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MORELLOFLAVONE, A 3-(8-) FLAVONYLFLAVANONE, FROM THE HEARTWOOD OF *GARCINIA MORELLA**

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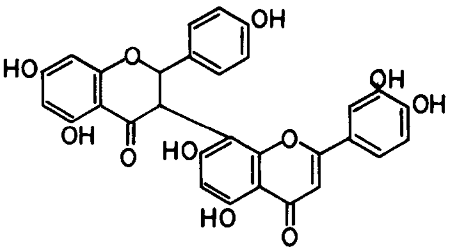
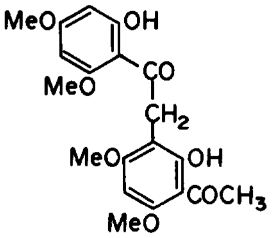
Morellin (1), a complex xanthone derivative occurring in the pericarp of the seeds of *Garcinia morella*, is accompanied by several closely related pigments (2). Morelloflavone, now isolated from the heartwood, has the structure (I) and is therefore a new type of biflavonoid.



I



III

Extraction of the coarsely powdered heartwood with cold acetone, followed by repeated column chromatography on silica gel using acetone-benzene (2:3) as solvent, gave the crude pigment. Preparative layer chromatography, using the same adsorbent and solvent gave morelloflavone, bright yellow cubes from methanol, m.p. 298° (*decomp.*). It gave a green ferric colour and a deep red with magnesium and hydrochloric acid. The UV spectrum in ethanol showed maxima at 345, 288, 275 and 255(sh) $m\mu$.

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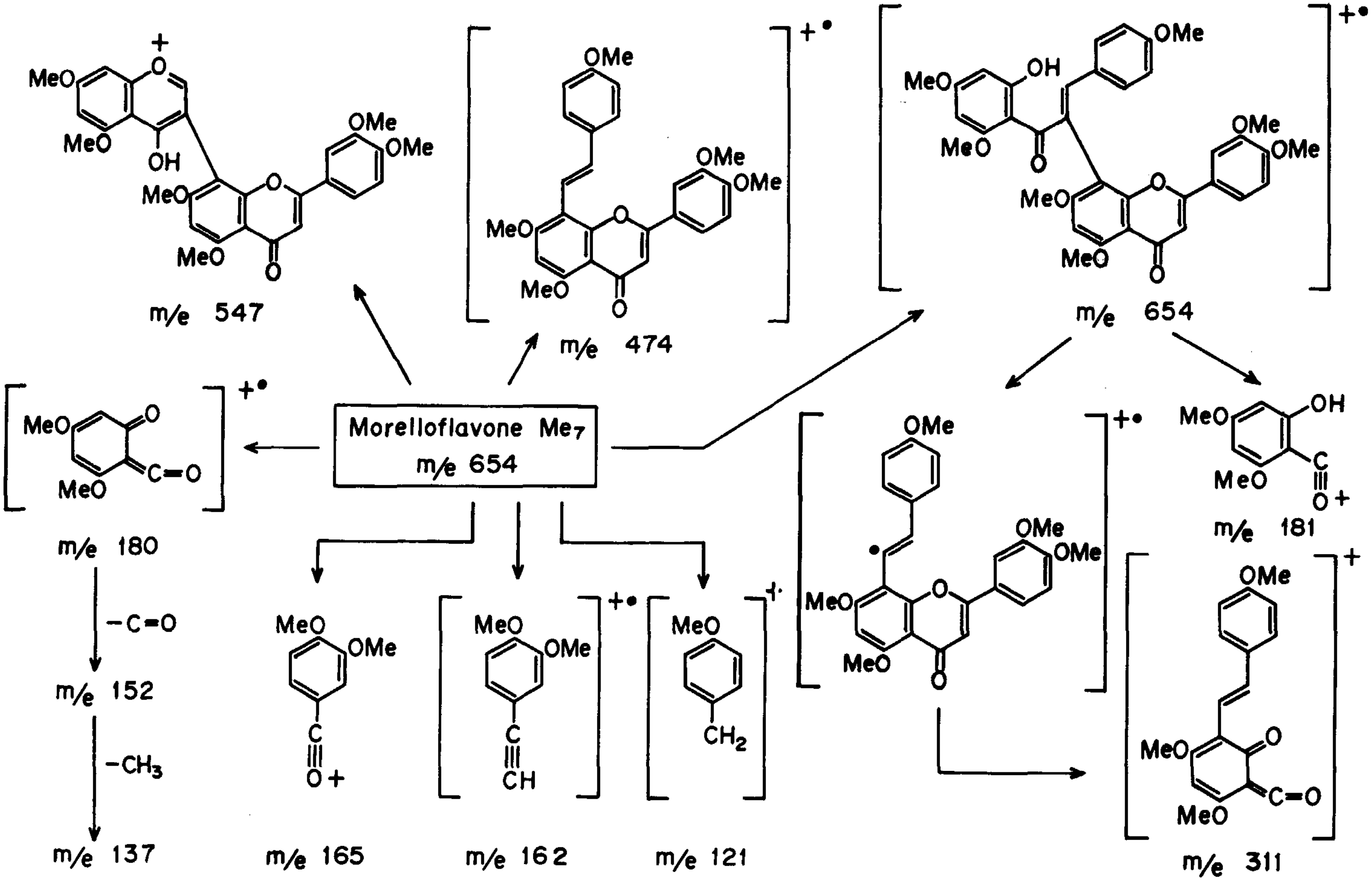
By methylation with dimethyl sulphate and potassium carbonate in acetone, (I) gave a heptamethyl ether (II), free from ferric colour. From the elemental analysis of (I) and (II) and the mass spectral *M* of (II) (654), (I) was assigned the molecular formula $C_{30}H_{20}O_{11}$. Hydrolysis of (II) with boiling 15 per cent ethanolic potassium hydroxide gave veratric acid, acetoveratrone and a crystalline compound(A), m.p. 116°, which showed a green ferric colour and a negative magnesium-hydrochloric acid test.

