The Tetracyclic Triterpenes from *Cedrela odorata* L.

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THE isolation of two new triterpenes, "X", (m.p. 230—231°, $[\alpha]_D$ −90°, ν_{max} 3333 and 1700 cm.$^{-1}$) and "Y", (m.p. 236—238°, $[\alpha]_D$ −45°, ν_{max} 3333 cm.$^{-1}$) from Jamaican cedar (*Cedrela odorata* L., Meliaceae) has recently been reported.[1] Chemical and spectroscopic evidence now lead to the structures (I) and (II) for "X" (odoratone) and "Y" (odoratol) respectively.

Periodate oxidation indicated a 1,2-diol in odoratol. As expected from its formulation as an equilibrium between the free aldehyde and the hemialdal (III), the product showed only weak carbonyl absorption in the infrared spectrum. Oxidation of odoratol acetonide (V), m.p. 199—200°, with chromium trioxide (Jones' reagent) gave odoratone acetonide, (IV), m.p. 207·5—209°, which has no hydroxyl absorption in the infrared region. High-resolution mass spectrometry† showed (IV) to be $C_{33}H_{52}O_4$ and hence odoratone and odoratol must be $C_{30}H_{48}O_4$ and $C_{30}H_{50}O_4$ and not as previously reported.[1]

Nuclear magnetic resonance (n.m.r.) spectroscopy‡ suggests the presence of a trisubstituted double bond, the spectra of both (I) and (IV) showing a broad band (1H) at 5·35 (H-7). The n.m.r. spectrum of (IV) further revealed the presence of nine tertiary [0·83, 1·02, 1·05(6H), 1·13, 1·24, 1·26, 1·34, and 1·54] and one secondary§ (0·88, $J = 7$) methyl groups. This spectrum had a quartet at 4·50 (H-23, $J = 7{\cdot}2$ and 5·0), a doublet at 4·26 (H-24, $J = 7{\cdot}2$) and a broadened doublet at 3·94 (H-22, $J = 5{\cdot}0$).

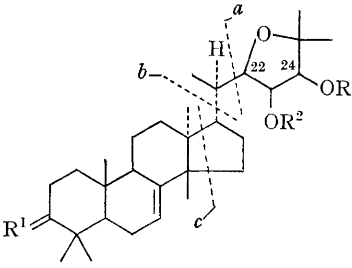
Ruthenium tetroxide oxidation[2] of (IV) yielded (VI), m.p. 193·5—195°, molecular ion at *m/e* 544 (5% relative intensity), ν_{max} 2800, 2700, 1725 (aldehyde), and 1700 cm.$^{-1}$ (ketone) whose mass spectrum showed the expected β-cleavage of the keto-group at C-8 (cleavage *a*) giving an ion at *m/e* 364 ($C_{22}H_{36}O_4$, 70%). This result locates the double bond in (IV) at C-7.

A similar oxidation of "B-diol" diacetate[3] gave the diketone (VII) whose mass spectrum showed characteristic α- and β-cleavage as indicated in the formula. As this fragmentation is only consistent with a 13,17-dione structure, the double bond in "B-diol" must be at C-13(17).[4] The base peak in the spectrum of "B-diol" corresponds to the loss of the C_8H_{17} side-chain, but fragmentation of a vinylic bond has recently been observed in some similar steroids.[5]

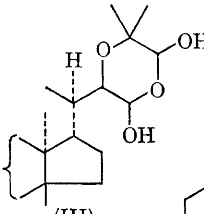
Odoratol triacetate was dehydrogenated with mercuric acetate[6] and the product hydrolysed to give the 7,9(11)-heteroannular diene (VIII), m.p. 282—286°, whose ultraviolet spectrum [λ_{max} 231 (ϵ 12,100), 238 (12,700) and 243 mμ (8300)] is characteristic of a euphol-type skeleton.[7]

The mass spectrum of (IV) was in agreement with the postulated structure. The cleavage of the C-20–C-22 bond (cleavage *a*) gave the base peak. Other fragments and their relative intensities are shown in (IV). The composition of the ions was confirmed by accurate mass measurements.

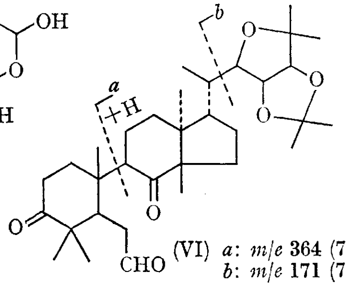
The circular dichroism curve of (IV) shows a negative Cotton effect ($\Delta\epsilon$ — 0·82 at 297 mμ) of the same sign and magnitude as shown by the optical rotatory curve of flindissone lactone[8]



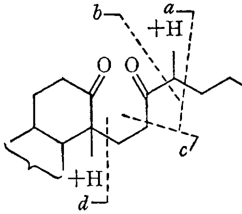
(I) R^1=O, R^2=R^3=H
(II) R^1=H, α-OH; R^2=R^3=H
(IV) R^1=O, R^2+R^3=CMe$_2$
a: *m/e* 171 (100%)
b: *m/e* 313 (4%)
c: *m/e* 271 (4%)
(V) R^1=H, α-OH; R^2+R^3=CMe$_2$
(VIII) R^1=H, α-OH; R^2+R^3=H; $\Delta^{9,11}$



(III)



(VI) *a*: *m/e* 364 (70%)
b: *m/e* 171 (79%)



(VII) *a*: *m/e* 434 (100%)
b: *m/e* 405 (55%)
c: *m/e* 377 (23%)
d: *m/e* 350 (44%)

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† Mass spectra were recorded on an Atlas CH 4 and an AEI MS-9 spectrometer using a direct inlet system.

‡ Spectra were recorded for deuterochloroform solutions on a Varian A60 spectrometer and chemical shifts are expressed as p.p.m. from Me_4Si. Coupling constants are in c./sec.

§ Confirmed by double irradiation.

indicating that rings-A and -B in the two compounds are the same.

The axial configuration of the C-3 hydroxyl in odoratol is indicated by a half-height width of less than 5 c./sec. for the C-3 proton in the triacetate. The suggested stereochemistry at C-17 and C-20 is based on an assumed relationship to tirucallol to which many of the tetracyclic triterpenes from the Meliaceae and Rutaceae are related.[9] The ready formation of the acetonide indicates that the glycol is *cis*. In (IV), the coupling constant of 7·2 between H-23 and H-24 suggests a small dihedral angle between the protons but because of the uncertainty of the conformation of the five-membered heterocyclic ring in (IV)[10] no definite conclusion can be drawn as to the relative configuration of H-22 and H-23 from their coupling constant. Models show that steric hindrance to rotation of the side chain is very severe if H-22, H-23, and H-24 are all *cis*, and this could explain the observed small coupling between H-20 and H-22. Small coupling between vicinal protons in an acyclic system has also been recently observed in chromomycinone hexa-acetate.[11]

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