X-Ray Crystal Structure of a Derivative of Salaspermic Acid

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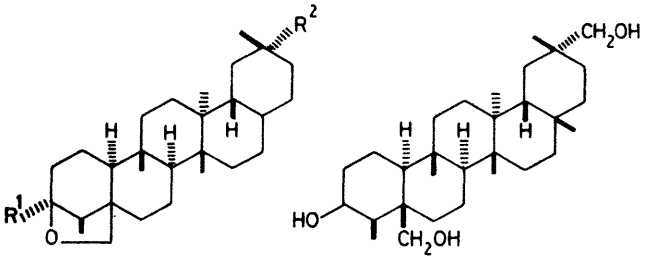
Summary The structure of salaspermic acid, isolated from *Salacia macrosperma* Wight., has been shown to be 24-hydroxyfriedelan-3-on-29-oic acid hemiacetal (**1a**) by an *X*-ray study of the compound (**3**) obtained from the acid by a sequence of reactions leading to enlargement of ring E.

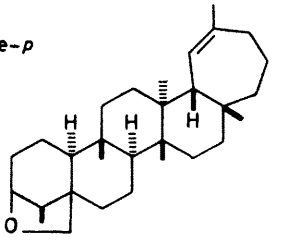
IN continuation of our work on the triterpenes of the *Salacia* species,[1] we have isolated from *Salacia macrosperma* Wight. a new acid designated salaspermic acid (**1a**), $C_{30}H_{48}O_4$, m.p. 335 °C. Although some structural information was available from chemical and spectral properties, no direct correlation with a friedelane of established structure proved possible, though it was probable on biogenetic grounds. Reduction

of (**1b**) with lithium aluminium hydride gave the triol (**2**), which on treatment with toluene-*p*-sulphonyl chloride afforded a mixture of the expected tosylate (**1c**) and a rearrangement product (**3**), $C_{30}H_{48}O$ (M^+ 424), m.p. 286–288 °C. Crystals of (**3**) grown from CH_2Cl_2 are colourless needles.



(1) (2)

a; R^1 = OH, R^2 = CO_2H
b; R^1 = OH, R^2 = CO_2Me
c; R^1 = H, R^2 = $CH_2OO_2SC_6H_4Me$-*p*
d; R^1 = H, R^2 = CH_2OAc



(3)

Crystal data: orthorhombic, space group $P2_12_12_1$, a = 28·160(1), b = 13·573(1), c = 6·431(1) Å; Z = 4. The intensities of 2744 reflexions (to θ = 71°) were measured with Cu–K_α radiation, and 2533 were considered observable. The structure was solved by direct methods and refined (C and O anisotropically; H isotropically) to R 0·042.† The molecular configuration of (**3**) depicted in the Figure shows that it is indeed a friedelane derivative in which ring E has been enlarged by the incorporation of the tosylate methylene. The *X*-ray study also confirms the formulation of salaspermic acid[2] as (**1a**) except for the stereochemistry of the carboxy-group. However, the ease of hydrolysis of the ester (**1b**), and the n.m.r. signals of the CH_2OAc group in compound (**1d**) indicate an equatorial disposition for the carboxy-group as shown in (**1a**). The stereochemical reconstruction of the oxo-ring in passing from (**2**) to (**3**) is at first sight unexpected, but seems in this context to be dictated by the relatively rigid pentacyclic ring system and the presence of the β-methyl group at C(4) which is in close contact with both O and C(24).

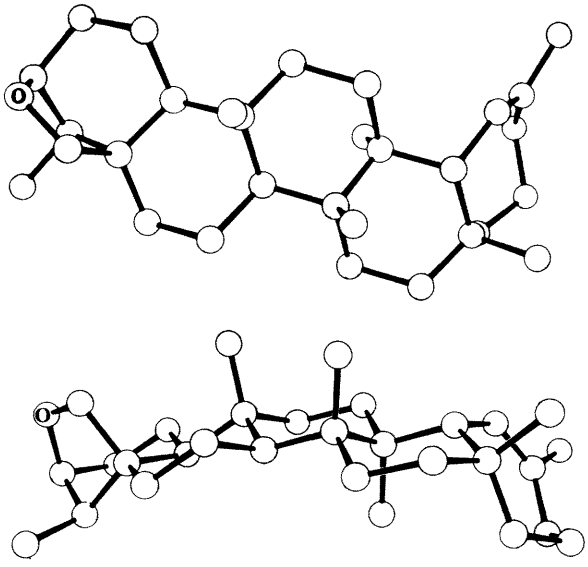


FIGURE. Two views of the molecular structure of compound (**3**).

This is the sixth reported *X*-ray determination of a friedelane derivative and it is the first well-established friedelane to incorporate a chair form of ring D. There has been considerable discussion in the literature on the conformation of the *cis*-fused D/E rings, but, as shown in the preceding Communication, the only instances of chair–chair conformation are in campanulin which is not a true friedelin, and in the very first assignment, that of 3α-friedelanol chloroacetate, which is based on an unconvincing two-dimensional map. The rearrangement of the tosylate (**1c**) to (**3**) offers an opportunity for the strained D/E end of (**1c**) to go over to a close approximation to the alternative chair–chair conformation as enlargement removes the interaction between C(27) and C(30) and leads to a geometry which appears to be nearly strain free. The n.m.r. spectrum of (**3**) reported in ref. 2 is consistent with the *X*-ray structure, but did not allow the D/E conformation to be identified unambiguously.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] B. S. Joshi, V. N. Kamat, and N. Viswanathan, *Tetrahedron*, 1973, **29**, 1365; D. Rogers, D. J. Williams, B. S. Joshi, V. N. Kamat, and N. Viswanathan, *Tetrahedron Lett.*, 1974, **63**; D. Rogers, F. L. Phillips, B. S. Joshi, and N. Viswanathan, preceding Communication.
[2] N. Viswanathan, *J. Chem. Soc., Perkin Trans.* 1, 1979, 349.