The IR spectrum of (I) indicates a chelated C=O at 1645 cm^{-1}, which is resolved into two bands at 1670 and 1645 cm^{-1} in the spectrum of (II). The appearance of a C=O band at higher frequency in (II) provided preliminary evidence of the presence of both a 5-hydroxyflavanone and a 5-hydroxyflavone nucleus in (I).

The NMR spectrum of (I) in acetone-*d*$_6$ shows signals in the region between 2 and 6 (τ scale), and in pyridine was transparent. A pair of doublets at 4.05 and 4.95 (J=12 cps), the former partly merged with a signal at 3.9, do not represent vinyl protons, since (I) failed to undergo catalytic hydrogenation under normal conditions. The doublet at 4.05 probably represents a proton α to oxygen and a phenyl ring as in a flavanone; since a methylene group is absent, it appeared probable that the doublet at 4.95 represents the 3-proton in a 3-substituted flavanone. The spectrum in DMSO shows the presence of two chelated hydroxyls at -2.66 and -3.50. The spectrum of (II) (acetone and $CDCl_3$) shows seven methoxyls (6.07 to 6.34) and a pair of doublets at 4.14 and 5.09 (J=12 cps). In the aromatic region signals appear between 2.3 and 3.9. The lowest is a quartet centered at 2.50; together with a *m*-coupled doublet at 2.67 (J=2.5 cps) and an *o*-coupled doublet at 3.30 (J=9 cps), it represents an ABC pattern arising from the B-ring of a flavone. A doublet at 2.75 (J=9.5 cps) probably represents the 2',6'-protons of the B-ring of a flavanone. A signal at 3.0 can be assigned to the 3-proton of a flavone.

Chart 1

Mass spectral fragmentation of morelloflavone heptamethyl ether



The NMR spectrum of (A) is very revealing and shows the presence of an acetyl group (7.40), four methoxyls (6.18 and 6.10), an uncoupled methylene group (5.75), three aromatic protons (~3.9), and two chelated hydroxyls (-3.8 and -3.9). Together with the mass spectral M 390, the data led to structure (III) for (A).

Since alkaline hydrolysis resulted in the liberation of an acetyl group, simultaneously with the disappearance of three methoxyls and seven aromatic protons, the cleavage must involve the loss of two aromatic rings, one being the B-ring of a flavone. Since there is evidence for (A) being a deoxybenzoin, the second aromatic ring is the B-ring of a flavanone. Morelloflavone therefore is constituted as (I). The linkage of the flavone nucleus in the 8-position is supported by its facile methylation (3).

The mass spectral fragmentation of (II) (Chart 1) lends strong support to the structure of (I) (4).

Morelloflavone is the first biflavonoid containing a flavone and a flavanone unit. Until very recently all the known biflavonoids were biflavonyls built from apigenin and its methyl ethers, the only variation being in the position of the linkage between the two apigenin units. When our work was approaching completion Jackson *et al.* (5) reported the isolation of three new biflavanonyls in which a naringenin unit is linked to a second naringenin unit or aromadendrin or taxifolin.

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4. Cf. C.J. Barnes and J.L. Occolowitz, *Austral.J.Chem.* **17**, 975 (1964); H. Audier, *Bull.Soc.Chim.Fr.* 2892 (1966).
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