New Antibacterial Polyphenol, Copalliferol A, from *Vateria copallifera* (Retz.) Alston (Dipterocarpaceae)

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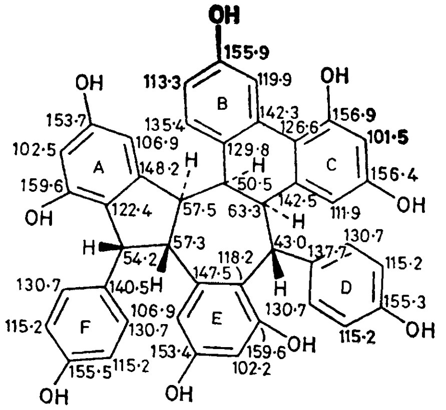
Summary A new resveratrol trimer, copalliferol A, isolated from *Vateria copallifera*, has been shown to have the structure (**1**) on the basis of u.v., i.r., ^1H, and ^{13}C n.m.r. spectroscopy, high resolution mass spectrometry, and biosynthetic considerations.

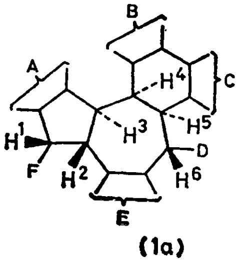
The structure of hopeaphenol,[1] a resveratrol tetramer from the Dipterocarpaceae, has been established by *X*-ray determination and shown to contain two seven-membered rings.[2] Structures for a resveratrol dimer and trimer from infected grapevine (*Vitis vinifera*)[3] have been proposed from spectral data.

From the cold acetone extract of the bark of *Vateria copallifera* (Retz.) Alston (Dipterocarpaceae), two antibacterial polyphenols, copalliferol A and copalliferol B, have been isolated.[4] Structure (**1**) for copalliferol A is now proposed.

Copalliferol A is amorphous, m.p. > 300 °C (decomp.), $[\alpha]_D^{25}$ + 115·6° (MeOH), M^+ 680·2075 ($C_{42}H_{32}O_9$). The formation of a nonamethyl ether, m.p. 145—147 °C, $[\alpha]_D^{25}$ + 92·8° ($CHCl_3$), M^+ 806·3600 ($C_{51}H_{50}O_9$), and of a nona-acetate shows that all the oxygen atoms are present as hydroxy groups. The u.v. spectrum shows absorption [(in EtOH) $\lambda_{max.}$ 282 nm (ϵ 867)] indicative of unconjugated phenolic chromophores. The spectrum is unchanged on addition of sodium acetate–boric acid, showing that *ortho*



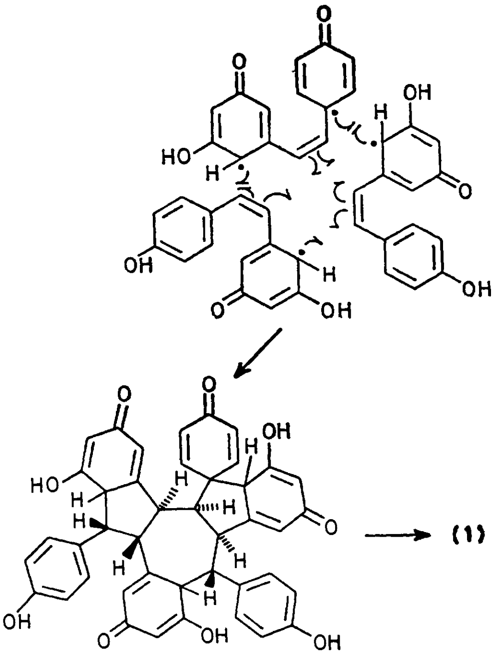
(**1**)



(**1a**)

dihydroxy groups are absent. The i.r. spectrum contained no carbonyl absorption but showed a broad hydroxy band at 3250 cm^{-1}, aromatic absorption at 1600 cm^{-1}, and a prominent band at 830 cm^{-1}, suggestive of 1,4-disubstituted benzene nuclei. Copalliferol A gives no colour with neutral iron(III) chloride solution.

Since copalliferol A did not give any recognisable products in degradation reactions, the structure proposed (**1**) is based on the following spectroscopic evidence and the presumed formation by oxidative phenolic coupling reaction of three resveratrol units (Scheme).



