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MEXOTICIN, A NEW COUMARIN FROM MURRAYA EXOTICA L. (1)

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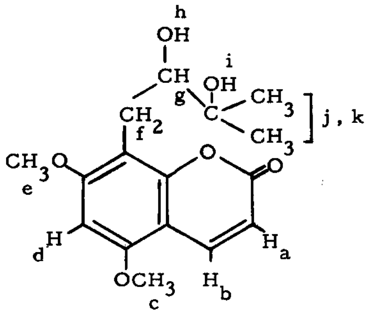
From taxonomic considerations we were interested to examine Murraya exotica L. (Fam: Rutaceae; Subfam: Aurantieae) which has been reported (2) to yield scopolin, $C_{16}H_{18}O_9$, m. p. 218°, and scopoletin, $C_{10}H_8O_4$, m. p. 204°. The present communication deals with the structure of a new coumarin isolated in a poor yield from the stem bark of M. exotica. The coumarin has been named mexoticin and on the basis of the studies reported here is formulated as (I).

Mexoticin (I), m. p. 185°, is an optically active, $[\alpha]_D + 37.6°$, ($CHCl_3$), neutral compound which with alcoholic potassium hydroxide gives a positive test for coumarins. Its homogeneity was established by paper (3) and thin-layer chromatography (4). The molecular formula of mexoticin has been determined as $C_{16}H_{20}O_6$ by high-resolution mass spectrometry: found 308.1262; calculated 308.1260. Its u. v. absoprtion spectrum shows maxima at 252 (log ϵ 4.09), 260 (log ϵ 4.14) and 326 mμ (log ϵ 4.26) and is very similar to that of 5:7-dimethoxy-coumarin (citropten) (5) : λ_{max} 247 (log ϵ 3.86) and 326 mμ (log ϵ 4.18). The i. r. spectrum (KBr) of mexoticin has bands at 3520 (OH), 1710 (δ-lactone), 1600, 1500 (unsaturation and aromatic system), 1360 (C-Me), 818, 790 cm^{-1} (substituted benzene derivative).

The analytical and spectral data suggest that mexoticin is a 5,7-dimethoxy coumarin bearing a $C_5H_{11}O_2$ substituent.

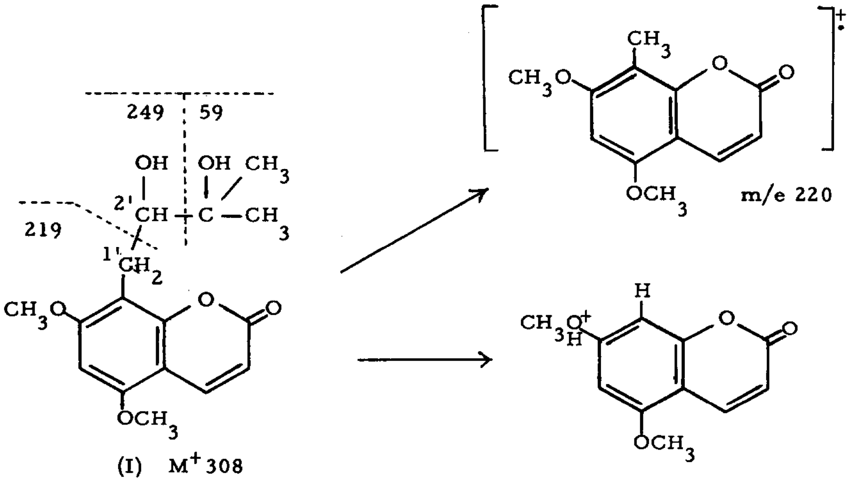
Like coumarins unsubstituted at the 3 and 4 positions (a,b ; structure I) the n. m. r. spectrum (60 Mc. in $CDCl_3$) of mexoticin shows doublets at δ 6.10 (J = 10 cps) and 7.98 (J = 10 cps). A sharp singlet at δ 3.92 (6H) reveals the presence of two aromatic methoxyl groups (c, e). The three-line signal at δ 2.90 (2 H) is assigned to the benzylic methylene (f) and a quartet at δ 3.58 (1 H) is due to the methine proton (g). The signal at δ 2.3, belonging to the two hydroxyl protons (h, i), disappears on deuteration. The singlet at δ 1.30 (6 H) corresponds to the gem dimethyl protons of the terminal hydroxy-isopropyl group (j, k), and a singlet at δ 6.32 (1 H) may be attributed to an aromatic proton (d) highly shielded (6) by two adjacent methoxyl groups situated at positions 5 and 7.

All the above data lead to the formulation of mexoticin as 5,7-dimethoxy-8-(2',3'-dihydroxy-isopentyl)-coumarin (I).



(I)

The mass spectrum (obtained with an A.E.I. MS 9 mass spectrometer operating at 70 eV) of mexoticin is in complete agreement with the proposed structure (I). The molecular peak at m/e 308 is displaced to m/e 310 upon deuteration, clearly demonstrating the presence of two hydroxyl groups in the molecule. A peak at m/e 59, shifted to m/e 60 after deuterium exchange, is consistent with the presence of a terminal hydroxy-isopropyl group. This is also evident from the occurrence of the M-59 and M-58 peaks (7) at m/e 249 and 250, respectively. Cleavage of the C-1' and C-2' bond leads to the appearance of the two peaks at m/e 219 and 220. The most abundant fragment in the mass spectrum is at m/e 207 and its composition $C_{11}H_{11}O_4$ (determined by high resolution mass measurement : found 207.0654; calculated 207.0657) points to the loss of the five-carbon substituent with acquisition of two hydrogen atoms by the rest of the molecule (e.g., see II)



(I) M^+ 308

(II) m/e 207 ($C_{11}H_{11}O_4$)

Mexoticin is evidently a position isomer of toddalolactone, i.e., 5:7-dimethoxy-6-(2':3'-dihydroxy-isopentyl)-coumarin, $C_{16}H_{20}O_6$, m.p. 132.5°, isolated from the bark of *Toddalia aculeata* Pers. (8) (Fam : *Rutaceae*; Subfam : *Toddalieae*).

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