West African Timbers. Part XVI. Ozic Acid, a New Diterpene Acid from *Daniellia ogea*

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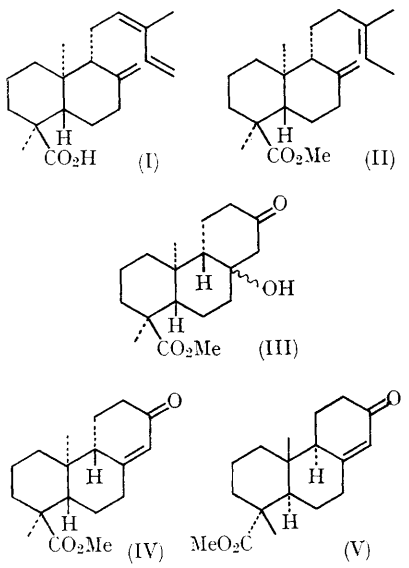
PETROLEUM extraction of the wood of *Daniellia ogea* gives a new diterpene acid, $C_{20}H_{30}O_2$, m.p. 141—143° $[\alpha]_D^{22}-47°$ ($CHCl_3$) named ozic acid (from Edo, *Oziya*, for Daniellia ssp.) to which structure (I) is assigned. Ultraviolet absorption maximum λ_{max} 237 mμ (ϵ, 19,000) indicates the presence of a conjugated diene. In the infrared it shows ν_{max} 1690 (CO_2H), 1642, 896 ($C=CH_2$), 1590, and 988 cm.$^{-1}$ (conjugated double bonds). The n.m.r. spectrum shows the presence of two tertiary methyl groups (τ 9·2 and 8·78) one methyl on an unsaturated carbon atom bearing no hydrogen (τ 8·17) and six vinyl hydrogens (five broad singlets and one quartet). On hydrogenation, ozic acid absorbs three moles of hydrogen, indicating the presence of three double bonds and hence two rings. These results are consistent with a gross structure (I). This structure agrees also with the mass spectrum of ozic acid which shows principal peaks at *m/e* 302, 256, 175, 121, and 81 corresponding to the molecular ion and the ion fragments a,b,c, and d respectively.

N.m.r. and i.r. spectra of its derivatives suggest an equatorial carboxyl at C–4. Reduction with sodium in propanol gives an iso-dihydro-compound which on treatment with diazomethane gives a liquid methyl ester $C_{21}H_{34}O_2$ (II); ν_{max} 1725 (CO_2Me), 1642, and 889 cm.$^{-1}$ ($C=CH_2$) and only end-absorption in the ultraviolet. Its n.m.r. spectrum also agrees with structure (II). In the region 1150—1250 cm.$^{-1}$ in the infrared, (II) as well as methyl oziate shows only one strong band at 1240 cm.$^{-1}$ consistent with an equatorial methoxycarbonyl group.[1]

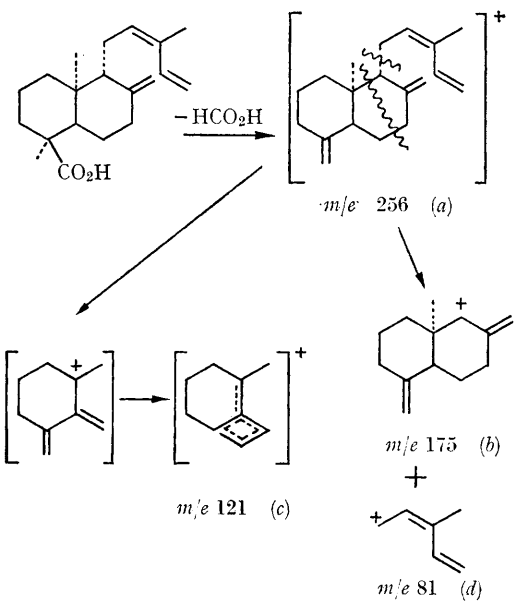
Reduction of (II) with lithium aluminium hydride gives an alcohol, the n.m.r. spectrum of

which shows the methylene hydrogens of the hydroxymethylene group as a quartet centred around τ 6·7. In the acetate of this alcohol these methylene hydrogens appear as a quartet centred around τ 6·2. These values indicate an equatorial configuration[2] for the hydroxymethylene group and hence for the carboxyl group in ozic acid. The corresponding values for daniellol and its acetate in which the groups are axial[3] are τ 6·38 and τ 5·9 respectively.



From analogy with daniellic acid[3] which we have also obtained from the wood of the closely related species *Daniellia oliverii*, the stereochemistry at C–5, C–9, and C–10 was inferred. This was confirmed by correlation with neoabietic acid. Ozonolysis of (II) gave a diketo-compound which on treatment with alkali cyclised to the ketol $C_{18}H_{28}O_4$ (III) m.p. 203—205° $[\alpha]_D^{22}$ −31° ($CHCl_3$); ν_{max} (nujol) 3,400 (OH), 1720 (CO_2Me) and 1700 cm.$^{-1}$ (C=O); two tertiary methyls in the n.m.r. spectrum. Dehydration of (III) with sodium methoxide in methanol gave the $\alpha\beta$-unsaturated ketone $C_{18}H_{26}O_3$ (IV), m.p. 123—126°; $[\alpha]_D^{22}$ −27° ($CHCl_3$); λ_{max} (methanol) 243 mμ (ϵ, 16,000) semicarbazone, m.p. 219—222°. The infrared and n.m.r. spectra of (IV) are identical with those of the $\alpha\beta$-unsaturated ketone (V), m.p.126—128°, obtained from neoabietic acid,[4,5] while the m.p. of its semicarbazone is the same as that reported for the semicarbazone of (V).[4] The optical rotation of (IV) is of approximately the same magnitude as that reported for (V) (+32°)[6] but opposite in sign. The two compounds are therefore antipodes and this confirms the configuration of ozic acid as in (I) leaving only the relative stereochemistry about the C–12—C–13 double bond to be determined.

Ozic acid is similar to communic acid[7] except that the former belongs to the less common stereochemical series with respect to the steroids and its carboxyl group is equatorial. Contrary to the reported instability of communic acid which could only be obtained as the sodium salt or the methyl ester,[7] ozic acid is a crystalline solid which remains stable for several months at room temperature. Like communic acid however it polymerises in the presence of minute traces of mineral acids.



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[1] S. Bory and M. Fetizon, *Bull. Soc. chim. France*, 1964, 570.
[2] E. Wenkert and P. Beak, *Tetrahedron Letters*, 1961, 358; A. Gaudemer, J. Polonsky, and E. Wenkert, *Bull. Soc. chim. France*, 1964, 407.
[3] J. Haeuser, R. Lombard, F. Lederer, and G. Ourisson, *Tetrahedron*, 1961, **12**, 205.
[4] W. M. Hoehn, U.S. Patent 2,682,555 (1954); (*Chem. Abs.*, 1955, **49**, 14033).
[5] We are grateful to Dr. W. M. Hoehn for a sample of this compound.
[6] C. Djerassi, R. Riniker, and B. Riniker, *J. Amer. Chem. Soc.*, 1956, **78**, 6362.
[7] V. P. Arya, H. Erdtman, and T. Kubota, *Tetrahedron*, 1961, **16**, 255.