Novel Resveratrol Tetramer, Vaticaffinol, from *Vatica affinis* Thw. (Dipterocarpaceae)[1]

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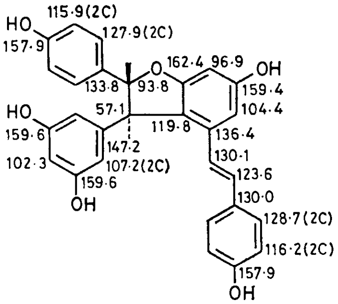
Summary The structure and possible structure, respectively, of a resveratrol dimer and tetramer (vaticaffinol) isolated from *Vatica affinis* Thw. have been elucidated on the basis of spectral data (u.v., i.r., ^{1}H and ^{13}C n.m.r. spectroscopy, high resolution mass spectrometry), chemical degradation, and biosynthetic considerations.

From the cold acetone extract of the bark of *Vatica affinis* Thw. (Dipterocarpaceae) two polyphenols have been isolated.

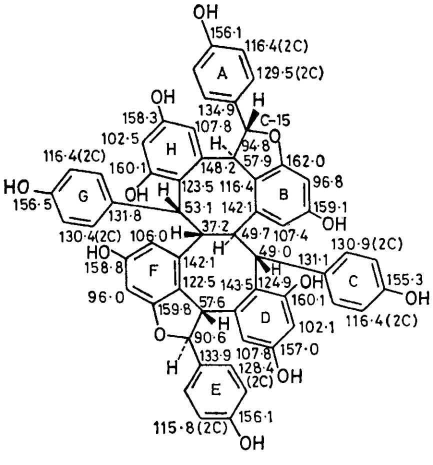
The first compound is a dehydro-resveratrol dimer and is identical to ε-viniferin[2] (**1**) (u.v., and ^{1}H and ^{13}C n.m.r. spectroscopy, m.s.). This is the first report of the dimer from the Dipterocarpaceae.

The second compound (**2**), called vaticaffinol, is a resveratrol tetramer different from the tetramer, hopeaphenol (**3**)[3] which has been isolated from several Dipterocarpaceae species.[4,5]

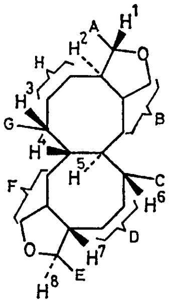
Vaticaffinol forms a pale cream solid, m.p. 280 °C, $[\alpha]_D^{25}$ $-22{\cdot}5°$. Molecular weight determination by high resolution mass spectrometry was unsuccessful but examination of the decamethyl ether, m.p. 160—162 °C, $[\alpha]_D$ $+20{\cdot}9°$ ($CHCl_3$), gave a molecular ion M^+ 1056·4253 ($C_{66}H_{62}O_{12}$). The formation of a deca-acetate, m.p. 154—156 °C, $[\alpha]_D$ $-33{\cdot}9°$ ($CHCl_3$) shows that only ten of the oxygen atoms are present as phenolic hydroxy-groups. The u.v. spectrum shows absorption (in MeOH) λ_{max} 286 nm (log ε 4·44) indicative of unconjugated phenolic chromophores. The spectrum is unchanged on addition of sodium acetate–boric acid showing that *o*-dihydroxy-functions are absent. The i.r. spectrum showed no carbonyl absorption but a broad hydroxy-band at 3200 cm^{-1}, and aromatic absorption at 1600 and 830 cm^{-1} were present, the last band being indicative of 1,4-disubstitution in benzene rings.



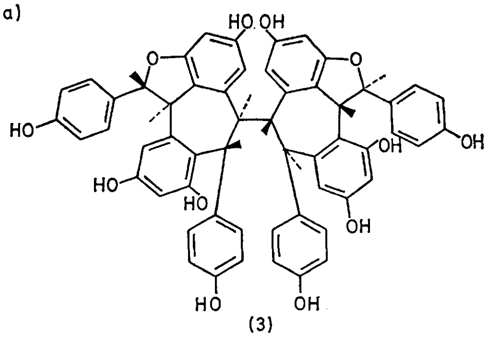
(1)



(2)



(2a)



