A Tirucall-7-ene to Apotirucall-14-ene Rearrangement Initiated by Bromine

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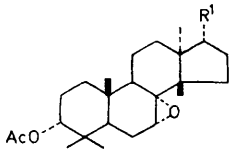
Summary Attack by bromine on the Δ^7-double bond of methyl 3α-acetoxytirucalla-7,24-dien-21-oate induces rearrangement to a 7α-bromoapotirucall-14-ene derivative.

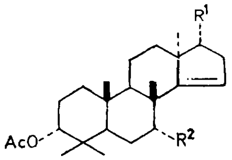
7α,8α-Epoxytirucallane derivatives (*e.g.* I) are rearranged with boron trifluoride–ether complex to give apotirucall-14-ene derivatives (*e.g.* II).[1] The epoxide (I) was prepared[1] by bromination in ether of a mixture of methyl Δ^7- and Δ^8-elemolates, acetylation, treatment of the acetylated product with ozone, and reductive work-up with zinc dust in boiling water when (I) was obtained from the Δ^7-isomer together with ketonic products from the Δ^8-isomer. This procedure has now been repeated using chloroform as solvent for bromination and a small yield of the 7α-bromoapotirucallane derivative (IV), m.p. 189—191°, $[\alpha]_D$ −99° has been isolated. It was also obtained starting from pure methyl Δ^7-elemolate acetate (V). Evidence for structure (IV) included the expected n.m.r. and m.s. data and its dehydrobromination to give the acid (VI).

Formation of the bromo-ketone (IV) must involve the bromonium ion (VII) which rearranges to (III). With ozone this gives the 14β,15β-epoxide which on treatment with zinc dust in boiling water undergoes debromination in the side chain and rearrangement of the 14β,15β-epoxy-group to the 14αH,15-ketone which is known to occur readily under very mild conditions.[2]

Earlier it was suggested[1] that a key feature of the rearrangement of the 7α,8α-epoxide (I) to the apotirucall-14-ene (II), rather than to an isotirucall-13(17)-ene as would be expected with mineral acid (*cf.* ref. 3), was a 1,3-diaxial type relationship between the C-15α proton and the epoxide oxygen, a feature also emphasised by ApSimon and his co-workers[4] with reference to the rearrangement of other terpenoid epoxides. The rearrangement now described suggests that a more important factor leading to the apotirucall-14-ene structure is the unfavourable 1,3-diaxial

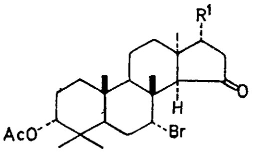


(I)



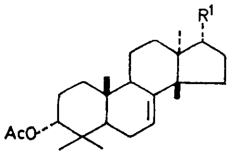
(II) $R^2 = OH$

(III) 24,25-dibromo-$R^1, R^2 = Br$

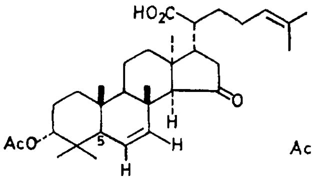


(IV)

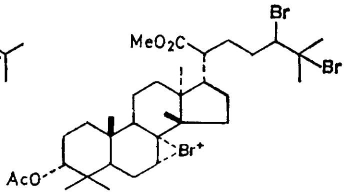
$R^1 = MeO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CH=CMe_2$



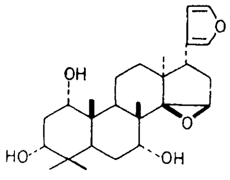
(V)



(VI)



(VII)



(VIII)

interaction which results with the 7α-substituent if the C-13α methyl substituent moves to C-14. This interaction could also explain why the epoxide group in havenensin (VIII) with a 7α-hydroxy-group rearranges[5] to give only a 14αH,15-ketone without any skeletal rearrangement, whereas related 7β-hydroxy- and 7-oxo-compounds give equal amounts of the corresponding 14α-H,15-ketones and 15α-hydroxy-vinyl($\Delta^{13,17}$)furans in which the C-13α methyl group has moved to C-14 into a 1,3-diaxial arrangement with only a 7α-proton.

The selectivity for attack on the side-chain double bond in (V) in ether compared with the attack on both double bonds in chloroform is similar to the effect of these solvents on the reactivity of aromatic peracids on the double bonds of euphol. Ourisson and his co-workers[6] have shown that in ether *p*-nitroperbenzoic acid selectivity oxidises the **24,25**-double bond but attacks both this and the 8,9-double bond in chloroform.

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