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Crenulatin, a Formyl Coumarin from *Hesperathusa crenulata* (Rutaceae)

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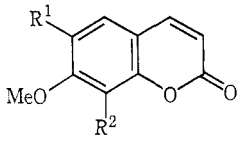
Abstract

A new coumarin, crenulatin (1), was obtained from the roots of *Hesperathusa crenulata*. By means of spectroscopic data and chemical degradation the compound was identified as 6-formyl-7-methoxycoumarin.

During a study on the isolation of possible anti-tumour constituents of the Indian Rutaceae, a new oxygen heterocyclic compound was encountered in the light petroleum extract of *Hesperathusa crenulata*. Previously[1] the coumarin derivatives suberosin, suberosin epoxide, marmesin and suberenol had been isolated from this source. The spectroscopic data and chemical reactions of this new compound suggest it to be a coumarin having a formyl substituent, the structure of which has been settled as 6-formyl-7-methoxycoumarin.

The coumarin had a molecular formula $C_{11}H_8O_4$ (M^+ 204), m.p. 252–253° and showed λ_{max} (EtOH) 256, 308 and 331 nm (log ε 4·17, 3·87 and 3·89); ν_{max} (Nujol) 1750 (α-pyrone), 1675 (aromatic aldehyde), 1620 (C=C), 860 and 840 cm^{-1} (1,2,4,5-tetrasubstituted aromatic nucleus).[2] Because of the small number of protons, the n.m.r. spectrum of the compound (100 MHz; $CDCl_3$: CF_3CO_2H 19 : 1) was distinct and showed signals for the C3 and C4 protons at δ 6·5 and 7·9 (d, 1H each, *J* 10 Hz); C5 and C8 protons at 8·16 and 6·96 (1H each, s). The methoxyl protons and the aldehydic proton resonated at δ 4·18 (3H, s) and 10·36 (1H, s). These arguments are in conformity with structure (1) for the new coumarin, which is further supported by its mass spectrum.



	R^1	R^2
(1)	CHO	H
(3)	H	CHO

	R^1	R^2
(2)	H	H
(4)	geranyl	H

Decarbonylation[3] of crenulatin (1) with 5% Pd/C resulted in the isolation of hernearin (2), thus supporting its structural assignment. Previously[4] 6-formyl-7-

[1] Nayar, M. N. S., and Bhan, M. K., *Phytochemistry*, 1972, **11**, 3333.
[2] Nakanishi, K., 'Infrared Absorption Spectroscopy' p. 27 (Holden–Day: San Francisco 1964).
[3] Hawthorne, J. O., and Wilt, N. H., *J. Org. Chem.*, 1960, **25**, 2215.
[4] Späth, E., and Klager, K., *Ber. Deut. Chem. Ges.*, 1934, **67**, 859 (*Chem. Abstr.*, 1934, **28**, 4721).

methoxycoumarin, m.p. 252–254°, was obtained as the CrO_3 oxidation product of ostruthin (4).

The occurrence of a formyl coumarin is now reported for the first time in the Rutaceae, the only other occurrence being angelical (3) in *Angelica pubescens*[5] (Umbelliferae). These are probably the biosynthetic intermediates of more complex coumarins.

Experimental

Melting points are uncorrected. Infrared spectra were measured in Nujol mulls, and the ultraviolet spectrum in ethanol solution; n.m.r. spectra were recorded on a Jeol spectrometer operating at 100 MHz. Each signal is described in terms of multiplicity, intensity, chemical shift in p.p.m. from tetramethylsilane.

Isolation of the Constituents of Hesperathusa crenulata

Milled, dry root bark of *H. crenulata* (5 kg) was extracted with light petroleum (60–80°) in a Soxhlet apparatus for 30 h. Evaporation of the extract gave a sticky oily residue (24 g). Acetone was added to the thick oily mass which was kept in a refrigerator overnight. The white solid separating out was filtered and taken up in ethyl acetate; the ethyl acetate solution on concentration furnished crenulatin, m.p. 252–253° (M^+ 204) (yield 0·0008%) (Found: C, 64·9; H, 4·1; O, 31·6. Calc. for $C_{11}H_8O_4$: C, 64·7; H, 3·9; O, 31·3%). It was insoluble in almost all organic solvents in the cold and showed a single spot on a t.l.c. plate, R_F 0·56 (silica gel; EtOAc : EtOH 4 : 1). Mass spectrum of crenulatin showed major fragmentation peaks at *m/e* 204 (100%), 175, 172, 159, 147, 133, 116, 105, 89, 77 and 69. The mother liquor left after the separation of crenulatin was chromatographed over silica gel for the isolation of other constituents.

Decarbonylation of Crenulatin

Crenulatin (200 mg) and palladized charcoal (5%, 100 mg) were thoroughly mixed together and heated at 250–260° for 2 h in a carbon dioxide atmosphere. The reaction mixture was cooled and extracted with ethanol. T.l.c. of the ethanol extract (silica gel; EtOAc : EtOH 4 : 1) showed three major spots, one of which had R_F identical with that of hernearin. Preparative t.l.c. of the concentrated extract furnished 20 mg of a product, m.p. 117°, identical with hernearin by m.m.p. and i.r.

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[5] Dean, F. M., 'Naturally Occurring Oxygen Ring Compounds' p. 185 (Butterworths: London 1963).