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STRUCTURE AND SYNTHESIS OF A DERIVATIVE OF FASCICULIFERIN, A NOVEL PELTOGYNOID FROM *ACACIA FASCICULIFERA*

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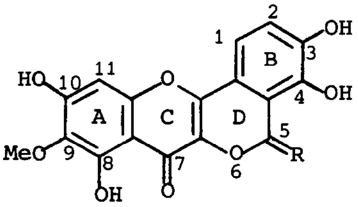
The structure and synthesis of the 5-*O*-ethyl-2,3-10-tri-*O*-methyl derivative of fasciculiferin (5-hydroxypeltogynin) a natural peltogynoid which exhibits an intermediate oxidation state of the C-5 methylene function in the D-ring are described.

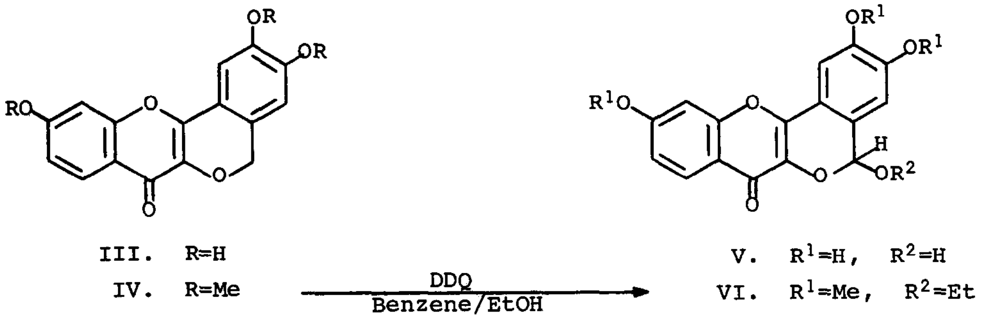
Hitherto only two natural variants of the oxidation state of the 'extra' D-ring carbon of C_{16}-peltogynoids have been recorded. These are illustrated by, and indeed limited to, the pair of flavonol analogues, benthamianin (I) with C-5 in the reduced form, and distemonanthin (II), with it fully oxidized; compounds which are associated in the heartwood of *Distemonanthus benthamianus*.[1,2,3]



I. R=H_2
II. R=O

Indirect evidence is now presented for the natural existence in another source of the first example of a peltogynoid with a C-5, or corresponding D-ring, in an intermediate oxidation state.

The heartwood of *Acacia fasciculifera* F. Muell *ex* Benth. contains amongst related flavonoid metabolites, also (+)-2,3-*trans*-3,4-*trans*-peltogynol, peltogynin (III),[4,5] and a novel peltogynoid (R_F 0.0 in 2% HOAc, and ~0.7 in water-satd. butan-2-ol), all in low proportion. The latter was isolated in 0.2% yield as racemic 5-ethoxy-2,3-10-trimethoxypeltogynin (VI), m.p. 160° (amorph.), following preparative paper chromatography in 2% acetic acid, stripping with 80% ethanol, and methylation with diazomethane.



