

Odoratin, an Undecanortriterpenoid from *Cedrela odorata* L.

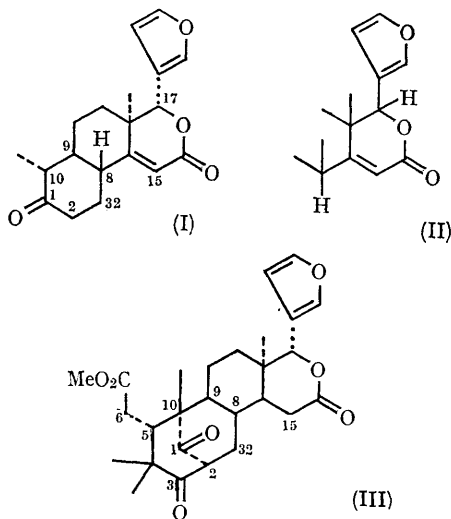
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EXTRACTION of the West Indian cedar (*Cedrela odorata* L., Meliaceae) has given variable results.^{1,2} The extract from one specimen has given in small amount, odoratin, $C_{19}H_{22}O_4$, m.p. 216–223°, $[\alpha]_D + 155^\circ$ ($CHCl_3$), for which we suggest structure (I).



The n.m.r.³ bands at 7.48 (α -furan H), 6.45 (β furan H), 5.89 (doublet, $J = 2.2$ c./sec., H-15- and 5.11 (singlet, H-17) suggested the part structure (II) also present in carapin (III).⁴ This is supported by the ultraviolet (λ_{max} 213 $m\mu$; ϵ 17,100) and infrared (ν_{max} 3050, 1710, 1630, 1580, 1500 and 877 cm^{-1}) spectral data. The n.m.r. spectrum further revealed the presence of a tertiary (1.10) and a secondary (1.04, doublet, $J = 7$ c./sec.) methyl group.

The fourth oxygen must be in a saturated six-membered (or larger) ring ketone since an ethylene ketal, $C_{21}H_{26}O_5$, m.p. 233–235°, $[\lambda_{max}$ 212 $m\mu$ (ϵ 14,700, ν_{max} 3050, 1710, 1630, 1580, 1500, 877 cm^{-1}) was obtained. The spectral data precludes the presence of further olefinic bonds and the molecule must be bicarbocyclic.

The part structure (II) combined with the occurrence of odoratin in a Meliaceae species suggests that odoratin is a degraded limonoid. A consideration of biogenetically derived structures consistent with the above data leads directly to (I) obtainable from carapin (III) by β -dicarbonyl cleavage (of the C-2-C-3 bond) followed by a

