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# 7-PHENYLACETOXY COUMARIN FROM *LIMONIA CRENULATA*

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**Key Word Index**—*Limonia crenulata*; Rutaceae; 7-phenylacetoxycoumarin.

**Abstract**—A new coumarin, 7-phenylacetoxycoumarin, has been isolated from *Limonia crenulata* along with luvangetin, xanthotoxin, umbelliferone and limonin. This is the first report of a coumarin phenol ester from a natural source.

## INTRODUCTION

In continuation of our work on naturally occurring coumarins [1–3] we have examined the aerial parts of *Limonia crenulata* Roxb. (Rutaceae), a plant which grows abundantly in the Himalayan range and is used extensively in the treatment of epilepsy [4]. In the course of this investigation we have isolated a new compound, 7-phenylacetoxycoumarin, the complete characterization of which is described in the present communication.

## RESULTS AND DISCUSSION

The new compound $C_{17}H_{12}O_4$ ($M^+$ 280), showed the typical UV absorption of a 7-oxygenated coumarin ($\lambda_{\max}^{\mathrm{EtOH}}$. 214, 283 and 313 nm: log $\varepsilon$ 4.28, 4.02 and 3.98). In alkali ($\lambda_{\max}^{\mathrm{NaOH/EtOH}}$. 216, 229 and 377.5; log $\varepsilon$ 4.17, 3.99 and 4.33) the spectrum was similar to that of umbelliferone. Several structural features could be ascertained from its 80 MHz $^1$H NMR spectrum ($CDCl_3$). The latter exhibited coumarinic doublets at $\delta$ 6.25 ($C_3$-H) and 7.54 ($C_4$-H) ($J$ = 9.6 Hz), the $C_5$-H appeared as a doublet at 7.32 ($J$ = 8.3 Hz) and the $C_6$-H as a double doublet at 6.91 ($J_o$ = 8.3; $J_m$ = 2.2 Hz). The doublet at 6.96 ($J$ = 2.2 Hz) was attributed to the $C_8$-H while the signal at 3.79 (2 H, *s*) and the five-proton singlet at 7.25 indicated the possibility of the presence of a $-CH_2Ph$ group in the molecule. On this basis structure **1** was assigned to this new coumarin.

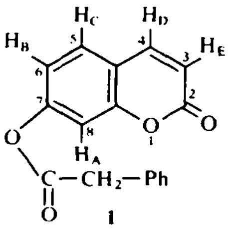

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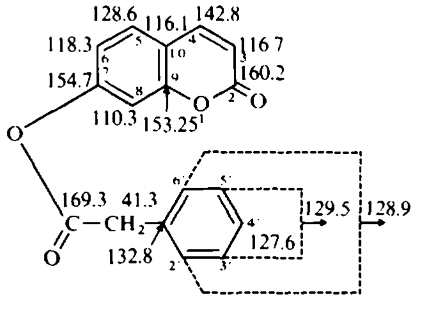
Table 1. Long range coupling constants of the protons $H_A$, $H_B$, $H_C$, $H_D$ and $H_E$ in 7-phenylacetoxycoumarin

| Proton number | Coupling constants (Hz) |
|---|---|
| $H_A$ | $J_{AB} = 2.2$ |
| | $J_{AC} = J_{AD} = 0.7$ |
| | $J_{AE} = 0.1$ |
| $H_B$ | $J_{AB} = 2.2$ |
| | $J_{BC} = 8.3$ |
| | $J_{BE} = 0.1$ |
| $H_C$ | $J_{BC} = 8.3$ |
| | $J_{CD} = 0.3$ |
| | $J_{AC} = 0.7$ |
| $H_D$ | $J_{DE} = 9.6$ |
| | $J_{CD} = 0.3$ |
| | $J_{AD} = 0.7$ |
| $H_E$ | $J_{DE} = 9.6$ |
| | $J_{AE} = 0.1$ |
| | $J_{BE} = 0.1$ |

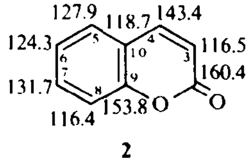
The presence of the ABC system was recognised by the plot expansions on a 1.0 Hz/cm scale. The long range couplings of the protons, $H_A$, $H_B$, $H_C$, $H_D$ and $H_E$ (Table 1) through 4, 5 and 6 bonds of 0.3, 0.7 and 0.1 Hz are typical of the expected patterns of a 7-substituted coumarin.

