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COUMARINS OF THE ROOT BARK OF *FERONIA ELEPHANTUM*

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Feronia elephantum (Rutaceae, subfamily Aurantioideae), a common Indian tree, belongs to the tribe Citreae and subtribe Balsamocitrinae.[1] *Feronia* is a single speciesed genus. Earlier work revealed the presence of aurapten in the root-bark,[2] essential oils, stigmasterol and bergapten in the leaves,[3] stigmasterol in the unripe fruits[3] and two uncharacterized alkaloids and marmesin in the stem-bark.[3] We now report the isolation and characterization of coumarins from the root-bark.

Powdered root-bark of *F. elephantum* was extracted with light petrol. (b.p. 60–80°) and $CHCl_3$ respectively. Both extracts were free from basic components. The residue from the light petrol. extract was chromatographed over silica gel. Light petrol. eluted as the main component aurapten[4] (I) crystallizing from light petrol. in stout needles, m.p. 66–67° (yield 0·7%.) Later fractions of the light petrol.–benzene (3:1) eluated another coumarin, bergapten[4] (II), m.p. 185–186° in very poor yield (0·0034%). The third coumarin, obtained from light petrol.–benzene (2:1), crystallized from light petrol.–MeOH in fine pale yellow needles, m.p. 148° (yield 0·021%) and was identified as isopimpinellin[4] (III). Light petrol.–benzene (1:1) eluted out a gummy solid from which another coumarin was isolated by repeated chromatography followed by slow crystallization from MeOH in needles, m.p. 87–88° (yield 0·006%), $C_{20}H_{24}O_4$; λ_{max} (EtOH) 229 nm (log ϵ, 4·17), 260 sh (4·47), 293 (4·56), unchanged in alkali, characteristic of 6,7-dialkoxycoumarin chromophore. The IR (KBr) spectrum indicated the presence of α,β-unsaturated δ-lactone (5·87 μ), *gem* dimethyl group (twin peaks at 7·25 and 7·37) and unsaturation (6·22).

The PMR spectrum[5] of this coumarin displayed signals for a 6,7-dialkoxycoumarin system (6·27, 1H *d*, $J_{3,4}$ 9·5 Hz, H-3; 7·63, 1H *d*, H-4; 6·87, 1H *s*, H-5; 6·82, 1H *s*, H-8), a methoxyl group at C-6 or at C-7 (3·89, 3H *s*) and a geranyloxy or neryloxy side chain at C-7 or C-6 (1·62 and 1·65, 3H *s* each, 7′ methyls; 1·75, 3H *s*, 3′-Me; 2·0–2·25, 4H *m*, 4′-H_2 and 5′-H_2; 4·70, 2H *d*, $J_{1',2'}$ 6·5 Hz, 1′-H_2; 4·85–5·32, 1H *bm*, 6′-H coupling with vicinal 5′-H_2 and allylic 7′-Me's; 5·48, 1H *bt*, 2′-H coupling with 1′-H_2, and also with allylic 4′-H_2 and 3′-Me) leading to its formulation as IV or IVa

The MS is consistent with structure IV and not IVa and is characterized by the extremely facile fragmentation of the allylic ether bond with H transfer from the allylic 3′-Me to the ether oxygen in a 6-membered cyclic TS resulting in the 6-methoxy-7-hydroxy coumarin

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[1] D. L. DREYER, M. V. PICKERING and P. COHAN, *Phytochem.* **11**, 705 (1972).

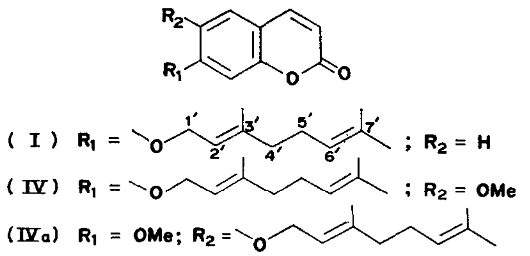
[2] T. R. GOVINDACHARI, N. S. NARASIMHAN and B. S. THYAGARAJAN, *Chem. Ber.* **91**, 34 (1958).

