

THE STRUCTURE OF A NEW COUMARIN FROM *Haplophyllum pedicellatum*

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We have previously reported the isolation from *Haplophyllum pedicellatum* Juss. of scopoletin, a new coumarin (I), and a substance of noncoumarin nature with mp 243-245.5°C [1]. Later, on chromatography, a coumarin derivative (II) with mp 84-84.5°C was obtained.

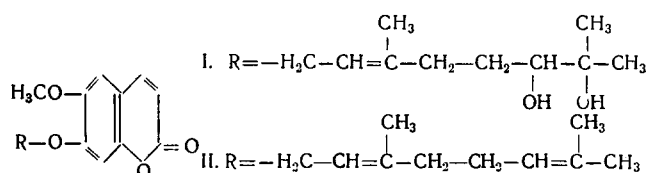
Substance (I), $C_{20}H_{26}O_6$, mp 119.5-120°C, $[\alpha]_D^{19} + 17.6^\circ$ (c 5.7; ethanol) possesses the properties of the coumarins. Its IR spectrum has absorption bands at 3420 cm^{-1} (OH group) and 1710 cm^{-1} (δ -lactone $C=O$). The UV spectrum has absorption maxima at 230, 252 (shoulder), 297, and 345 nm, which is characteristic for 6,7-disubstituted coumarins [3].

Compound (I) contains two hydroxy groups, forms a monoacetate with mp 106-106.5°C, and is very readily hydrolyzed. Scopoletin has been isolated from the products of acid hydrolysis and identified. The formation by the usual method [2] of an acetonide with mp 103-103.5°C proved the presence of two adjacent hydroxy groups in the side chain of substance (I).

From the products of its chemical transformation and its UV, IR, and NMR spectra we have proposed for the new coumarin the structure of 7-(6,7-dihydroxy-3,7-dimethyloct-2-enyloxy)-6-methoxycoumarin (I). This compound may be called 6-methoxymarmin, since it is different from marmin only by the presence of a methoxy group in position 6 of the coumarin ring.

The proposed structure of the side chain of compound (I) is confirmed by the isolation of levulinic acid from the products of its oxidation with chromic acid. The IR spectrum of the levulinic acid isolated coincided with that of an authentic sample. The mass spectrum of (I) shows fragmentation of the same nature as that of the structurally close 7-geranyloxy-6-methoxycoumarin [4]. The peak of the molecular ion is absent, which is explained by the ease with which the allyl aliphatic chain of ethers of 7-hydroxycoumarin are split off.

Thus, the new coumarin is characterized by structure (I):



Substance (II) possesses the typical properties of coumarins, exhibits a blue fluorescence, and is optically inactive. On the basis of a chemical analysis and UV, IR, and NMR spectra, substance (II) was identified as 7-geranyloxy-6-methoxycoumarin [4].

LITERATURE CITED

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