The Mechanism of the Rearrangement of Havanensin

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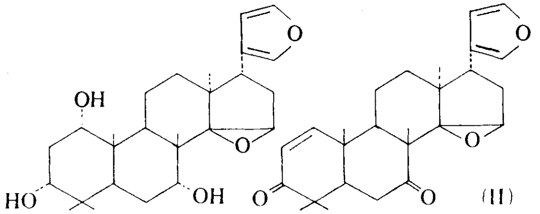
CHAN, GIBBS, and TAYLOR[1] have reported the presence of the limonoid havanensin (I), together with its 1,7- and 3,7-di and 1,3,7-tri-acetate, in the timber of *Trichilia havanensis*, and have found that with dilute acid the oxide-ring opens to give the 15-ketone, neohavanensin. A similar reaction also takes place in heudelottin.[1,2]

We have now investigated the possibility that ring-opening under such mild conditions might involve participation of the oxygen function at C(7). Havanensin acetates are the main limonoid constituents of the seed of the West African variety of *Khaya anthotheca* (Welw.) C.DC., together with smaller amounts of the 14,15-deoxy-compounds. Havanensin is readily converted by 0·05 N-acid to neohavanensin. We find that havanensin triacetate and the related 3,7-dione (II) are similarly easily isomerised, but in these cases the product is a mixture of the 15-ketone and the product of Wagner-Meerwein rearrangement in which the 13-methyl group migrates to C(14), and the product contains a 13,17 double bond and a 15-hydroxy-group; as in the similar case of isocedrelone.[3]

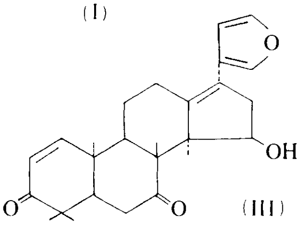
The derived 3β,7β-saturated alcohol, m.p. 191–194°, prepared by borohydride reduction of the dione (II), is also isomerised by acid under mild conditions, giving a mixture of the derived 15-ketone and the 14-methyl-15-hydroxy-isomer.

In this case, assistance by a neighbouring group is not stereochemically possible, and the reaction must proceed by direct acid-catalysed opening of the oxide ring. It may be significant that havanensin, the 7α-hydroxy-compound, apparently gives only the 15-ketone; whereas the 7α-acetate, the 7-ketone, and the 7β-hydroxy-compound give *ca.* equal mixtures of the 15-ketone and the 14-methyl-15-hydroxy-compound obtained by Wagner–Meerwein rearrangement.

In all cases the first stage appears to be the opening of the epoxide ring by acid catalysis to give a 15-hydroxy-14-carbonium ion, which either undergoes Wagner–Meerwein rearrangement or loses a proton to give the 15-ketone enolate. In the case of the ketone, acetate, and 7β-hydroxy-compound, these reactions compete equally: but in the case of the 7α-hydroxy-compound we suggest that the 7α-OH is bonded to the carbonium ion, possibly to form a 7–14-oxide ring or possibly merely as a charge-association complex, and that this shields the carbonium ion from the 13α-methyl group so that Wagner–Meerwein rearrangement does not occur.



(I) (II)



(III)

14,15-Deoxyhavanensin 3,7-diacetate has m.p. 204—208°, the n.m.r. spectrum lacks the oxide proton present in the havanensin acetates, and H(7) is shifted downfield to δ 5·31, in a way characteristic of $\Delta^{14(15)}$ compounds.[4] There is also a new signal appearing as a broad singlet at δ 5·18, which we ascribe to the H(15) vinyl proton. Oxidation with chromic acid in acetone, followed by chromatography over alkaline alumina, gave an amorphous unsaturated ketone, which was shown to be the $\Delta^{2(3)}$-1-ketone, and not the isomeric 7-deacetoxy-7-oxoazadirone,[5] by the n.m.r. spectrum (coupled doublets at δ 6·34, 5·68, *J* 10 c./sec. characteristic of $\Delta^{2(3)}$-1-ketones). Deoxyhavanensin triacetate did not crystallise.

The Wagner-Meerwein product (III) from the dione (II) has m.p. 182—185°, $\nu_{\max}$ 1670 cm.$^{-1}$ (cyclohexenone and hydrogen bonded cyclohexanone); $\lambda_{\max}$ 237 (ϵ 1·8 × 10^4), $\lambda_{\max}$ (trichilenone as reference compound) 240 mμ (ϵ 1·2 × 10^4) (vinyl furan). The n.m.r. spectrum showed the expected features.

The spectra and analyses of the other new compounds mentioned have been recorded, but show no features of special interest.

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