The Synthesis of Cycloartenol

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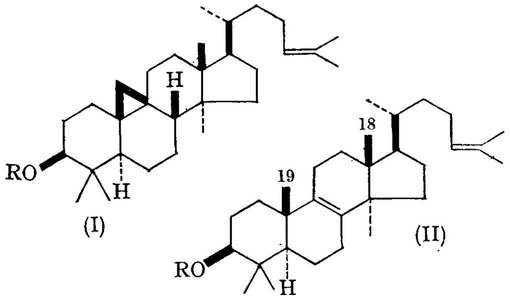
THE triterpenoid cycloartenol (I; R=H) is the parent of a large family of triterpenoids and alkaloids characterised by the 9β,10β-cyclopropane ring. Cycloartenol has recently been envisaged as a possibly important intermediate in the biosynthesis of tetracyclic triterpenoids and steroids in plants.[1] 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.

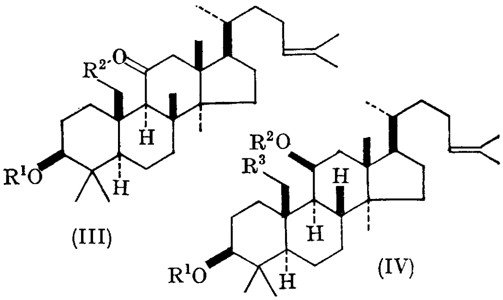
3β-Acetoxylanost-24-en-11-one[3] (III; R^1=Ac, R^2=H) was reduced with lithium aluminium hydride in ether, and the product benzoylated in pyridine to give 3β-benzoyloxylanost-24-en-11β-ol (IV; R^1=COPh, R^2=R^3=H), m.p. 229—230°, $[\alpha]_D$ + 68° (all $[\alpha]_D$ in $CHCl_3$ at c, *ca.* 1·0). Treatment 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]

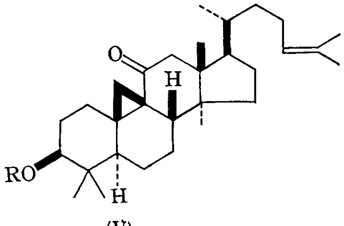
In another series of experiments cycloartenyl acetate dibromide[7] was oxidised with chromic acid in acetic acid according to the directions of Corsano and Nicita[8] to give, after debromination with sodium iodide in acetone and chromatography over alumina (grade III), 11-oxocycloartenyl acetate (V; 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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