Isomerisation of a β-Amyrin Derivative to an α-Amyrin Derivative[1]

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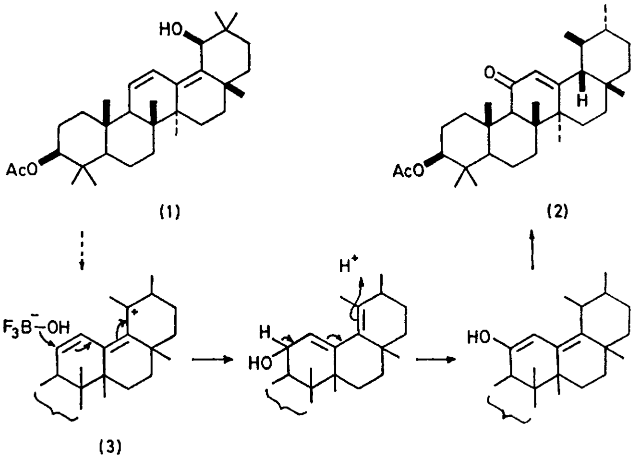
Summary Treatment of 19β-hydroxyolean-11,13(18)-dien-3β-yl acetate with boron trifluoride etherate yields 11-oxo-α-amyrin acetate, together with olean-9(11),12,18-trien-3β-yl acetate and an unidentified trienyl acetate.

SKELETAL rearrangements involving interconversion of the various members of the oleanane group of pentacyclic triterpenes, and formation of the oleanane skeleton from members of the lupane and ursane series, are well known.[2] In all cases the thermodynamically most stable product is an oleanane derivative. We now report the first example of the formation of a simple derivative of α-amyrin from a compound possessing the oleanane skeleton.

When 19β-hydroxyolean-11,13(18)-dien-3β-yl acetate (**1**) is left overnight at room temperature with excess (30—40 mol.) boron trifluoride etherate (15—20% in ether), the product (*ca.* 90% yield) is a mixture of approximately equal amounts of olean-9(11),12,18-trien-3β-yl acetate,[3] an as yet unidentified trienyl acetate, and 11-oxo-α-amyrin acetate (**2**). The α-amyrin derivative (**2**), which was identified by comparison with an authentic sample,[1] presumably arises from nucleophilic attack by a trifluoroborate species on the rearranged carbonium ion (**3**). Compound (**2**) is also formed when the dienol (**1**) is treated with phosphorus oxychloride in pyridine or when olean-11,13(18)-dien-3β-yl acetate[4] is photo-oxidised in the presence of mercury(II) bromide.[5]

The 19β-hydroxydiene (**1**), m.p. 235—237° (from EtOH), $[\alpha]_D$ $-30 \pm 0{\cdot}5°$ (in $CHCl_3$), was prepared in *ca.* 80% yield by irradiation,[1] at 70°, of a solution of olean-11,13(18)-dien-3β-yl acetate[4] in dioxan containing *N*-bromosuccinimide.



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[1] Previous paper in this series: B. W. Finucane and J. B. Thomson, *J.C.S. Perkin I*, 1972, 1856.

[2] J. F. King and P. de Mayo in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1964, pp. 815—829.

[3] L. Ruzicka, O. Jeger, and J. Redel, *Helv. Chim. Acta*, 1943, **26**, 1235.

[4] G. G. Allan and F. S. Spring, *J. Chem. Soc.*, 1955, 2125.

[5] *Cf.* N. Friedman, M. Gorodetsky, and Y. Mazur, *Chem. Comm.*, 1971, 874.