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ISOPONCIMARIN: NEW COUMARIN FROM *PONCIRUS TRIFOLIATA**

A. GUIOTTO, P. RODIGHIERO, U. QUINTILY and G. PASTORINI

Istituto di Chimica Farmaceutica dell'Universita'di Padova, via Marzolo 5, 35100 Padova, Italy

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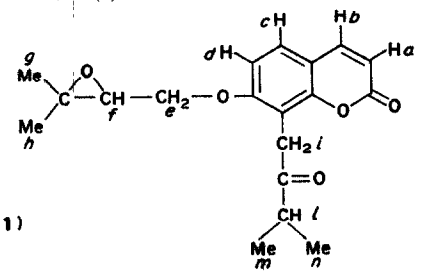
Key Word Index—*Poncirus trifoliata*; Rutaceae; new coumarin; isoponcimarin.

Plant. Poncirus trifoliata L. (Botanical Institute of University Padua Herbarium) *Source.* Padua surroundings. *Previous work.* Essential oil [1], bitter principles [2], coumarins and furocoumarins from seeds [2–5] unripe fruits [6] and roots [7].

In an earlier communication [6] the isolation of a 7-*O*, 8-*C*-diepoxyisoprenylcoumarin, poncimarin, was reported from unripe fruits of the above plant. We now report the isolation from the petrol extract of the same material of a new unknown coumarin, isoponcimarin. From chemical and spectral evidence isoponcimarin is 7-(3′-methyl-2′,3′-epoxybutyloxy)-8-(3″-methyl-2″-oxobutyl)coumarin (**1**).



(1)

The extract was chromatographed on a silica gel column eluting with a mixture of solvents of slowly increasing in polarity; EtOAc–C_6H_6 (1:1; v) fractions gave a crystalline compound, which after recrystallization from *n*-hexane had mp 85° and gave a single blue-fluorescent spot in UV light in several TLC systems.

The elemental analysis of isoponcimarin agrees with a molecular formula $C_{19}H_{22}O_5$, molecular weight 333·3 (calcd. 330·37; osmometric method; $CHCl_3$) and $[\alpha]_{465}^{20}$ − 6·94 ($CHCl_3$; $c = 3·75$). UV absorption spectrum, characteristic of a 7-alkoxycoumarin chromophore, is virtually identical with that of poncimarin [6] and it is not affected by addition of alkali, indicating the absence of a free phenolic hydroxyl group [(95% EtOH) λ_{max} nm (log. ϵ) 217 (4·16, (sh); 255 (3·63); 320 (4·20)].

The H^1-NMR spectrum of isoponcimarin (60 Mc; $CDCl_3$; TMS internal standard) confirmed the presence of a 7,8-disubstituted coumarin system showing doublets at δ 6·23 (1 H; J 9·5 Hz) and δ 7·64 (1 H; J 9·5 Hz), assigned to C_3 and C_4 protons *a* and *b* respectively and doublets at δ 6·87 (1 H; J 8·6 Hz) and δ 7·38 (1 H; J 8·6 Hz) assigned to C_6 and C_5 *ortho* benzenic protons *d* and *c* respectively. A sharp singlet at δ 4·07 (2 H) due to the benzylic protons *i*, because of the combined diamagnetic effects of the aromatic nucleus and contiguous carbonyl group [8]. An incompletely resolved septet at δ 2·86 (1 H) assigned to the methyne proton *l* and a doublet at δ 1·23 (6 H; J 7 Hz) for the terminal methyl groups *m* and *n*. A four line signal of an AB_2 system centered at δ 4·19 (2 H) assigned to methylene *e* and a triplet at δ 3·08 (1 H) due to the epoxide proton *f*. Two singlets at δ 1·35 and δ 1·37 (3 H each) for the methyls *g* and *h*. Decoupling experiments are in agreement with the attributions. In HOAc solution isoponcimarin gave on addition of conc. H_2SO_4 a mixture of 3 compounds, the major of which was identified as the corresponding diketo product arising from isomerization of epoxy group. However, isoponcimarin is not an artifact from poncimarin, since the latter compound did not undergo isomerization under the condition of isolation and both coumarins are present in the original petrol extract of the plant material as indicated by TLC.

* Part 4 in the series, Coumarin and furocoumarin from *Poncirus trifoliata*. For part 3 see A. Guiotto *et al.* (1975) *Z. Naturforsch.* **30 c**, 420.

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4,2′,4′,6′-TETRAHYDROXYCHALCONE IN POLLEN OF *PETUNIA HYBRIDA*

P. DE VLAMING* and K. F. F. KHO†

* Institute of Genetics, University of Amsterdam; † Department of Plant Physiology, University of Amsterdam, The Netherlands

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Key Word Index—*Petunia hybrida*; Solanaceae; pollen; flavonoids; chalcones.

In pollen of the inbred line V11 of *Petunia hybrida*, maintained in the collection of the Institute of Genetics, University of Amsterdam, a yellow pigment has been found. On paper chromatograms the colour of this pig-