Guayin: An Unusual Oxalactone Dibenzxanthone from *Tabebuia guayacan*

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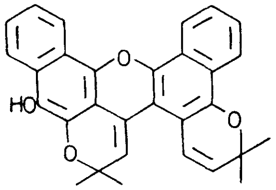
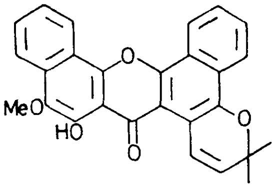
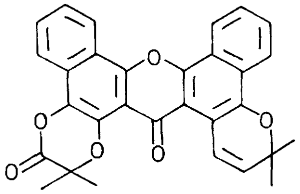
Summary A unique oxalactone dibenzxanthone has been identified in *Tabebuia guayacan* wood and its dihydro derivative has been successfully synthesised.

IT has previously been reported[1] that the marine borer resistant heartwood of *Tabebuia guayacan* Hemsl. contains a novel phenolic xanthene derivative guayacanin (I), tectol, and several of the naphthaquinones found in other *Tabebuia* species.[2] A new and unusual compound, guayin, (III) m.p. 277—278 °C, has now been isolated from the ether extract of the heartwood.


(I)

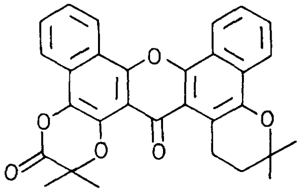


(II)


(III)

Guayin, $C_{30}H_{22}O_6$, λ_{max}(EtOH) 414 (log ϵ 3·84), 323 (4·22), *ca.* 294 (4·53), 282 (4·57), *ca.* 250 (4·51), 226 nm (4·81) is non-phenolic and contains one conjugated carbonyl (i.r. 1660 cm^{-1}) and one six-membered lactone carbonyl (i.r. 1785 cm^{-1}). The 100 MHz n.m.r. spectrum in $CDCl_3$ shows two geminal dimethyl groups [δ 1·56 (6H, s), 1·77 (6H, s)], two vicinal vinylic (chromene) protons [δ 5·75 (1H, d, J 10 Hz), 8·01 (1H, d, J 10 Hz)] and eight aromatic protons [δ 8·56—8·74 (8H, m)].

The presence of the lactone function was confirmed by alkaline methylation of guayin to form the *OO*-dimethyl derivative of the corresponding hydroxyacid ($C_{32}H_{28}O_7$, m.p. 186—187 °C). Hydrolysis of the ester yielded the acid, decarboxylation of which was accompanied by the loss of a $C_4H_6O_2$ unit, yielding a product with the properties of a catechol monomethyl ether derivative, $C_{27}H_{20}O_5$. The u.v. spectrum of this phenol showed a pronounced bathochromic shift (24 nm) upon addition of aluminum chloride,[3] indicating the free phenolic hydroxy group to be *peri* to the remaining carbonyl group. On the basis of this and other spectral properties this phenol was considered to be (II) and guayin is formulated as the dibenzxanthone derivative (III). *X*-ray crystallographic analysis of guayin has confirmed this structural assignment. The similarity of structure (I) and (III) suggest the derivation of guayin from guayacanin (I) by oxidative cleavage and subsequent rearrangement of the benzylically substituted chromene ring.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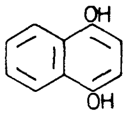
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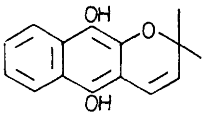
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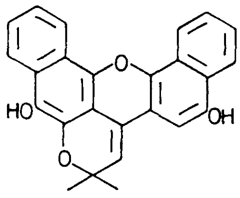
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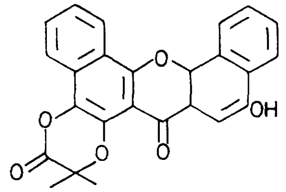
(VIII)

The structure of guayin as (III) has also been confirmed by a successful synthesis of dihydroguayin (IV). Compounds (V) and (VI) were condensed in aqueous formic acid to yield the analogue (VII) of guayacanin. Oxidation of (VII) with 30% hydrogen peroxide gave (VIII) which, on prenylation in aqueous formic acid, gave (IV), identical in all respects (t.l.c., i.r., u.v., n.m.r., mixed m.p.) with dihydroguayin obtained from the natural product.

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[1] G. Manners, L. Jurd, and K. Stevens, *J.C.S., Chem. Comm.*, 1974, 388.

[2] A. R. Burnett and R. H. Thomson, *J. Chem. Soc.* (*C*), 1967, 1710; 1968, 850.

[3] L. Jurd, in 'The Chemistry of Flavonoid Compounds', Pergamon Press, New York, 1962, p. 119.