

6-GERANYLOXY-7-METHOXYCOUMARIN — A NEW COMPONENT FROM Haplophyllum
pedicellatum

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UDC 577.15/17.582.89

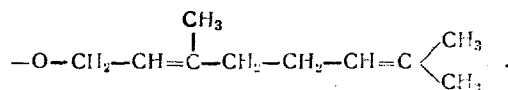
Continuing an investigation of the coumarin composition of Haplophyllum pedicellatum Juss, we have isolated a new crystalline substance (I) with the composition $C_{20}H_{24}O_4$, mp 66.5–68°C possessing the properties of coumarins.

The IR spectrum of (I) showed, in addition to other absorption bands, the bands characteristic for the carbonyl in an α -pyrone ring (1720 cm^{-1}) and for an aromatic nucleus (1615 , 1565 , 1510 cm^{-1}).

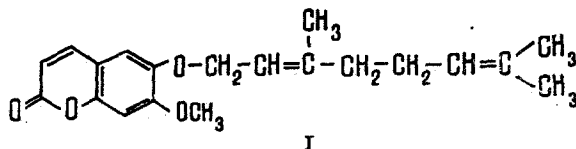
In the PMR spectrum of (I) in the region of aromatic protons there are two doublets with chemical shifts of 6.33 and 7.68 ppm (1 H each), $J = 10\text{ Hz}$, and one singlet at 6.91 ppm (2 H), which are due to the protons in positions 3, 4, 5, and 8 of the coumarin ring. Consequently, the substance studied is a 6,7-disubstituted coumarin, one of the substituents being a methoxy group (singlet at 3.95 ppm, 3 H).

The structure of the second substituent was unambiguously determined from the results of the PMR spectrum in the region of aliphatic protons, which include the signals of the protons of three methyl groups on a double bond (singlets at 1.62, 1.66, and 1.80 ppm, 3 H each), of methylene groups (unresolved signal at 2.11 ppm, 4 H, appearing in the form of a singlet), two olefinic protons (triplets at 5.11 and 5.55 ppm, $J = 7\text{ Hz}$, 1 H each), and a $\text{Ar}-\text{CH}_2-\text{C}=\text{C}$ grouping (doublet at 4.72 ppm, $J = 7\text{ Hz}$, 2 H). Hence, the side chain has the

following structure:



The positions of the substituents in the molecule of (I) were determined on the basis of physicochemical constants, and also by comparing the PMR spectra of (I) with those of analogs of it known in the literature and, in particular, 7-geranyloxy-6-methoxycoumarin (mp 84–84.5°C) [1] (5-geranyl-7-methoxycoumarin with mp 86–87°C [2] and 7-geranyl-8-methoxycoumarin with mp 67–68°C [3] were excluded from consideration by the characteristics of the PMR spectrum of (I)). The facts given permit the suggestion of the most probable structure for the compound under investigation as 6-geranyl-7-methoxycoumarin (I)



The IR spectra were taken on a UR-20 spectrometer (in paraffin oil) and the PMR spectra on a HX-90 spectrometer (in CDCl_3 , 0 – TMS). Melting points were determined on a Kofler block.

LITERATURE CITED

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2. W. L. Stanley and S. H. Vannier, *J. Am. Chem. Soc.*, **79**, 3488 (1957).
3. F. Anet, F. Blanks, and G. Hughes, *Austr. J. Sci. Res.*, **2A**, 127 (1949).

Leningrad Sanitary-Hygienic Medical Institute. Institute of Chemistry, Academy of Sciences of the Turkmen SSR, Ashkabad. Translated from *Khimiya Prirodnykh Soedinenii*, No. 6, p. 846, November-December, 1979. Original article submitted June 11, 1979.