Hirtin and Deacetylhirtin: New "Limonoids" from *Trichilia hirta*

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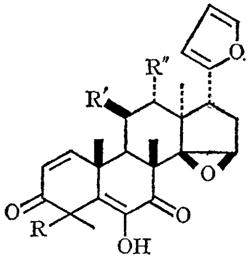
Extraction of the seeds and leaves of *Trichilia hirta* L. (Meliaceae) has yielded a new crystalline limonoid, hirtin, $C_{32}H_{36}O_{11}$, molecular ion at *m/e* 596,[1] m.p. 159—161°, $[\alpha]_D + 26{\cdot}0°$ ($CHCl_3$) for which we propose the structure (I).

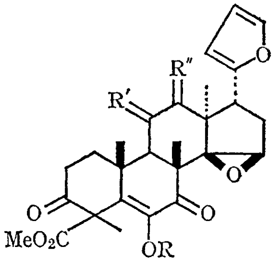
The spectral properties [λ_{max} 217, 277 mμ (ε, 10,280 and 7450) shifting in base to 326 mμ (ε, 4470); ν_{max} 3290, 1750, 1686, 1630, 1502, and 876 cm.$^{-1}$] suggested that hirtin contained all the chromophores present in cedrelone (II).[2] This is supported by the n.m.r. spectrum[3] with signals at 7·30, 7·13, 6·08 (β-substituted furan), 7·03 and 6·18 (doublets, $J = 10$ c./sec.) [C-1(H) and C-2(H) respectively] and 6·57 (diosphenol, lost on deuteration). The n.m.r. spectrum further revealed the presence of four tertiary *C*-methyl groups (0·80, 1·43, 1·45, and 1·83), a methyl of an ethyl group (1·03, triplet, $J = 7$ c./sec.), an acetate (2·20), a methyl ester (3·77), a deshielded epoxide (3·93) and two broadened singlets (5·23 and 5·41) suggestive of two groups of the type *H*-C-OCO·R.

The spectral evidence presented is consistent with hirtin being related to cedrelone, with one *C*-methyl transformed into a methoxycarbonyl group and with two additional ester groups, one of which is an acetate. Assuming a C_{26} limonoid skeleton, and taking cognizance of the ethyl group, the other ester must be a propionate.

Hydrogenation of hirtin with palladium–carbon in ethanol afforded dihydrohirtin (IV), m.p. 248—250°, λ_{max} 277 mμ (ε, 8700) which showed the disappearance of the appropriate bands in the n.m.r. spectrum. Treatment of dihydrohirtin with dimethyl sulphate and alkali gave the methyl ether (V), m.p. 205—206°, λ_{max} 211, 263 mμ (ε, 5600 and 5400), which on basic hydrolysis followed by oxidation with chromium trioxide afforded the stable yellow α-diketone (VI), molecular ion at *m/e* 510, m.p. 235—237°, λ_{max} 210, 266 mμ (ε, 8440 and 6100). The formation of (VI) from (V) with the loss of five carbon atoms confirms that hirtin contains an acetate and a propionate ester. The diketone (VI) was converted into its methyl ether (VII) m.p. 185—186°, λ_{max} 210, 270 mμ (ε, 12,400 and 14,530) with dimethyl sulphate and alkali.

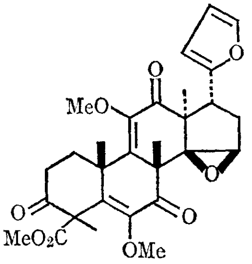


(I) $R{=}CO_2Me$; $R'{=}OAc$
$R''{=}O{\cdot}COEt$
(II) $R{=}Me$; $R'{=}R''{=}H$
(III) $R{=}CO_2Me$; $R'{=}OH$
$R''{=}O{\cdot}COEt$

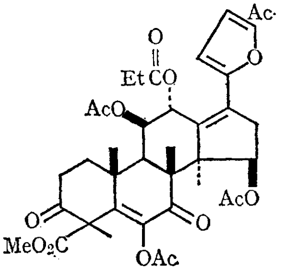


(IV) $R{=}H$; $R'{=}\beta$-OAc, H;
$R''{=}\alpha$-O·COEt, H
(V) $R{=}Me$; $R'{=}\beta$-OAc, H;
$R''{=}\alpha$-O·COEt, H
(VI) $R{=}Me$; $R'{=}R''{=}O$

Confirmation of the presence of the epoxide was obtained as follows: treatment of dihydrohirtin in acetic anhydride with the boron trifluoride—ether complex gave an acetate $C_{38}H_{44}O_{14}$, (VIII) λ_{max} 235, 280 mμ (ε, 12,800 and 12,500). The n.m.r. spectrum showed the presence of three acetate residues in addition to the acetyl attached to the furan ring. There were no olefinic protons. This reaction defines the relative configuration of C-13, C-17, and the epoxide.[2] The stereochemistry at C-9, C-11, and C-12 follows from the small coupling constants for the protons at C-11 and C-12. The stereochemistry at the other centres is based on the assumed relationship to cedrelone.



(VII)



(VIII)

Spectral evidence, to be discussed in the full Paper, indicates that the acetate is at C-11 and the propionate is at C-12. The methoxycarbonyl group, which must be tertiary since it resists hydrolysis (*vide supra*), is placed on a carbon bearing a *C*-methyl (C-4) to explain the appearance of one of the methyls at very low field (1·83) in hirtin.[4]

The seeds of *Trichilia hirta* L. also contain the amorphous compound deacetylhirtin (III). The amorphous compound had the same ultraviolet absorption spectrum as hritin. The n.m.r. spectrum was particularly informative, showing all the main peaks of hirtin except those due to the acetate (2·20) and the proton on carbon bearing acetate (5·41). The relationship of the two limonoids was confirmed by converting the amorphous compound into the methyl ether of dihydrohirtin.

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[1] Mass-spectral data were obtained on the A.E.I. MS9 instrument through the courtesy of Dr. T. G. Halsall.

[2] (a) R. Hodges, S. G. McGeachin, and R. A. Raphael, *J. Chem. Soc.*, 1963, 2515; (b) K. W. Gopinath, T. R. Govindachari, P. C. Parthasarathy, N. Viswanathan, D. Arigoni, and W. C. Wildman, *Proc. Chem. Soc.*, 1961, 446.

[3] N.m.r. data refer to deuterochloroform solutions and are in p.p.m. from tetramethylsilane as internal standard.

[4] C. A. Henrick and P. R. Jefferies, *Austral. J. Chem.*, 1964, **17**, 915.