Scheme

The ^{13}C n.m.r. spectrum [$(CD_3)_2CO$] shows the following resonances: six aliphatic doublets (δ_C 43—64), nine phenolic singlets (153—160 p.p.m.), ten aromatic doublets assigned to a total of 17 atoms, and ten quaternary carbon singlets. (The designations 'singlet' and 'doublet' refer to the appearance of the resonances in single-frequency off-resonance proton-decoupled experiments.) The assignments based on substituent parameters[5] are shown in structure (**1**).

^{1}H N.m.r. spectra at high frequency (270, 360 MHz) show resonances due to the presence of nine hydroxy-groups, seventeen aromatic protons, and a series of six aliphatic methine protons in the region δ 3·5—4·9.

These protons are present at the junction of the 5-, 7-, and 6-membered ring systems, and their chemical shifts and couplings (confirmed by decoupling experiments) form the basis of the stereochemistry proposed (the 7-membered ring in the chair conformation). Referring to partial structure (**1a**) the assignments are: δ_H 3·51 (d, 1-H), 3·86 (dd, 2-H), 4·90 (d, 3-H), 4·10 (s, 4-H), 4·63 (d, 5- or 6-H), and 4·55 (d, 6- or 5-H), $J_{1,2}$ 6·75, $J_{2,3}$ 2·0, and $J_{5,6}$ 3·75 Hz.

Fragmentation of copalliferol A in the mass spectrometer gives several odd-electron ions of structural significance. The Figure shows the relation of these to structure (**1**).

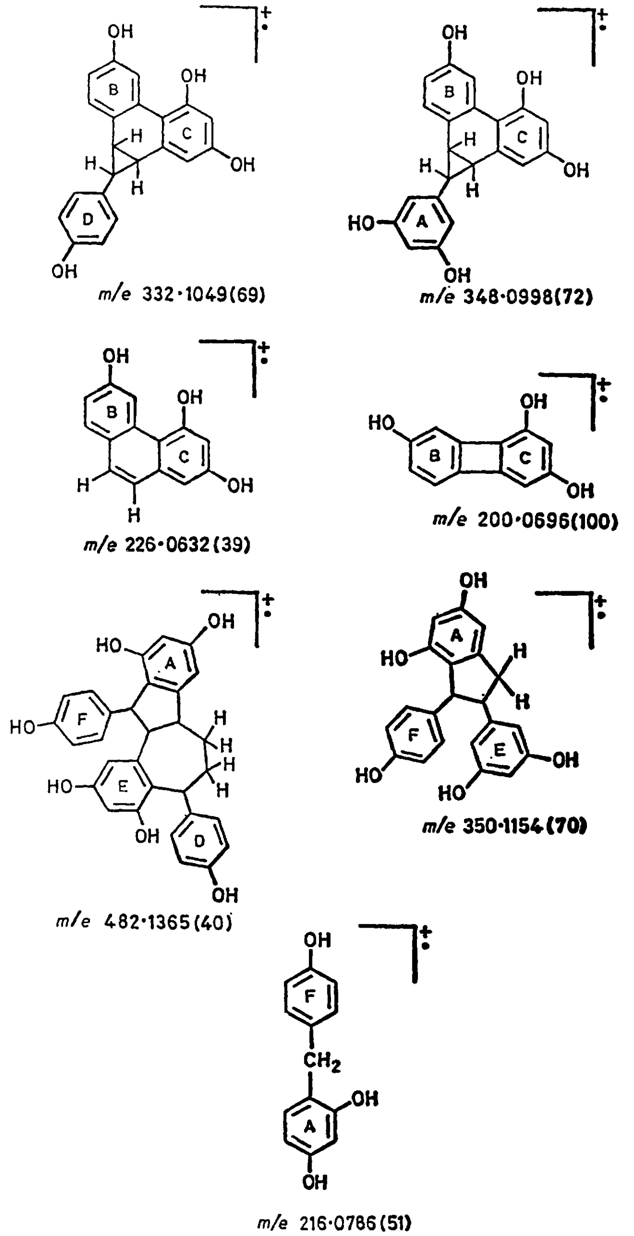


Figure. Mass spectral fragments of copalliferol A.

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