suggest a structure similar to that of isomasticadienonic acid[3] for the keto acid, the hydroxy acid being the corresponding 3α alcohol.

Separation of the Triterpene Alcohols

A portion of the neutral fraction (40 g) was chromatographed on silica gel (480 g); 5% ether in petrol. ether eluted a mixture of 3-*epi*-α-amyrin and 3-*epi*-lupeol (gum, 13 g) and an α-amyrin containing (mass spectrum) solid (crystals, 9 g). 30% ether in petrol. ether eluted a small amount of a solid which crystallized from methanol-ether and had m.p. 258–261° $[\alpha]_D - 31°$ ($c = 0{\cdot}05$), *M* (mass spectrum) 444. ν_{max} (nujol) 3390 cm^{-1}, 1073 cm^{-1}, 1032 cm^{-1}, 990 cm^{-1} and 893 cm^{-1}.

3-Epi-α-*Amyrin and* 3-epi-*lupeol Acetates*

The mixture of the 3-*epi*-alcohols was acetylated and the acetates (3·5 g) chromatographed on silica gel impregnated with $AgNO_3$ (62 g). 3-*epi*-α-amyrin acetate (2·2 g) was eluted with 2% ether in petrol. ether. 5 and 10% ether in petrol. ether eluted 3-*epi*-lupeol acetate (0·8 g).

The 3-*epi*-α-amyrin acetate after three recrystallizations from methanol-ether had m.p. 130–133° $[\alpha]_D + 31°$ ($c = 0{\cdot}094$) *M* (mass spectrum) 468 (lit.[4] m.p. 134–135° $[\alpha]_D + 36°$ ($c = 0{\cdot}689$)). NMR bands at τ 7·9 (CH_3CO) 5·33 (1H, triplet, $J^* = 5$ c/s equatorial *H*C-OCOR) 4·84 (1H, multiplet, vinyl H). The 3-*epi*-lupeol acetate crystallized in ether. Recrystallization from methanol–ether gave crystals m.p. 163° $[\alpha]_D - 8°$ ($c = 0{\cdot}122$) (lit.[5] m.p. 163° $[\alpha]_D - 1°$ ($c = 0{\cdot}99$) *M* (mass spectrum) 468. NMR bands at τ 8·3 (3H, broad, vinyl CH_3) 7·9 (CH_3CO), 5·36 (3H, multiplet, *H*C-OCOR overlapping with $C{=}CH_2$). Hydrolysis of the 3-*epi*-α-amyrin acetate (1·2 g) in benzene (22 ml) and KOH (10 g), water (4 ml), and methanol (55 ml) gave a gum (1 g) which later solidified. Three crystallizations from aqueous acetone afforded 3-*epi*-α-amyrin as crystals m.p. 135–138° $[\alpha]_D + 65°$ ($c = 0{\cdot}066$) (lit.[5] m.p. 138° $[\alpha]_D + 75°$) *M* (mass spectrum) 426. NMR bands at τ 6·57 (1H, triplet $J^* = 4{\cdot}5$ c/s equatorial *H*C—OH)

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[3] E. Seoane, *J. Chem. Soc.* 4158 (1956).

[4] L. Razicka and H. Gubser, *Helv. Chim. Acta* **28**, 1056 (1945).

[5] (Miss) I. L. Allsop, A. R. H. Cole, D. E. White and R. L. S. Willix, *J. Chem. Soc.* 4868 (1956).

4·83 (1H, multiplet, vinyl H). Perbenzoic acid oxidation of the 3-*epi*-α-amyrin (1·8 g) in $CHCl_3$ for 22 hr and chromatography on activated alumina (100 g) gave *ursan*-12-*on*-3α-*ol* which crystallized from methanol-$CHCl_3$ and had m.p. 255–8° $[\alpha]_D - 45°$ ($c = 0·076$). Found: C, 81·7; H, 11·5 per cent *M* (mass spectrum) 442. $C_{30}H_{50}O_2$ required: C, 81·4; H, 11·4 per cent; *M* 442 ν_{max} (nujol) 3560 (OH), 1680 cm^{-1} (C=O).

α-Amyrin Acetate

The crude α-amyrin-containing fraction was acetylated and the acetate on chromatography on silica gel impregnated with $AgNO_3$ gave crystals of α-amyrin acetate, which after two recrystallizations from ethanol-ether had m.p. 220–223° $[\alpha]_D + 77°$ ($c = 0·06$) *M* (mass spectrum) 468 (lit.[6] m.p. 225–226° $[\alpha]_D + 83·3°$ ($c = 0·724$)) NMR bands at τ 8·0 (3H, singlet, CH_3CO), 5·55 (1H, multiplet, $J^* = 15$ c/s, axial *H*C-OAC), 4·9 (1H, multiplet, vinyl H).

This appears to be the first report of 3-*epi*-amyrin and 3-*epi*-lupeol as natural products. In the Meliaceae the C-3 hydroxy-group of the triterpenes is also normally α and axial, and this may indicate a relationship between *D. edulis* and the Meliaceae.

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[6] L. Ruzicka and W. Wirz, *Helv. Chim. Acta* **22**, 948 (1939).