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STRUCTURE OF A NEW TRITERPENE ETHER FROM *SALACIA PRINOIDES* DC: X-RAY INVESTIGATION OF THE DIBROMO DERIVATIVE

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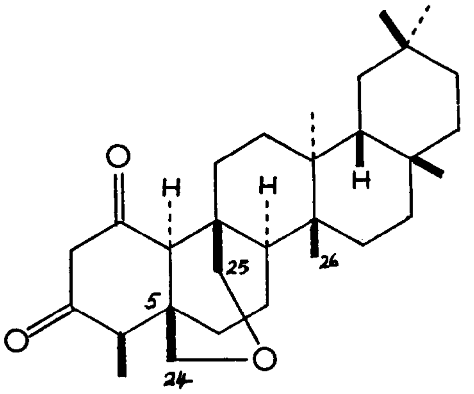
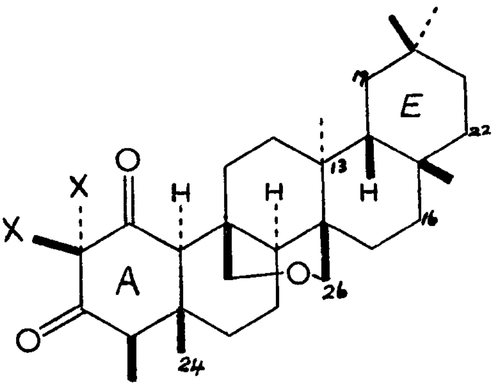
Abstract: An X-ray diffraction study has established the structure of the dibromo derivative of a new triterpene ether isolated from *Salacia prinoides* DC. as (IIb), a derivative of friedelane.

Because *Salacia prinoides* DC, an Indian shrub, has been used for the treatment of diabetes[1], the Indian authors have studied its constituents and have recently submitted for publication a paper describing the isolation, characterisation and chemistry of six crystalline compounds from the root bark, designated P,Q,R,S,T and U. All except R were, with varying degrees of confidence and directness, identified as 1,3-diketo derivatives of friedelane.

Compound R, $C_{30}H_{46}O_3$ (M^+454), m.p. 300°, $[\alpha]_D = -4.3°$, shared the spectroscopic features characteristic of a 1,3-diketone, but could not convincingly be correlated with the other compounds. It gave an enol acetate, m.p. 285 - 8°, which on catalytic reduction formed the 1-keto derivative, and Wolff-Kishner reduction of the latter gave the des-keto compound, $C_{30}H_{50}O$, m.p. 244 - 6°. As there is no other carbonyl or hydroxyl function in the molecule, the third oxygen is present as an ether linkage. The (100 MHz) n.m.r. spectrum showed three AB quartets, of which the doublets (1H each) at δ 3.48 and 3.22 (J = 16 Hz) are due to the methylene protons of the 1,3-diketone, and the pair of doublets (1H each) at δ 4.56 and 4.01 (J = 11 Hz) and δ 4.3 and 3.35 (J = 11 Hz) are attributed to the protons in a $-CH_2-O-CH_2-$ group. If a friedelane skeleton was assumed by analogy with the congeners, it became possible to interpret the mass spectral fragmentations for R and the properties of its derivatives in terms of either I or IIa.



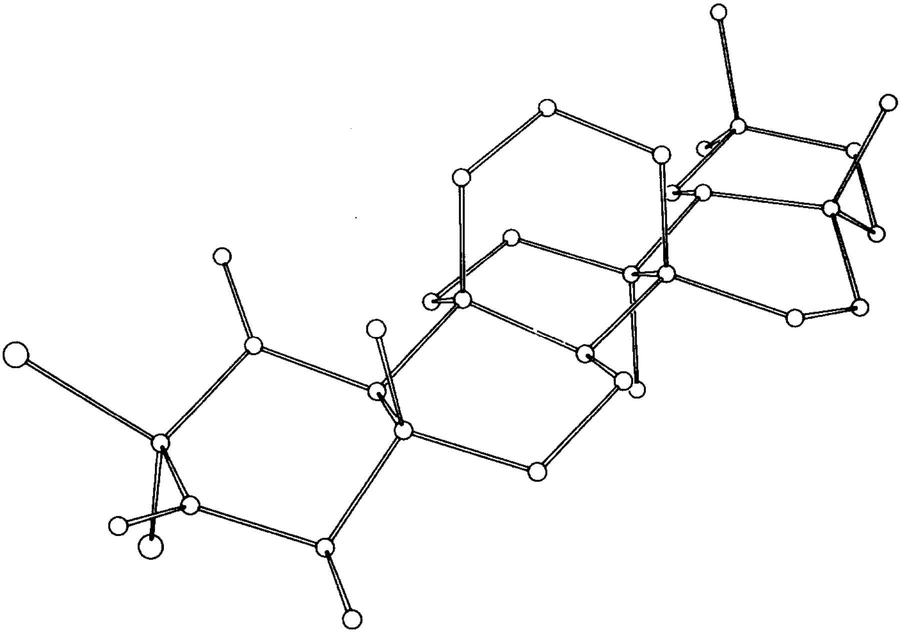
I



II a; X = H
b; X = Br

One of the methyls involved in the ether bridge should be C_{25}, but the other could be C_{24} or C_{26}. Structure I was preferred as most of the congeners of R have the methyl group attached to C_5 in an oxidised state, but, because of the uncertainties and absence of direct correlation of R with any derivative of friedelane, an X-ray study of the dibromoderivative (IIb) was undertaken in London.

Crystals, m.p. 340°, (from $CHC\ell_3$:MeOH) are monoclinic, $\underline{P}2_1$, a = 6.398, $\underline{b}$ = 12.043, $\underline{c}$ = 18.216 Å, β= 99.796°, $\underline{D}_c$ = 1.646 g.cm^{-3} for Z = 2. Measurements made with a Siemens diffractometer using Cu-$\underline{K}_\alpha$ radiation to θ = 70° gave 2677 observable intensities. The structure, which was solved by standard heavy-atom procedures and is currently refined to $\underline{R}$ = 0.096, has established the constitution as IIb, thus confirming compound R to be a derivative of friedelane, *viz.* 25, 26-oxido-friedel-1, 3-dione. This appears to be the first instance of a friedelane derivative having an oxygen function attached to C_{26}. Its stereochemistry, shown in the figure, corresponds very closely to that found by Kikuchi *et al.*[2] for 3β-O-acetyl-16β-O-p-bromobenzoylpachysandiol-B, the only other friedelane derivative to have been studied by X-rays in 3-D. Thus the A,B,C and tetrahydropyran rings are chairs, whereas rings D,E are boats with atoms C_{13}, C_{16}, C_{19}, C_{22} at prow and stern.



This conformation for rings D,E, which Kikuchi designates S̲, differs from the E̲ (cis-decalin like) conformation deduced by Corey and Ursprung[3] from a 2-D X-ray study of friedelan-3α-ol chloroacetate. The bridge between atoms C_{25} and C_{26} in the present structure removes much of the extensive strain that occurs between the five β-methyl groups in friedelane, so our ring system is much less warped than that depicted by Kikuchi *et al.*

References

1. V. Krishnan and S. Rangaswami, *Tetrahedron Letters*, 1967, 2441.
2. T. Kikuchi, M. Niwa and N. Masaki, *Tetrahedron Letters*, 1972, 5249.
3. E.J. Corey and J.J. Ursprung, *J. Amer. Chem. Soc.*, 1956, *78*, 5041.