

Poncitrin, a New Coumarin: Structure and Nuclear Overhauser Effects

By TOSHIAKI TOMIMATSU and MITSUKO HASHIMOTO

(Faculty of Pharmaceutical Sciences, Tokushima University, Tokushima, Japan)

TETSURO SHINGU

(Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto, Japan)

and KAZUO TORI*

(Shionogi Research Laboratory, Shionogi and Co., Ltd., Fukushima-ku, Osaka, Japan)

WE report the elucidation of the structure of a new coumarin, poncitrin, isolated from the root of *Poncirus trifoliata* Rafinesque.

Poncitrin (I), $C_{20}H_{22}O_4$, m.p. 93—94°, $[\alpha]_D 0^\circ$ ($CHCl_3$), crystallized from ethanol as colourless pillars. It shows the presence of an $\alpha\beta$ -unsaturated δ -lactone in its i.r. spectrum, the presence of a conjugated coumarin ring in its u.v. spectrum, and a parent peak at m/e 326 in its mass spectrum. The 1H n.m.r. and n.m.d.r. spectra† show an isolated ABX-type signal arising from a vinyl group (τ 3.70, 5.07, and 5.13;

J 17.6, 10.6, and 1.2 Hz.) and two sharp AB-type quartets due to olefinic protons (τ 2.14 and 3.84; J 9.8 Hz; τ 3.43 and 4.31; J 10.2 Hz), in addition to a methoxy-singlet (τ 6.18) and two sharp singlets arising from two magnetically equivalent *gem*-dimethyl groups (τ 8.33 and 8.54); these findings suggest the presence of a methoxy-substituted coumarin ring, a 2,2-dimethylchromene ring,¹ and a 1,1-dimethylallyl group² on the benzene ring.

Hydrogenation of (I) over Pd-C in AcOH gave tetrahydroponcitrin (II), $C_{20}H_{26}O_4$, m.p. 94—95°, as colourless

† The 1H n.m.r. spectra were taken with a Varian HA-100 spectrometer (100 MHz) in the frequency-swept and internal $SiMe_4$ -locked mode, for $\sim 10\%$ (w/v) degassed solutions in $CDCl_3$. N.m.d.r. experiments were performed by use of the same spectrometer with a Hewlett-Packard HP-200ABR audio-oscillator and HP-5212A electronic counter. Accuracies are $\tau \pm 0.01$ for chemical shifts and ± 0.2 Hz for coupling constants.

The observed NOE's for (I) in CDCl₃ (percentages)

Protons saturated	Increase in integrated intensities and heights (in parentheses) of signals of						
	H-3	H-4	H-6	H-7	H-12	H-13 (cis)	H-13 (trans)
5-OCH ₃	τ3.84	2.14	3.44	4.31	3.70	5.07	5.13
τ6.18	nil	11	16	nil	nil	nil	nil
8-(CH ₃) ₂	nil	(9)	(13)	22	nil	nil	nil
τ8.54	nil	nil	nil	(13)	nil	nil	nil
11-(CH ₃) ₂	nil	nil	nil	nil	12	25	nil
τ8.33					(19)	(39)	

prisms (from ethanol). Its i.r. and u.v. spectra still showed the presence of the coumarin ring. In its ¹H n.m.r. spectrum, an isolated A₂B₃-type signal due to -CH₂-CH₂- and

an isolated A₃B₂-type signal (Et) appeared in the high-field region in place of the olefinic proton signals due to the vinyl and dimethylchromene groups in (I). These facts led us to a partial structure (III) for poncitrin.

We were able, using the nuclear Overhauser effects (NOE)³ recently developed,^{4,5} to establish the complete structure.

The signals of the methoxy- and the two *gem*-dimethyl protons were successively saturated by double irradiation, and increases of integrated intensities and heights[†] of all the olefinic proton signals were measured. The observed NOE's are summarized in the Table. Structure (I) is the only one possible for poncitrin because both the H-4 and H-6 signals increase in intensity on saturation of the methoxy-protons. The NOE measurements also confirmed the presence of the 2,2-dimethylchromene and 1,1-dimethylallyl groups, and the assignment of their *gem*-dimethyl groups.

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[†] The NOE measurements were performed with sweep rates of 1 Hz. sec. for integrations and 0.2 Hz. sec. for signal heights. Accuracies for NOE values are about ±2%. Since long-range spin couplings were hardly detected, the increases in signal heights are also described in the Table.⁴

¹ T. Tomimatsu and M. Hashimoto, *J. Pharm. Soc. Japan*, 1968, **88**, 1357; M. W. Jarvis and A. G. Moritz, *Austral. J. Chem.*, 1968, **21**, 2445, and references therein.

² M. M. Ballantyne, R. D. H. Murray, and A. B. Penrose, *Tetrahedron Letters*, 1968, 4155, and references therein.

³ F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 1965, **87**, 5250.

⁴ M. C. Woods, I. Miura, Y. Nakadaira, A. Terahara, M. Maruyama, and K. Nakanishi, *Tetrahedron Letters*, 1967, 321.

⁵ K. Tori, M. Ohtsuru, I. Horibe, and K. Takeda, *Chem. Comm.*, 1968, 943, and references therein.

