The Limonoids of *Trichilia havanensis* Jacq.: an Epoxide Rearrangement

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THE limonoids of *Trichilia havanensis* occur as a complex mixture of esters, mainly acetates, some of which have been separated by column chromatography and recrystallisation. Three of the esters afford havanensin (I), $C_{26}H_{38}O_5$, m.p. 235—237°, ν_{max} 3350 cm.$^{-1}$, on basic hydrolysis. N.m.r. spectral data and chemical transformations allow the parent esters to be formulated as the triacetate (II), m.p. 188—191°, and the two diacetates (III), amorphous, and (IV), m.p. 174—175°. The stereochemistry shown at C-1, C-3, and C-7 follows from the small (< 8 c./sec.) half-height width of the protons in the n.m.r. spectra of (II), (III), and (IV).

Sarett oxidation of (III) and (IV) followed by hydrolysis yielded trichilenone (V) (naturally occurring as the amorphous acetate) $C_{26}H_{34}O_4$, m.p. 199—201°, ν_{max} 3450 and 1650 cm.$^{-1}$, λ_{max} 222 mμ (ϵ 9800), and isotrichilenone (VI), m.p. 205—207°, ν_{max} 3450 and 1680 cm.$^{-1}$, λ_{max} 220 mμ (ϵ 9750) respectively. The orientation of the enone chromophore in (V) and (VI) is shown by the n.m.r. spectra, circular dichroism data, and mass spectral fragmentation patterns† which will be detailed in the full paper.

The chemistry of compounds in this series with a 7α-hydroxy-group or the corresponding acetate is characterised by a ready and quantitative isomerisation by acid (0·05M-HCl in methanol for 30 min. or during several days in ethyl acetate or chloroform) or heating to 240°. Thus havanensin (I) gives neohavanensin (VII), m.p. 286—288°, ν_{max} 3380 and 1716 (H-bonded cyclopentanone) cm.$^{-1}$; the triacetate (II) affords neohavanensin triacetate (VIII), m.p. 238—240°, ν_{max} 1740 cm.$^{-1}$; and trichilenone (V) yields neotrichilenone (IX), m.p. 215—218°, ν_{max} 3390, 1724, and 1667 cm.$^{-1}$ (acetate, m.p. 207—211°, ν_{max} 1742 and 1670 cm.$^{-1}$). The n.m.r. spectra of (VIII) and (IX) compared with those of their precursors showed the loss of the epoxide proton and the appearance of a wide triplet at 3·64 and 3·54 (J = 10 c./sec.) respectively, which must be assigned to H-17. The multiplicity agrees with that observed for H-17 in androstan-17-ols and their acetates.[1] The spectra further define the environment of the carbonyl group generated in the transformation (see Table). Confirmation of the assignments was provided by the n.m.r. spectrum of the product from base-catalysed deuteration of neotrichilenone. This showed the disappearance of the signals attributed to H-2, H-14, and H-16, while H-17 sharpened to a broad singlet (w_H = 3 c./sec.) as expected from H,D coupling.[2] Neotrichilenone is recovered quantitatively from base treatment under conditions which effected the deuteration. This suggests that ring-C exists in the more stable chair conformation (*i.e.*, 14-α) in the *neo*-series.

Jones' oxidation of either havanensin or neohavanensin gave the tetraketone (X), $C_{26}H_{32}O_5$, m.p. 131—132°, λ_{max} 257 mμ (ϵ 10,700) shifting in base to 288 mμ (ϵ 18,000), ν_{max} 1740 (cyclopentanone), 1724 and 1706 (cyclohexanones) cm.$^{-1}$ which was characterised as the enol acetate, ν_{max}

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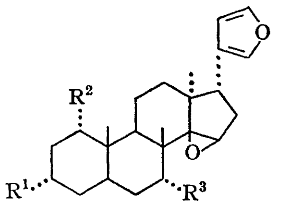
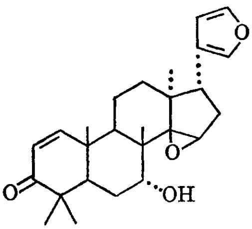
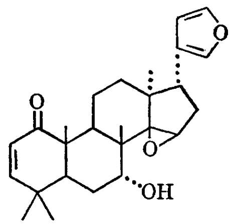
† Circular dichroism measurements were done by Dr. G. Snatzke and mass spectra by Dr. H.-W. Fehlhaber and Dr. R. T. Aplin.



