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THE CONSTITUTION OF CEANOTHIC ACID, A RING-CONTRACTED TRITERPENOID

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CEANOTHIC acid was first isolated by Julian, Pikl and Dawson from Ceanothus americanus (Jersey Tea).[1] It was characterised as a hydroxy dicarboxylic acid and, further, it was reported that at the melting point it lost one molecule each of carbon dioxide and water.

Reinvestigation has required the revision of the empirical formula of ceanothic acid, m.p. 356-7°, $[\alpha]_D$ + 38° (in EtOH)[2] to $C_{30}H_{46}O_5$. The presence of a band in the infrared spectrum at 883 cm.$^{-1}$ together with the isolation of betulinic acid (I) (characterised by conversion to betulin diacetate and comparison with an authentic specimen) suggested that ceanothic acid belonged to the lupeol-betulin series of triterpenoids. This was confirmed when treatment with refluxing formic acid let to a monocarboxylic acid, $C_{30}H_{46}O_5$, m.p. 303-5°, $[\alpha]_D$ + 90°, in which the band at 883 cm.$^{-1}$ (attributed to the isopropenyl group) had disappeared and was replaced by a band at 1760 cm^{-1} attributed to a γ-lactone.[3]

The dehydration-decarboxylation reported[1], required that the hy-

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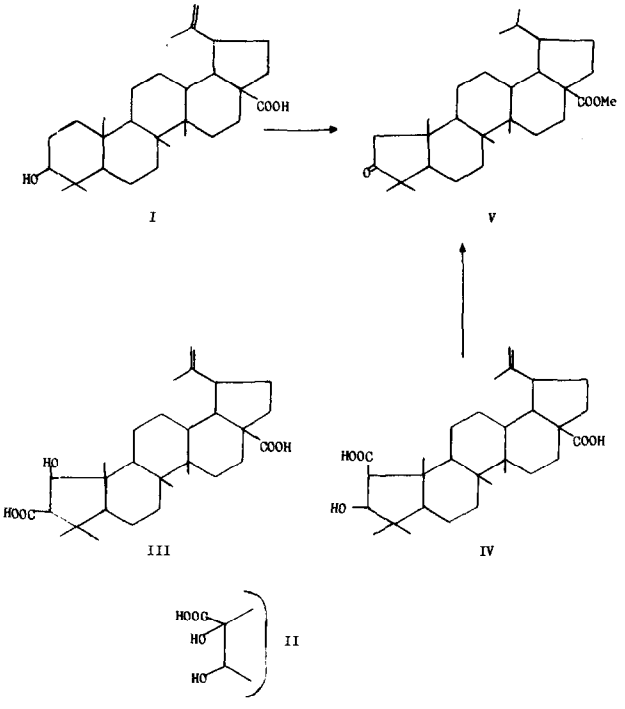
1 P.L. Julian, J. Pikl and R. Dawson, J. Amer. Chem. Soc. 60, 77 (1938).

2 Rotations were determined in chloroform unless otherwise stated. Melting points were determined on the Kofler block.

3 G.S. Davy, T.G. Halsall and E.R.H. Jones, J. Chem. Soc. 2696 (1951).

droxyl group be β to one of the carboxyl groups. This was confirmed as follows. Ceanothic acid dimethyl ester, m.p. 221-3°, $[\alpha]_D$ + 41° was converted into an oily benzoate which was pyrolysed to give, with loss of benzoic acid, the αβ-unsaturated ester, m.p. 166-8°, $[\alpha]_D$ - 16° which showed the expected absorption in the ultraviolet (λ_{inf} 215 mμ, 67,500). The NMR spectrum[4] showed the presence of one vinyl hydrogen (τ = 3.9) as well as those bands (τ = 5.4, doublet) to be attributed to the isopropenyl group. The dehydration-decarboxylation product, which is not a lactone[1]



4 The NMR spectra were determined in ca. 10% w v solution in CCl_4 using a Varian V-4302 spectrometer with TMS as internal standard.

but an unsaturated acid, showed bands in the NMR spectrum indicative of two vinyl hydrogen atoms in addition to those due to the isopropenyl group. This required that both the hydroxyl group and the carboxyl be secondary, and this was confirmed by the NMR spectrum of ceanothic acid dimethyl ester itself which showed bands at τ = 5.98 and 7.51, attributed to methine hydrogen on carbon bearing oxygen and methine hydrogen α to carbonyl respectively.

Since no secondary carboxyl is possible in an unmodified lupeol-betulin type structure it seemed possible that the carboxyl group was produced, biogenetically, by a benzilic acid or acyloin type rearrangement. To contain the part structure -CH(OH)·CH(COOH)- would require the biogenetic precursor of ceanothic acid to have three contiguous carbon atoms all being methylene groups substituted by oxygen functions. This is possible in the lupeol-betulin system only in Ring A, whence (III) or (IV) follow for ceanothic acid.

Hydrogenation of ceanothic acid dimethyl ester in acetic acid solution (PtO_2) gave dihydroceanothic acid dimethyl ester, m.p. 262-3°, $[\alpha]_D$ + 21°. Oxidation (sodium dichromate-acetic acid) gave the corresponding ketone, m.p. 183-184°, $[\alpha]_D$ + 94°, ν_{max} 1750 cm^{-1}. Hydrolysis of this gave (with loss of carbon dioxide) (V) identical in every respect with an authentic specimen prepared from (I)[5], further characterised as the 2:4-dinitrophenylhydrazone, m.p. 161-163°. The ring contraction to give ceanothic acid (IV), though so far unique in the triterpenoid field, is biogenetically unexceptional and must occur, for instance,

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5 L. Ruzicka and O. Isler, Helv. Chim. Acta 19, 506 (1936); L. Ruzicka, M. Brenner, and E. Rey, 24, 515 (1941).

in the genesis of gibberellic acid. A similar ring contraction would accomodate the part structure (II) reported for senegenin.[6]

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6 M. Shamma and L.P. Reiff, Chem. and Ind. 1272 (1960).