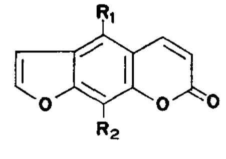
[3] *Supplement to Glossary of Indian Medicinal Plants* (edited by R. N. CHOPRA, I. C. CHOPRA and B. S. VARMA), p. 29, Publications and Information Directorate, New Delhi (1969); and references cited therein.

[4] These compounds were identified in the conventional way by direct comparison (m.m.p., IR, TLC) with the respective authentic samples isolated previously in this laboratory. The PMR and the MS of coumarins I and II studied were also consistent with their structures.

[5] The PMR spectra were studied in $CDCl_3$ in Varian A60 spectrometer and the chemical shifts are expressed in ppm using TMS as the internal standard.

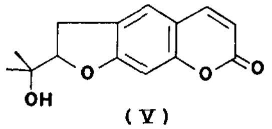
radical ion (*a*), appearing as the base peak at *m/e* 192 and consequently the parent ion at *m/e* 328 is extremely weak (0·5 %).[6] The other diagnostically important peaks are at *m/e* 259 (0·4 %, M − 69, 4′-5′ cleavage), 193 (34 %, 1′-O cleavage with intramolecular capture of 2H), 191 (5 %, M − 137, 1′-O cleavage), 177 (10 %, *a* − Me, generated as shown, thus locating the OMe at 6 position),[7] 164 (5 %, *a* − CO), 149 (4·5 %, 177 − CO or 164 − Me), 136 and 137 (9 and 6 %, side chain after 1′-O cleavage, with or without H loss to the ether oxygen), 121 and 93 (4 and 6 %, sequential loss of 2 CO from 149), 68 and 69 (8 and 51 %, 5′-4′ cleavage with or without H loss).





(II) R_1 = OMe; R_2 = H

(III) R_1 = R_2 = OMe



(V)

The only other significant ion at *m/e* 81 (17 %), the genesis of which is not obvious, might arise from the geranyl side chain by its isomerization, involving simultaneous 5′-4′ cleavage and 2′-1′ formation followed by cleavage of O-1′ bond with H transfer from 3′-Me to ether O and subsequent loss of one Me from the doubly allylic quaternary carbon.

All the above data indicate the 6-methoxy-7-geranyloxycoumarin structure (IV) for this coumarin, but the possibility of the *cis* stereochemistry of the 2′,3′ double bond (i.e. 7-neryloxy substituent) could not be eliminated at this stage. After the completion of our work our attention was drawn to a new coumarin having structure IV, recently reported from *Thapsia garganica*,[8] Umbelliferae. The structure was finally confirmed by direct comparison (m.m.p., IR, TLC) with an authentic sample of 6-methoxy-7-geranyloxycoumarin kindly supplied by Prof. P. K. Larsen.[8] The MS peaks of the two compounds, although differing slightly in relative intensities, were also similar.

The UV, IR and PMR spectral data and the genesis of the mass peaks of this coumarin not being published earlier[8] are recorded here. To our knowledge the occurrence of 6-methoxy-7-geranyloxycoumarin in the Rutaceae seems not to have been reported earlier.

Further elution of the main chromatogram with increasing polar solvent systems led to no isolable product. The chloroform extract of the plant material upon working up in a similar way furnished in addition to all the four coumarins (in lower yields: I 0·2 %; II 0·0016 %; III 0·0083 %; IV 0·004 %), another coumarin marmesin[4] (V), m.p. 188°, $[\alpha]_D + 23°$ ($CHCl_3$), from the $CHCl_3$ eluates. No limonoid or alkaloid could be isolated or detected from either light petrol. or $CHCl_3$ extract of the plant material.

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[6] C. S. BARNES and J. L. OCCOLOWITZ, *Austral. J. Chem.* **17**, 975 (1964).

[7] R. H. SHAPIRO and C. DJERASSI, *J. Org. Chem.* **30**, 955 (1965).

[8] P. K. LARSEN and F. SANDBERG, *Acta Chem. Scand.* **24**, 1113 (1969).