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Poncimarin, a New Coumarin from *Poncirus trifoliata* L.

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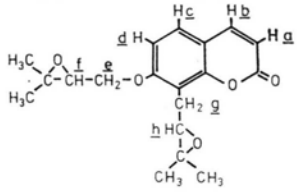
A new coumarinic derivative (Poncimarin; $C_{19}H_{22}O_5$; m.p. 140 °C) was isolated from unripe fruits of *Poncirus trifoliata* L. which from spectroscopic evidences was formulated as 7-(2,3-epoxy-3-methyl butyloxy)-8-(2,3-epoxy-3-methyl butyl) coumarin.

In a systematic study of the coumarinic components of *Poncirus trifoliata* L. (Fam. Rutaceae; subfam. Aurantioideae), we recently described the presence of the coumarins aurapten and 6-methoxy-7-geranyloxy coumarin [1] and the furocoumarins isopimpinellin, prangenin and pragenin hydrate [2] in addition to the already reported bergapten and imperatorin [3]. From the roots of the same plant the coumarins seselin, marmesin [4] and poncitrin [5] were also isolated.

We are now reporting the characterization of a unknown coumarin present in low amount in the unripe fuits. This coumarin, which we call poncimarin, is formulated from the evidences reported here as 7-(2,3-epoxy-3-methylbutyloxy)-8-(2,3-epoxy-3-methylbutyl) coumarin (**1**).



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Poncimarin (**1**) is an optically active $[\alpha]_D^{25}$ $-56.2°$ ($CHCl_3$, *c* 9.4), neutral coumarin, which crystallized from CH_3OH in white needles, m.p. 140 °C, and showed violet-blue fluorescent to UV light. Elemental analysis yielded $C_{19}H_{22}O_5$ and the molecular weight is 328.6 (calcd. 330.37) (osmometric method; $CHCl_3$). The UV absorption spectrum [(95% C_2H_5OH) λ_{max} nm (log ε) 320 (4.19); 255.5 (3.61); 246 (3.60); 235 (3.57); 216 (shoulder; 4.14) and λ_{min}: 262 (3.28); 250.5 (3.55); 240.5 (3.54); 233 (3.56)] is very similar to that of osthol and auraptenol [6].

The IR spectrum (KBr) of poncimarin shows absorption at 1725 (vs), 1600 (s), 1500 (m) [coumarin system], 1390 and 1380 (m) $\left[>C(-O-)C<^{CH_3}_{CH_3}\right]$ 1250 (s) [epoxide] and 830 cm^{-1} (s) [substituted benzene ring].

The H^1-NMR spectrum of poncimarin (90 Mc; $CDCl_3$; TMS internal standard) shows doublets at δ 6.26 (1H; $J = 9.5$ cps) and δ 7.65 (1H; $J = 9.5$ cps), assigned to C_3 and C_4 protons **a** and **b** respectively and doublets at δ 6.90 (1H; $J = 8.6$ cps) and δ 7.37 (1H; $J = 8.6$ cps) assigned to C_6 and C_5 *ortho* benzenic protons **d** and **c** respectively.

A four-line signal of AB_2 system centered at δ 4.23 (2H) assigned to methylene **e**. A broad multisignal absorption from δ 3.0 to δ 3.40 (4H) assigned to benzylic methylene **g** and to the epoxide protons **f**, **h**. Four singlets at δ 1.30; 1.39; 1.41; 1.51 (3H each) for the two geminal methyls.

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