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TRITERPENES OF THE FRIEDELANE SERIES. PART V. ACIDS

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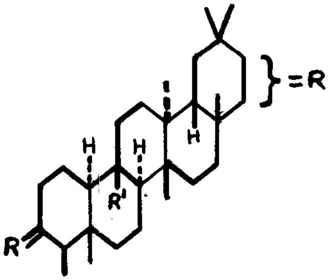
The bark of Siphonodon australe Benth. contains a great many triterpenes of the friedelane series. These compounds have been classified as follows: ketones, hydroxy-ketones and polyhydroxy compounds (1,2). This last fraction is extremely difficult to resolve and it was therefore oxidised with chromium trioxide-pyridine reagent and chromatographed. Friedelane-3,x-dione, friedelan-3-one-25-al, friedelane-3,x-dione-25-al and three new acids were obtained by this procedure. This paper gives characteristics of the three acids and presents the proof of structure of one of them, this being relevant to a forthcoming publication.

The acids all gave negative tests with tetranitromethane and showed no evidence of unsaturation in their infrared and n.m.r. spectra. In view of their origin and the fact that they are saturated, it is highly likely all of them are members of the friedelane series. The characteristics of these compounds are given in the table.

TABLE

Formula	M.p.	$[\alpha]_D$	Ester m.p.
$C_{30}H_{48}O_3$	304-306°	-46°	233-235° (monomethyl)
$C_{30}H_{46}O_4$	334-336°	+83°	264-269° (monomethyl)
$C_{30}H_{46}O_5$	>360°	-68°	183-185° (dimethyl)

The acid, $C_{30}H_{46}O_4$, has been shown by the following evidence to have structure 1a. The infrared spectrum of this acid has peaks at 1692, 1715 and 1728 cm.$^{-1}$ whilst the infrared spectrum of its methyl ester, 1b, has no absorption band in the hydroxyl region. The absence of aldehydic, acidic or olefinic protons in the methyl ester was demonstrated by the n.m.r. spectrum* which exhibited no peaks in the region δ 2.5 - 12.0 except a sharp singlet due to the methyl ester grouping at δ3.6 (3 protons).



Ia R = O, R' = CO_2H

Ib R = O, R' = CO_2CH_3

Ic $R = <^{OH}_{H}$, R' = CO_2CH_3

Id R = O, R' = CHO

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* Spectra were taken on deuterochloroform solutions by a Varian A60 spectrometer using tetramethylsilane as an internal standard.

When treated with an excess of lithium aluminium hydride in ether for sixteen hours the methyl ester, 1b, yielded almost quantitatively a dihydroxy-methyl ester, 1c. The infrared spectrum of this product has a band at 1730 $cm.^{-1}$ and the n.m.r. spectrum has a signal at δ 3.6 (3 protons) due to the methyl ester group and a multiplet at δ 3.65 - 3.8 (2 protons) ascribed to the hydrogens on carbons attached to secondary hydroxyl groups. The dihydroxy-ester on acetylation afforded a diacetyl-methyl ester, as plainly indicated by its n.m.r. spectrum; on oxidation with Jones' reagent it was readily converted into the diketo-ester, 1b.

Treatment of the diketo-ester, 1b, with lithium aluminium hydride in boiling dioxane for sixteen hours yielded a mixture which presumably consists of epimeric alcohols since its infrared spectrum exhibited no absorption in the carbonyl region. Oxidation of the crude product with Jones' reagent yielded friedelane-3,x-dione-25-al, 1d,[*] identical in every respect with an authentic specimen. Thus the "O_4 acid" is friedelane-3,x-dione-25-oic acid.

The question as to the nature of possible naturally occurring precursor(s) of this acid remains to be answered. Initially it was

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[*] The position of the x-oxo group is either at C_{21} or C_{22} but its precise location is not known. cf. J. L. Courtney and J. S. Shannon, Tetrahedron Letters, 13 (1963).

thought that the diketo acid arose from the oxidation of the corresponding triol(s) since the extract of Siphonodon australe had been washed with alkali to remove acidic materials. However, when friedelane derivatives possessing the 25-aldehyde or 25-hydroxymethylene group were treated with chromium trioxide-pyridine or with chromic acid in acetic acid on the steam bath, no acidic compounds were formed. The precursor(s) of friedelane-3,*x*-dione-25-oic acid must therefore be one or more of the epimeric 3,*x*-dihydroxyfriedelane-25-oic acids. As is to be expected of a compound possessing a hindered carboxylic acid group, the diketo acid is a very weak acid; it is not therefore surprising that the dihydroxy-acid(s) should remain in the "neutral" extract of the bark.

REFERENCES

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