Poncitrin, a New Coumarin: Structure and Nuclear Overhauser Effects

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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°, $[\alpha]_D 0^\circ$ (CHCl₃), 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 ($\tau 2.14$ and 3.84; J 9.8 Hz; $\tau 3.43$ and 4.31; J 10.2 Hz), in addition to a methoxy-singlet ($\tau 6.18$) and two sharp singlets arising from two magnetically equivalent gem-dimethyl groups ($\tau 8.33$ and 8.54); these findings suggest the presence of a methoxy-substituted coumarin ring, a 2,2-dimethylchromene ring,¹ and a 1,1dimethylallyl 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

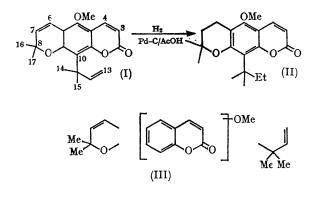
[†] The ¹H n.m.r. spectra were taken with a Varian HA-100 spectrometer (100 MHz) in the frequency-swept and internal SiMe₄locked mode, for $\sim 10\%$ (w/v) degassed solutions in CDCl₃. N.m.d.r. experiments were performed by use of the same spectrometer with a Hewlett-Packard HP-200ABR audio-oscillater and HP-5212A electronic counter. Accuracies are $\tau \pm 0.01$ for chemical shifts and ± 0.2 Hz for coupling constants.

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

Protons	Increase in integrated intensities and heights (in parentheses) of signals of						
saturated	H-3	H-4	H-6	H-7	H-12	H-13 (cis)	H-13 (trans)
	$\tau 3.84$	$2 \cdot 14$	3.44	4.31	3.70	5.07	5.13
5-OCH ₃	nil	11	16	nil	nil	nil	nil
$\tau 6.18$		(9)	(13)				
8-(CH ₃) ₂	nil	nil	nil	22	nil	nil	nil
$\tau 8.54$. "1	.,	(13)		~~	
$11-(CH_3)_2$ $\tau 8.33$	nil	nil	nil	nil	12	25	nil
73.33					(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 A₂B₂-type signal due to -CH₂·CH₂- and



an isolated A_3B_2 -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 $\pm 2\%$. Since long-range spin couplings were hardly detected, the increases in signal heights are also described in the Table.4

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