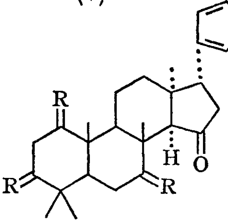
(I) $R^1{=}R^2{=}R^3{=}OH$
(II) $R^1{=}R^2{=}R^3{=}OAc$
(III) $R^1{=}OH$, $R^2{=}R^3{=}OAc$
(IV) $R^1{=}R^3{=}OAc$, $R^2{=}OH$



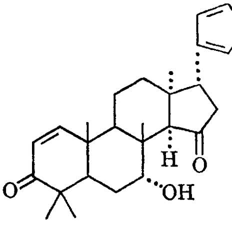
(V)



(VI)



(VII) R=H, α-OH
(VIII) R=H, α-OAc
(X) R=O



(IX)

TABLE

Nuclear magnetic resonance signals (given in δ-values for $CDCl_3$ solutions)

									Furan			
Compound	H-1	H-3	H-7	H-2	H-14	H-15	H-16	H-17	α-H	β-H	Ac	C-Methyls
(II)	4·71	4·71	4·71			3·42			7·11 7·37	6·16	2·03 2·12 (2)	0·81, 0·92, 1·01 (2), 1·06
(III)	4·95	3·41	4·78			3·42			7·14 7·40	6·19	2·09 2·12	0·86, 0·94, 0·99 (2), 1·06
(IV)	3·54	4·92	4·70			3·42			7·10 7·35	6·17	2·15 (2)	0·79, 0·91, 0·94, 1·05, 1·08
(V)	7·18d		3·59	5·82d		3·59			7·09 7·34	6·16		0·97, 1·07, 1·09, 1·14, 1·18
(VI)		6·34d	3·57	5·68d		3·57			7·11 7·35	6·20		1·03, 1·06 (2), 1·09, 1·27
(VIII)	4·67	4·81	4·88		2·46		2·48d	3·47t	7·26 7·38	6·27	2·03 2·07 2·15	0·77, 0·82, 0·91, 0·98, 1·11
(IX)	7·12d		3·88	5·86d	2·77		2·52d	3·54t	7·30 7·40	6·30		0·79, 1·10 (3), 1·15
(X)				3·48	3·04		2·52d	3·39t	7·29 7·40	6·31		0·86, 1·18, 1·24, 1·32, 1·41

d=doublet, J = 10c./sec.; t=triplet, J=10c./sec.

1773 (acetate), 1742 (cyclopentanone), 1715 (cyclohexanone), 1680 (cyclohexenone) cm.$^{-1}$ As expected from the *cis*-C/D ring junction, there is a downfield shift of H-14 on conversion into the 7-ketone.

These results suggest that derivatives of heudelottin[3] assigned trimethylene oxide structures are the analogous 15-keto-compounds. This is in agreement with all the physical data quoted. The downfield position of the H-17 triplet in the compound with an 11β-hydroxyl could be explained by the proximity of the hydroxyl group.

Compounds of the *neo*-series are naturally occurring, neohavanensin being obtained from careful base hydrolysis of an incompletely characterised ester. All the limonoids so far isolated from *Trichillia spp.* have a carbocyclic ring-D[3,4] but the major limonoid from *T. trifolia* is gedunin.[5]

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[1] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, 1964, p. 78.
[2] Ref. 1, p. 55.
[3] D. A. Okorie and D. A. H. Taylor, *Chem. Comm.*, 1967, 83.
[4] W. R. Chan and D. R. Taylor, *Chem. Comm.*, 1966, 206.
[5] A. Akisanya, C. W. L. Bevan, T. G. Halsall, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.*, 1961, 3705.