The proposed structure **1** received unambiguous support from the $^{13}$C NMR spectrum of the compound and also from a comparison of the carbon signals with those of coumarin (**2**). The shift in the values of the carbons C-5, C-6, C-7, C-8 and C-10 in **1a** compared to that in coumarin **2** are due to the presence of the acetoxy group.

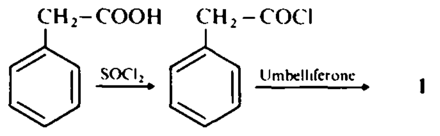
**1** was subsequently synthesized from phenylacetic acid and umbelliferone and found to be identical with the natural product. This is the first report of a coumarin phenol ester from a natural source.



**1a**



**2**



Phenylacetic acid Phenylacetyl chloride 7-Phenylacetoxycoumarin

## EXPERIMENTAL

Mps are uncorr. UV spectra were measured in EtOH and NMR spectra were determined in $CDCl_3$ using TMS as int. standard. Column chromatography was carried out with Si gel (Gouri Chemical Works, 60–100 mesh) and TLC with Si gel G (Merck). $Na_2SO_4$ was used to dry the organic solvents and samples were routinely dried over $P_2O_5$ for 24 hr.

*Isolation of chemical constituents.* Air-dried and powdered aerial parts of *Limonia crenulata* (5 kg) were extracted with petrol (60–80°) in Soxhlet extractor and the defatted material percolated at room temp. with EtOH. The concd petrol extract on chromatography afforded luvangetin and xanthotoxin from the $C_6H_6$ eluates and limonin from the 5% methanolic $CHCl_3$ eluate.

*7-Phenylacetoxycoumarin* (**1**) *and umbelliferone.* The EtOH concentrate afforded 7-phenylacetoxycoumarin (**1**) in the $C_6H_6$–$CHCl_3$ (3:1) eluate. It was purified by further chromatography, mp 101° (colourless needles from MeOH); yield: 0.00002%; *m/e* 280 ($M^+$, 16%), 162 (50%), 134 (34%), 133 (18%), 119 (52%), 118 (92%), 105 (28%), 91 (100%) and 77 (32%). The 10% methanolic $CHCl_3$ eluate yielded umbelliferone.

*Synthesis of 7-phenylacetoxycoumarin* (**1**). Phenylacetic acid (500 mg) and freshly dist. thionyl chloride (1 ml) was heated over a steam bath for 1 hr in dry conditions. Excess thionyl chloride was removed under red. pres., umbelliferone (150 mg) added and the mixture refluxed for 2 hr. The reaction mixture was then cooled in an ice bath, poured over crushed ice, stirred and extracted with $CHCl_3$ (3 × 25 ml). The total $CHCl_3$ extract was washed with 1% aq. NaOH, followed by $H_2O$. The $CHCl_3$ concentrate upon chromatography afforded 7-phenylacetoxycoumarin (**1**) (yield: 55%), mp 100 101° (MeOH). The synthetic coumarin was found to be identical with the natural compound from mp, mmp, co-TLC and superimposable IR spectra.

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## REFERENCES

1. Chatterjee, A., Banerji, J. and Basa, S. C. (1972) *Tetrahedron* **28**, 5175.
2. Majumder, P. L., Sengupta, G. C., Dinda, B. N. and Chatterjee, A. (1974) *Phytochemistry* **13**, 1929.
3. Chatterjee, A., Sen, R. and Ganguli, D. (1978) *Phytochemistry* **17**, 328.
4. Chopra, R. N., Nayer, S. L., Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants.* Council of Scientific and Industrial Research, New Delhi.