

### Arnottianin: A New Dihydropyranocoumarin

In the course of the studies on the Alkaloids of Rutaceous Plants,<sup>1)</sup> we occasionally isolated a new nonphenolic dihydropyranocoumarin,<sup>2)</sup> mp 197—198°,  $[\alpha]_D^{25} \pm 0^\circ$ ,<sup>3)</sup> designated as arnottianin by us, from the wood of *Xanthoxylum Arnottianum* Maxim.<sup>4)</sup> in 0.0024% yield. We reported here the structural establishment of it from consideration of the spectral data.

Arnottianin gave elemental analyses in agreement with the molecular formula  $C_{15}H_{16}O_5$ , mass spectrum  $m/e$ : 276 ( $M^+$ ). And it shows the following spectral properties: IR  $\nu_{\text{max}}^{\text{CHCl}_3}$ ,  $\text{cm}^{-1}$ : 3600 (OH), 1728 (C=O), 1621, 1572 (C=C). UV  $\lambda_{\text{max}}^{\text{EtOH}}$  m $\mu$  (log  $\epsilon$ ): 250 (3.57), 260.5 (3.61), 329 (4.20). NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.41 (6H, singlet,  $2 \times (\text{C})\text{CH}_3$ ), 2.00 (1H, broad singlet, OH), 2.82 (1H, quartet,  $J=16.6$  and 6.0 Hz,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OR})-$ ), 3.06 (1H, quartet,  $J=16.6$  and 6.0 Hz,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OR})-$ ), 3.86 (1H, triplet,  $J=6.0$  Hz,  $\text{CH}_2\text{CH}(\text{OR})\text{C}-$ ), 3.93 (3H, singlet,  $\text{OCH}_3$ ), 6.18 (1H, doublet,  $J=9.4$  Hz,  $\text{C}_3\text{-H}$ ), 6.90 (1H, singlet,  $\text{C}_5\text{-H}$ ), 7.53 (1H, doublet,  $J=9.4$  Hz,  $\text{C}_4\text{-H}$ ). These spectral data indicate that arnottianin **1** is a coumarin having a partial structure of **2**, one methoxy group and one aromatic proton on its benzene portion. The ultraviolet spectrum of arnottianin is superimposable to that of (+)-rutaretin methylether<sup>5)</sup> **3** which was isolated from the same plants. This fact remains only two possibilities for arnottianin that a racemate of rutaretin methylether or the structure **1**. Since infrared spectrum in solution and nuclear magnetic resonance (NMR) spectrum of arnottianin are different from those of (+)-rutaretin methylether **3**, the former should be depicted by formula **1**.

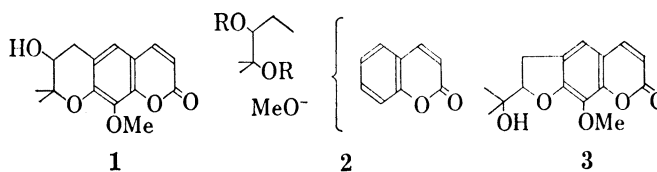


Chart 1

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- 1) Preceding paper; Part XIX: H. Ishii, H. Ohida and J. Haginiwa, *Yakugaku Zasshi*, **92**, 118 (1972).
- 2) Isolation work will be shown in a full paper. (H. Ishii, K. Hosoya and J. Haginiwa, unpublished.)
- 3) It was confirmed by measurement of the ORD curve. From this result, we wondered at first if it might be an artefact produced from other coumarin contained in the same plant during preparation of the extract. Thin layer chromatography of the methanol extract of this plant has shown the spot at the  $R_f$  value corresponding to the new coumarin and refluxing of all of the isolated coumarins from the same plant in 10% AcOH aq. which was a condition used for isolation work of alkaloids did not give the material. These experimental facts are enough to exclude the possibility of an artefact of it.
- 4) This material was collected in Bonin-islands and called as "Iwazansho" in Japanese name.
- 5) G. Schneider, H. Müller and P. Pfaender, *Arch. Pharm.*, **300**, 73 (1967).