III. R=H

IV. R=Me $\xrightarrow[\text{Benzene/EtOH}]{\text{DDQ}}$

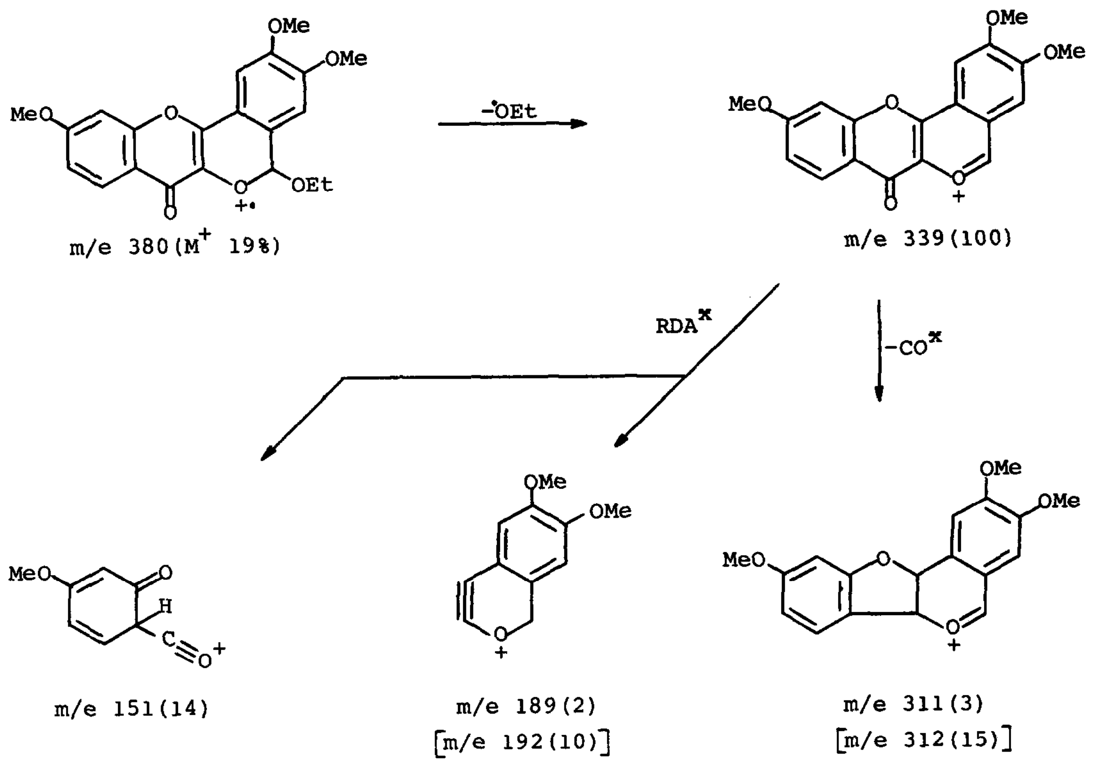
V. R^1=H, R^2=H

VI. R^1=Me, R^2=Et

The structure of the trimethyl ether of 5-ethoxypeltogynin (VI), $C_{21}H_{20}O_7$, [R_F 0.40 in benzene-acetone 4:1 on Kieselgel PF_{254}, followed by separation (2x), R_F 0.13 in benzene-EtOAc 7:3; yellow with H_2SO_4-HCHO] is consistent with its n.m.r. [δ($CDCl_3$) 8.10(d, J 7.5, H-8), 7.28(s, H-1), 6.88(d, J 2.0, H-11), 6.85 (dd, J 7.5 and 2, H-9), 6.76(s, H-4), 6.03(s, H-5), 3.87,3.92,3.97(s, 3 x OMe), 3.81(q, J 7.5, $O\underline{CH_2}CH_3$) and 1.19(t, J 7.5, $OCH_2\underline{CH_3}$)] and mass fragmentation spectra (*cf.* scheme). Chemical shift of the 5-proton (δ 6.03) is also in close agreement with that of 5-methoxy-β-photomethylquercetin (δ 5.93)[6] in the same solvent ($CDCl_3$).

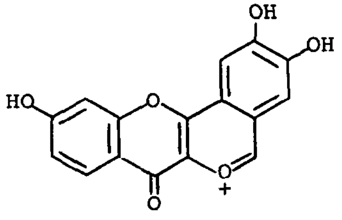
Proof of structure of the derivative was obtained by selective functionalization of the methylene group at C-5 of 2,3,10-tri-*O*-methylpeltogynin (V)[5] with DDQ in benzene-ethanol (50:1 v/v), according to a variation of the method of Buchan *et al.*,[8] to give a 30% yield of the desired product (VI) in a single step conversion (*cf.* scheme).

The 5-ethoxy compound derived from *A. fasciculifera* is considered to be an

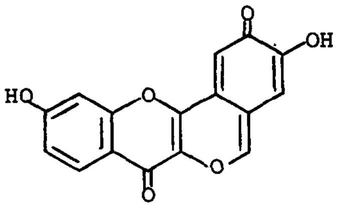


*Presumably accompanied by H-transfer (*cf.* ref. 7)

artefact which originates from 5-hydroxypeltogynin (V) *via* a stable oxonium ion (VII), formed under the acid conditions applied during preparative paper chromatography or during subsequent stripping and by its solvolysis with ethanol under the latter conditions (80% ethanol:residual acetic acid). Such



VII



VIII

presumption for the natural presence of 5-hydroxypeltogynin, is supported by the observation that oxidative synthesis of its tri-*O*-methyl ether from 2,3,10-tri-*O*-methylpeltogynin (IV) is also accompanied by spontaneous reaction with ethanol; formation of an intermediate quinone methide (*cf.* ref. [8]) which is trapped by ethanol being excluded in this instance.

The susceptibility of the C-5 methylene function in peltogynoids to oxidation was demonstrated by Waiss *et al.*[6] under conditions of oxidative photolysis of penta-*O*-methylquercetin in methanol when 5-methoxy-*O*-photomethyl=quercetin, an analogue of V, is formed albeit in very low yield. Accordingly fasciculiferin (V) is speculatively considered to have its biogenetic origin in a quinone methide intermediate (VIII) originating from peltogynin (III) *via* an oxidative mechanism.

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