

## The Structure of Heudelottin, an Extractive from *Trichilia heudelottii*

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LIGHT PETROLEUM extraction of the timber of *Trichilia heudelottii* Planch ex. Oliv. (Meliaceae), followed by column chromatography has given two substances, dregeanin, a compound of unknown structure previously isolated from *Trichilia dregeana*<sup>1</sup> (syn. *T. splendida*), and a crystalline solid m.p. 178—180°, which we name heudelottin. Analysis and mass spectra give the formula

$C_{42}H_{60}O_{11}$ , absorption spectra show the presence of a furan ring ( $\nu_{\max}$  875  $\text{cm}^{-1}$ , n.m.r. 2 $\alpha$ -furan H,  $\delta$  7.36,  $\beta$ -furan  $\delta$  6.34) and an  $\alpha\beta$ -unsaturated ketone ( $\nu_{\max}$  1690  $\text{cm}^{-1}$ , n.m.r. coupled doublets at  $\delta$  7.2, 5.8,  $J = 10$  c./sec.). Hydrolysis does not give crystalline products. Hydrogenation under mild conditions gives a dihydro-compound, m.p. 164—166°, which is a saturated ketone. The u.v.

spectrum of heudelottin, recorded against dihydroheudelottin as standard, gives  $\lambda_{\max}$  228  $m\mu$ ,  $\epsilon$   $9.25 \times 10^3$ , which is similar to that of typical  $\Delta^1$ -3-ketomeliacins. (Anthothecol against dihydroanthothecol, 227  $m\mu$ ,  $\epsilon$   $9.2 \times 10^3$ ). Hydrolysis of dihydroheudelottin gave one mol. each of acetic acid and  $\alpha$ -methylbutyric acid, identified spectroscopically,<sup>2</sup> a nonvolatile acid, and a crystalline solid,  $C_{26}H_{36}O_6$ , m.p. 238—240°, which still contains the furan ring. The nonvolatile acid, isolated as its *p*-phenylphenacyl ester, is an unidentified saturated dihydroxy-acid,  $C_9H_{18}O_4$ .

The n.m.r. spectrum of heudelottin shows a 1H doublet ( $\delta$  4.90,  $J = 2.5$  c./sec.) probably coupled to a 1H multiplet ( $\delta$  4.74), and a 1H multiplet ( $\delta$  4.70). These are ascribed to hydrogens at the base of three secondary acyl groups. There are also two secondary hydroxyl groups ( $\delta$  4.26, 1H m., coupled to a hydroxyl proton at  $\delta$  3.9, to a 1H m. at  $\delta$  2.60, and to something else:  $\delta$  3.90, apparent doublet in  $D_2O$ ,  $J = 4.5$  c./sec.), and a broad singlet at  $\delta$  3.40 ( $W_H = 2.5$  c./sec.) which is of the right chemical shift and band width to be (C-15)-H in a 14,15-epoxide.<sup>3</sup> Oxidation of dihydroheudelottin and hydrolysis gives the same crystalline product, hence the free hydroxyl groups are in the  $C_9$  acid residue. This evidence is consistent with the formulation of heudelottin as an unsaturated trihydroxy-ketone, closely related to cedrelone and anthothecol.

The hydrolysis product gives a diacetate, m.p. 280—283°, with pyridine and acetic anhydride (triacetate with toluenesulphonic acid catalyst). The n.m.r. spectrum of the diacetate shows the usual furan bands, a doublet at  $\delta$  4.96 ( $J = 4$  c./sec.) and a narrow multiplet at  $\delta$  4.84 ( $W_H = 3$  c./sec.) which we take to be at the base of acetyl groups, an unusual triplet ( $J = 10$  c./sec.) at  $\delta$  4.40, and a 1H multiplet at  $\delta$  4.30, which is coupled to the  $\delta$  4.96 doublet above, to a hydroxyl proton at  $\delta$  3.50 and to some other proton ( $J = 2.5$  c./sec.). The  $\delta$  4.84 multiplet is coupled to protons at  $\delta$  1.84, and the  $\delta$  4.40 multiplet to protons at  $\delta$  2.5. There are five tertiary methyl groups.

After chromic acid oxidation the product, m.p. 272—274°, has no hydroxyl group, the wide triplet moves to  $\delta$  3.33, and the two acetyl protons shift downfield to  $\delta$  5.50 (s) and  $\delta$  5.22 (m).

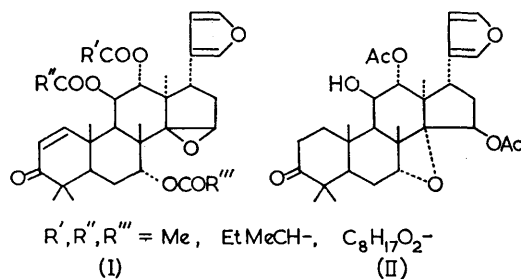
Clearly, heudelottin contains an  $\alpha$ -glycol function, which must be at C-6,C-7, or at C-11,C-12. In agreement with this, the hydrolysis product of

dihydroheudelottin on oxidation gives a yellow  $\alpha$ -diketone (m.p. 178—180°)  $\lambda_{\max}$  215  $m\mu$ ,  $\epsilon$   $5.03 \times 10^3$  which with alkali isomerises to a diosphenol (m.p. 202—203°,  $\lambda_{\max}$  215  $m\mu$ ,  $\epsilon$   $7.9 \times 10^3$ , 288  $m\mu$ ,  $\epsilon$   $9.2 \times 10^3$ , shifted in alkali to 227  $m\mu$ ,  $\epsilon$   $4.2 \times 10^3$ , 330  $m\mu$ ,  $\epsilon$   $4.3 \times 10^3$ ). These compounds show the wide triplet in the n.m.r. spectrum (at  $\delta$  3.68, 3.62) and in the infrared spectrum show a cyclopentanone. ( $\nu_{\max}$  1745, 1750  $cm^{-1}$  respectively).

The only explanation of these results is that dihydroheudelottin is a 14,15-epoxide, but that on alkaline hydrolysis one of the liberated hydroxy-groups attacks position-14, giving a 15-hydroxy-compound with a new oxide ring; the only sterically credible position for this is 7 $\alpha$ ,14 $\alpha$ , from which it follows that heudelottin has the structure (I), and dihydroheudelottin hydrolysis product acetate the structure (II). The hydroxyl groups are all shown to be axial from the low coupling constants of the protons at their bases.

Such 7,14-oxides are well known as intermediates in the hydrolysis of limonol and allied compounds,<sup>4</sup> but this is the first time that one has been isolated as a stable compound.

The large coupling constant which we ascribe to the 7 $\beta$ -proton is unusual, but examination of the dihedral angles on a model shows that it is not unreasonable. The chemical shift of this proton in the keto-compounds is normal, the down-field shift in compound (II) is perhaps due to the proximity of the 15 $\beta$ -acetate.



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<sup>1</sup> D. A. H. Taylor, *J. Chem. Soc.*, 1965, 3495.

<sup>2</sup> D. H. Calam and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1966, 949.

<sup>3</sup> J. W. Powell, *J. Chem. Soc. (C)*, 1966, 1794.

<sup>4</sup> Cf. A. D. Cross, *Quart. Rev.*, 1960, 14, 326.