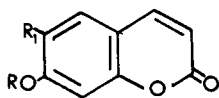


# CONSTITUENTS OF *HESPERATHUSA CRENULATA*

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In the frame work of our continuing search for anti-tumor constituents of Indian Rutaceae, we examined *Hesperathusa crenulata*. Earlier work on this species has resulted in the isolation of a number of coumarins and alkaloids (1-4). We now report the structural elucidation and synthesis of 6-formyl-7-methoxycoumarin (1) isolated from the root extracts of this species.



- 1 R=CH<sub>3</sub>, R<sub>1</sub>=CHO  
 2 R=R<sub>1</sub>=CH<sub>3</sub>  
 3 R=CH<sub>3</sub>, R<sub>1</sub>=H

On the basis of elemental analysis and mass spectrometry, the molecular formula for 1 was found to be C<sub>11</sub>H<sub>8</sub>O<sub>4</sub>. That it is a substituted coumarin was revealed from its uv and ir spectra (*vide* experimental). The 100 MHz nmr spectrum displayed the characteristic singlets for the methoxyl and aldehydic signals at  $\delta$  4.18 and 10.36, and that of the aromatic C-5 and C-8 protons at  $\delta$  8.16 and 6.96, respectively. The <sup>13</sup>C nmr parameters which corroborated the <sup>1</sup>H nmr assignments are summarized in table 1.

TABLE 1. <sup>13</sup>C nmr chemical shifts of (1) & (2).<sup>a</sup>

Carbon/compound	1	2
2.....	164.15	161.22
3.....	114.54	112.97
4.....	143.24	142.97
4a.....	112.46	112.00
5.....	128.88	128.60
6.....	122.13	124.01
7.....	159.73	160.94
8.....	99.96	98.00
8a.....	159.47	154.70
-OMe.....	56.36	55.84
-CHO.....	187.71	—
-CH <sub>3</sub> .....	—	15.45

<sup>a</sup>In parts per million down field from TMS:  $\delta$  TMS =  $\delta$  (CDCl<sub>3</sub>) + 76.9 ppm.

Decarbonylation (5) of 6-formyl-7-methoxycoumarin 1 with 5% Pd/C resulted in the isolation of 3 which was also isolated during the column chromatography of the light petroleum extracts. Moreover, following the procedure of Seshadri *et al.* (6), 6-methyl-7-methoxycoumarin 2 was synthesized from resorcinol, which in turn was oxidized with chromyl chloride (7) to give 6-formyl-7-methoxycoumarin, thus establishing its structure.

6-Formyl-7-methoxycoumarin has also been isolated from other Rutaceous species, i.e., *Zanthoxylum suberosum* (8), *Boenninghausenia albiflora* (9), *Citrus nobilis* (10) and from the Umbelliferous species *Angelica pubescens* (11). The 6-methyl-7-methoxycoumarin 2 was isolated from *Trachyspermum roxburghianum* (12).

## EXPERIMENTAL<sup>1</sup>

PLANT MATERIAL.—The plant material was collected on the campus of the Laboratory. A voucher specimen has been kept in the herbarium of the Laboratory.

ISOLATION OF 6-FORMYL-7-METHOXYCOUMARIN.—Milled, air dried root bark of *H. crenulata* (5 kg) was extracted with light petroleum (60–80°) in a Soxhlet apparatus for 30 h. Excess solvent was distilled off. Acetone was added to the thick oily mass, which was kept in the refrigerator overnight. The white solid that separated was repeatedly crystallized from ethyl acetate which gave 6-formyl-7-methoxycoumarin, mp 252–53° (M<sup>+</sup> 204), (Found: C, 64.9, H, 4.1, O, 31.6, Calc for C<sub>11</sub>H<sub>8</sub>O<sub>4</sub>: C, 64.7, H, 3.9, O, 31.31%). Uv  $\lambda$  max (EtOH) 256, 308 and 331 nm (log  $\epsilon$  4.17, 3.87 and 3.89); ir  $\nu$  max (nujol) 1750, 1675, 1620, 860 and 840 cm<sup>-1</sup>, mass spectra: *m/z* 204 (M<sup>+</sup>, 100%) 175, 172, 159, 147, 133, 116, 105, 89, 77, and 69.

ISOLATION OF 7-METHOXYCOUMARIN.—The mother liquor of the above was chromato-

<sup>1</sup>Melting points are uncorrected. The ultraviolet spectrum was measured in a Beckmann DK 2A spectrophotometer in ethanol solution, and infrared spectra were measured in Nujol mulls with a Perkin Elmer 337 instrument. The <sup>1</sup>H nmr spectrum was run on a JEOL PS-100 spectrometer, and the <sup>13</sup>C nmr spectra were recorded on a JEOL FX60 instrument.

graphed over silica gel with benzene as eluent; 7-methoxycoumarin was isolated as white needles mp 117°. Its identity was established from its mp, mmp and ir spectra which were superimposable with an authentic sample.

**DECARBONYLATION OF 6-FORMYL-7-METHOXYCOUMARIN.**—The 6-formyl-7-methoxycoumarin (200 mg) and palladized charcoal (5%; 100 mg) were thoroughly mixed together and heated at 250–60° for 2 hr in a carbon dioxide atmosphere.

The reaction mixture was cooled and extracted with ethyl acetate. Preparative tlc (Si gel; ethyl acetate-ethanol 4:1) of the concentrated extract furnished 20 mg of a solid, mp 117°, identical with 7-methoxycoumarin by mmp and ir.

**SYNTHESIS OF 6-FORMYL-7-METHOXYCOUMARIN.**—To a solution of 6-methyl-7-methoxycoumarin (100 mg) in carbon disulfide (10 ml) was added a solution of chromyl chloride (4 gm) in carbon disulfide (25 ml) with shaking, and the mixture was kept at room temperature for 96 hours. The red precipitate obtained was filtered and washed with carbon disulfide, and the product suspended in water (100 ml). After one hour the residue obtained was filtered, washed, dried and crystallized from ethyl acetate, mp 250°, yield 12 mg. This had an undepressed mmp and a superimposable ir in comparison with the sample isolated from the natural source.

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#### LITERATURE CITED

1. M. N. S. Nayar, C. V. Sutar and M. K. Bhan, *Phytochemistry*, **10**, 2843 (1971).
2. M. N. S. Nayar, M. K. Bhan and V. George, *Current Science*, **40**, 570 (1971).
3. M. N. S. Nayar, and M. K. Bhan, *Phytochemistry*, **11**, 3331 (1972).
4. S. C. Basa, *Aust. J. Chem.*, **28**, 1159 (1975).
5. J. O. Hawthorne and M. H. Wilt, *J. Org. Chem.*, **25**, 2215 (1960).
6. M. Bandopadhyay, N. P. Pardeshi and T. R. Seshadri, *Ind. J. Chem.*, **12**, 295 (1974).
7. W. R. Boon, *J. Chem. Soc.*, S 230 (1949).
8. G. B. Guise, E. Ritchie, R. G. Senior and W. C. Taylor, *Aust. J. Chem.*, **20**, 2429 (1967).
9. S. K. Talapatra, S. K. Mukhopadhyay and B. Talapatra, *Phytochemistry*, **14**, 836 (1975).
10. J. Reisch, I. Mester and E. A. Sofowora, *Planta Medica* (Supplement), **56** (1980).
11. K. Hata, Y. Taneka, *Yakugaku Zasshi*, **77**, 937 (1957).
12. B. R. Sharma and P. Sharma, *Ind. J. Chem.*, **19 B**, 85 (1980).