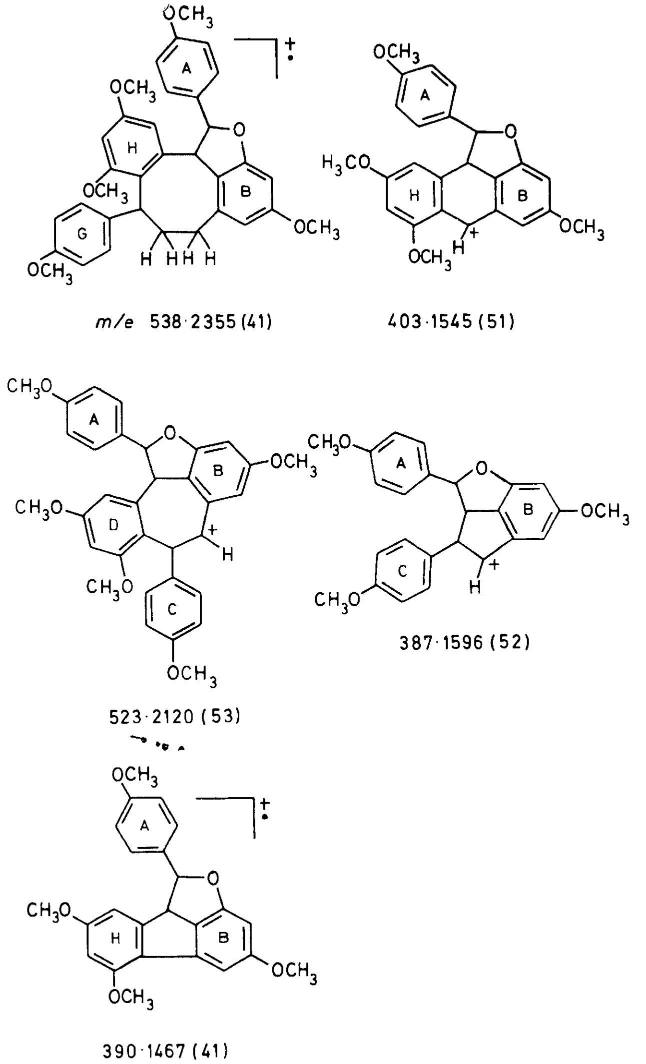
(3)

Vaticaffinol gave picric acid on oxidation with nitric acid.

On the basis of detailed spectroscopic evidence (see below) and the assumption that it is formed by an oxidative phenolic coupling reaction of four resveratrol units (or two dehydro-dimer units), vaticaffinol is assigned the structure (**2**).

The ^{13}C n.m.r. spectrum of vaticaffinol in $(CD_3)_2CO$ shows the following resonances: eight aliphatic doublets (δ_C 37—95 p.p.m.), ten phenolic singlets (155—163 p.p.m.) for twelve carbons, eleven quaternary carbon singlets (116—149 p.p.m.) for twelve carbon atoms, and thirteen aromatic doublets (96—131 p.p.m.) assigned to a total of twenty-four atoms. (The designation, 'singlet' and 'doublet' refer to the appearance of the resonance in the single-frequency off-resonance mode experiments). Probable assignments based on substituent parameters[4] are shown in structure (**2**).

The ^{1}H n.m.r. spectra at high frequency (270, 360 MHz) show resonances due to the presence of hydroxy-groups, twenty-four aromatic protons, and a series of eight aliphatic methine protons in the region δ_H 3·1—5·8 p.p.m. Decoupling experiments on these aliphatic protons showed four coupled protons on adjacent carbon atoms, and two



m/e 538·2355 (41)

403·1545 (51)

523·2120 (53)

387·1596 (52)

390·1467 (41)

Figure. Mass spectral fragments of vaticaffinol.

isolated coupled pairs of protons. The assignments [see (**2a**)] are δ_H 5·76 d (H^1), 4·44 d (H^2), 5·21 d (H^3), 3·19 (H^4), 4·5 dd (H^5), 4·44 d (H^6), 4·68 d (H^7), and 5·37 p.p.m. d (H^8), $J_{1,2}$ 11·5, $J_{3,4}$ 3·66, $J_{4,5}$ 11·0, $J_{5,6}$ 10·0, and $J_{7,8}$ 5·15 Hz.

Fragmentation of vaticaffinol in the mass spectrometer gives two odd-electron ions of structural significance. The Figure shows the relation of these ions and some even-electron ions to the structure (**2**).

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[1] For an earlier paper concerning a related species of Dipterocarpaceae see M. U. S. Sultanbawa, S. Surendrakumar, and P. Bladon, *J. Chem. Soc., Chem. Commun.*, 1980, 619.
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