Guayacanin—A Novel Phenolic Xanthen Derivative from *Tabebuia guayacan*

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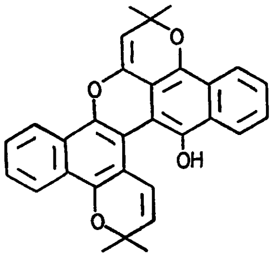
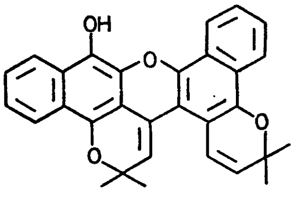
Summary The structure of guayacanin, a novel phenolic xanthen derivative from *Tabebuia guayacan*, has been investigated by chemical and spectral methods.

Examination of the heartwood of *Tabebuia guayacan* Hemsl., a Central American timber resistant to attack by marine borers, has shown the presence of lapachol, α- and β-lapachone, dehydro-α-lapachol, tetcol, and tetrahydrotectol, substances previously isolated from other *Tabebuia*[1] and *Tectonis*[2] species. In addition, a new compound, guayacamin, $C_{30}H_{24}O_4$ (m.p. 225—226°) crystallized from ether extracts of the wood. Guayacanin, λ_{max} (EtOH) 405 (log ε 3·95), 385 (3·95), *ca.* 365 (3·86), *ca.* 295 (4·31), *ca.* 270 (4·67), 257 (4·76), *ca.* 251 (4·73), 238 (4·72), 218 (3·82) nm, has one phenolic group, forms a monoacetate (m.p. 248—249°) and monomethyl derivative (m.p. 205°), and yields immediately a characteristic deep purple pyrylium salt (λ_{max} 550 nm) on addition of HCl. The 100 MHz n.m.r. spectrum in $CDCl_3$ shows two gem dimethyl groups [δ1·56 (6H, s), 1·58 (6H, s)], an aromatic hydroxyl (δ 5·60, 1H, s), two vicinal vinylic (chromene) protons [δ 5·73 (1H, d, *J* 10 Hz), 7·05 (1H, d, *J* 10 Hz)] an uncoupled vinylic proton (δ 5·80 1H, s), and eight aromatic protons [δ 7·42—7·70 (4H, m), 8·0—8·35 (2H, m) and 8·36—8·65 (2H, m)]. These data are in accord with three possible structures, (I) (II), or (III), in which one chromene ring is benzylically substituted.


(I)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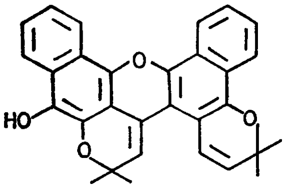
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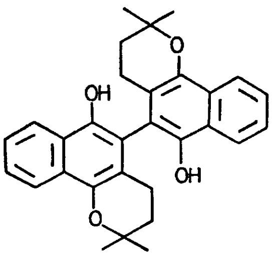
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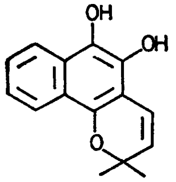
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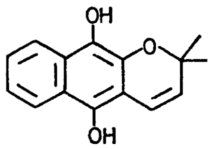
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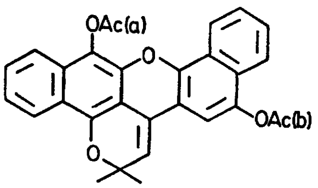
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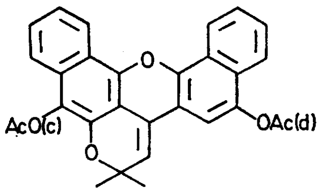
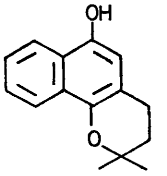

(VIII)


(IX)

Guayacanin can be formulated as (II) or (III) on the basis of its catalytic hydrogenation. Structure (I) would be expected to consume three moles of hydrogen with benzylic ether hydrogenation to form tetrahydrotectol (IV). Guayacanin takes up only two moles of hydrogen to form tetrahydroguayacanin. In accord with structure (II) or (III), tetrahydroguayacanin is oxidized readily in air in acid media to dihydroguayacanin which, in turn, yields a deep purple pyrylium salt. Ready oxidation of xanthens to xanthylium salts in acid media has frequently been reported.[3]

Since the chemical and spectral data do not distinguish the xanthen structures (II) and (III) an attempt was made to synthesize the tetrahydro derivatives of each of these structures. As models for these syntheses, the naphthalene diols (V) and (VI), prepared from lapachol, were successfully condensed with naphthalene-1,4-diol in 80% aqueous formic acid to yield (VII) and (VIII) (as acetates), respectively. When, however, (V) and (VI) were condensed with (IX) to yield the tetrahydro derivatives of (II) and (III), each reaction gave a common product, m.p. 249—250°, identical in all respects (t.l.c., m.m.p., n.m.r., i.r., m.s.) with tetrahydroguayacanin.

Although tetrahydroguayacanin has now been synthesized by reactions which establish the guayacanin structure as (II) or (III), the rearrangement of an intermediate in the reaction of (V) with (IX) or of (VI) with (IX) does not permit an unambiguous assignment. However, a comparison of acetate n.m.r. resonances of guayacanin acetate with those of diacetates (VII) and (VIII) strongly suggests structure (II) for guayacanin. The acetates (a) and (b) of (VII) resonate as a 6H singlet at δ 2·47 while the acetates (c) and (d) of (VIII) resonate as two 3H singlets at δ 2·47 and 2·62. Since acetates (b) and (d) are chemically equivalent, acetates (a) and (c) must resonate at δ2·47 and 2·62 respectively. Guayacanin monoacetate shows an n.m.r. 3H singlet at δ 2·47 consistent with acetate (a) of (VII) and structure (II) for guayacanin. An *X*-ray crystallographic study is currently being undertaken to establish this.

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[2] W. Sandermann and M. H. Simatupang, *Chem. Ber.*, 1964, **97**, 588.

[3] L. Jurd and T. C. Somers, *Phytochemistry*, 1970, **9**, 419; F. Kröhnke and K. Dickoré, *Chem. Ber.*, 1959, **92**, 46.