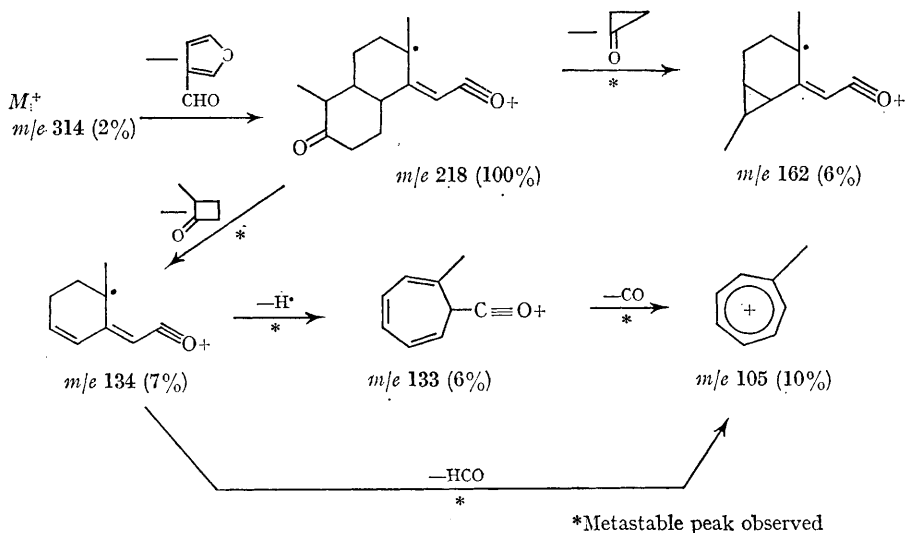


FIGURE 1

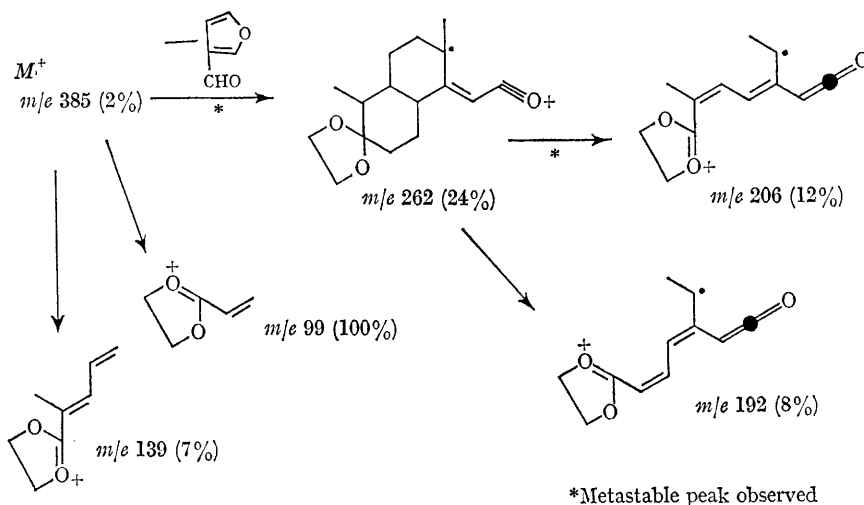


FIGURE 2

reverse Michael reaction (cleavage of the C-5-C-10 bond).

The structure of odoratin as (I) is fully supported by its mass-spectral fragmentation pattern and that of its derived ethylene ketal. Figures 1 and 2 detail the essential features. The fragments observed for the ethylene ketal (Fig. 2) confirm the structure (I) by defining the relative positions of the atoms not apparent in the part structure (II).

The absolute stereochemistry written into (I) assumes formation from carapin without stereochemical change at C-9. The large allylic coupling

(2.2 c./sec.) of H-15 shows that the C-8-H bond must be perpendicular to the plane of the C-14-C-15 bond.⁵ The circular dichroism curve⁶ shows a positive Cotton effect at 264 m μ , $\Delta\epsilon$ 7.0 for the ene-lactone and a negative Cotton effect at 302m μ , $\Delta\epsilon$ - 1.21 for the ketone. This proves the stereochemistry of the ene-lactone to be as shown⁷ and is in agreement with the other stereochemical features written into (I).

Odoratin thus represents a variation in the possible degradation of the limonoids.⁸

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¹ W. R. Chan, K. E. Magnus, and B. S. Mootoo, forthcoming publication.

² C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.*, 1963, 980.

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

⁴ E. O. Arene, C. W. L. Bevan, J. W. Powell, and D. A. H. Taylor, *Chem. Comm.*, 1965, 302; we are grateful to Professor C. W. L. Bevan and Dr. J. W. Powell for further information on the n.m.r. spectrum of carapin.

⁵ S. Sternhell, *Rev. Pure Appl. Chem. (Australia)*, 1964, 14, 15.

⁶ The circular dichroism curve was obtained through the courtesy of Dr. G. Snatzke, University of Bonn, Germany.

⁷ R. Tschesche, H. Schwang, H. W. Fehlhaber, and G. Snatzke, *Tetrahedron*, 1966, 22, 1129.

⁸ J. B-son Bredenberg, *Chem. and Ind.*, 1964, 73; D. L. Dreyer, *Experientia*, 1964, 20, 297.