The Synthesis of Cycloartenol

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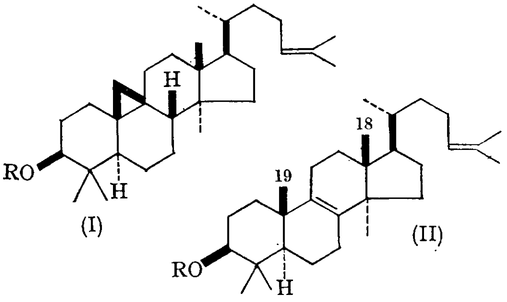
THE triterpenoid cycloartenol (I; R=H) is the parent of a large family of triterpenoids and alkaloids characterised by the $9\beta,10\beta$-cyclopropane ring. Cycloartenol has recently been envisaged as a possibly important intermediate in the biosynthesis of tetracyclic triterpenoids and steroids in plants.[1] We report the first synthesis of cycloartenol from readily available lanosterol (II; R=H). Since the latter has been totally synthesised[2] our synthesis amounts to a total synthesis of cycloartenol.

3β-Acetoxylanost-24-en-11-one[3] (III; R^1=Ac, R^2=H) was reduced with lithium aluminium hydride in ether, and the product benzoylated in pyridine to give 3β-benzoyloxylanost-24-en-11β-ol (IV; R^1=COPh, R^2=R^3=H), m.p. 229—230°, $[\alpha]_D$ + 68° (all $[\alpha]_D$ in $CHCl_3$ at c, *ca.* 1·0). Treatment of the latter with nitrosyl chloride in pyridine afforded the corresponding 11β-nitrite (IV; R^1=COPh, R^2=NO, R^3=H), m.p. 156—157°, which on photolysis[4] in dry benzene containing iodine (6 mole) under oxygen-free nitrogen using a 125 w medium pressure mercury lamp (Pyrex filter) gave the iodo-derivative (IV; R^1=COPh, R^2=H, R^3 = I). This was immediately oxidised with Kiliani's chromic acid solution to furnish 3β-benzoyloxy-19-iodolanost-24-en-11-one (III; R^1 =COPh, R^2=I), (60%), m.p. (from $CHCl_3$–MeOH) 143—144°, $[\alpha]_D$ + 36°. There was no detectable formation of an 18-iodo-compound, the minor product from the reaction being 3β-benzoyloxylanost-24-en-11-one (III, R^1=COPh, R^2=H), m.p. 168—170°, $[\alpha]_D$ + 75°.

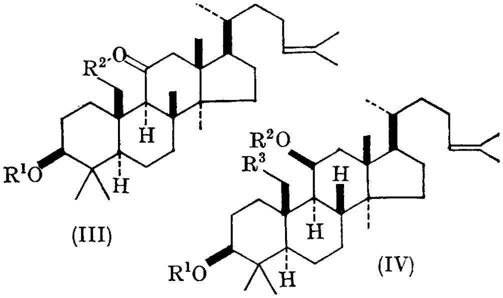
On treatment with potassium t-butoxide in t-butanol at room temperature for 2 hr. the γ-iodoketone (III; R^1=COPh, R^2=I) afforded smoothly 11-oxocycloartenyl benzoate (V; R=COPh), m.p. 144—145°, $[\alpha]_D$ + 119°. Reduction of this ketone with an excess of lithium aluminium hydride in dioxan[5] afforded cycloarternol (I; R=H), characterised as its acetate (m.p., mixed m.p., $[\alpha]_D$ and i.r. spectrum).[6]

In another series of experiments cycloartenyl acetate dibromide[7] was oxidised with chromic acid in acetic acid according to the directions of Corsano and Nicita[8] to give, after debromination with sodium iodide in acetone and chromatography over alumina (grade III), 11-oxocycloartenyl acetate (V; R=Ac), (15%), m.p. 126—127°, $[\alpha]_D$ + 129°. On hydrogenation this compound gave 11-oxocycloartenyl acetate identical with an authentic specimen kindly provided by Professor Corsano.



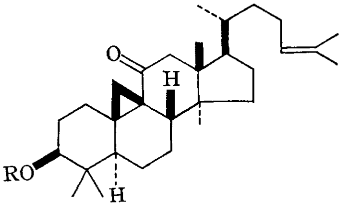
(I)

(II)



(III)

(IV)



(V)

Alkaline hydrolysis of 11-oxocycloartenyl acetate (V; R=Ac) gave 11-oxocycloartenol (V;

R=H), m.p. 185—187°, $[\alpha]_D + 139°$, which on benzoylation afforded the 3-benzoate (V; R=COPh) already described above.

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[1] J. D. Ehrhardt, L. Hirth, and G. Ourisson, *Compt. rend.*, 1965, **260**, 5931; *Phytochemistry*, 1967, **6**, 815; G. Ponsinet and G. Ourisson, *Phytochemistry*, 1967, **6**, 1235.

[2] R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelly, *J. Chem. Soc.*, 1957, 1131.

[3] W. Lawrie, F. S. Spring, and H. S. Watson, *Chem. and Ind.*, 1956, 1458.

[4] M. Akhtar, D. H. R. Barton, and P. G. Sammes, *J. Amer. Chem. Soc.*, 1964, **86**, 3394; 1965, **87**, 4601.

[5] D. Herlem-Gaulier, F. Khuong-Huu-Lainé, and R. Goutarel, *Bull. Soc. chim. France*, 1966, 3478.

[6] D. H. R. Barton, *J. Chem. Soc.*, 1951, 1444.

[7] K. Schreiber and G. Osske, *Tetrahedron*, 1964, **20**, 1805.

[8] S. Corsano and G. Nicita, *Ricerca. Sci.*, 1967, **37**, 351.