BRIEF COMMUNICATIONS

HAPTUSINOL — A NEW COUMARIN FROM Haplophyllum obtusifolium

A. Z. Abyshev and N. F. Gashimov

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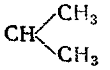
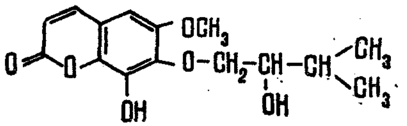
Continuing an investigation of the coumarin derivatives from Haplophyllum obtusifolium Lbd., we have isolated a new substance (I) with the composition $C_{15}H_{18}O_6$, mp 119-120°C, which we have called haptusinol. Compound (I) is optically inactive, shows the bright blue fluorescence that is characteristic for coumarins, and gives a positive reaction with ferric chloride. Conseuqently (I) belongs to the group of phenolic coumarins.

The IR spectrum of (I) contains, together with other bands, the characteristic absorption bands of hydroxy groups (3370 cm^{-1}), of a C=O group in an α-pyrone ring (1705 cm^{-1}), and of an aromatic nucleus (1615, 1580, 1505 cm^{-1}).

In the PMR spectrum of (I), in the weak field appear the signals of the H-3 and H-4 protons (doublets, 6.29 and 7.55 ppm, J = * Hz, 1 H each) and of H-5 or H-8 (singlets, 6.85 ppm, 1 H). In the strong field of the spectrum there are the signals of the protons of an Ar—O—CH_2—CH— grouping (multiplets, 4.21 and 3.77 ppm, 3 H), of a methoxy group (singlet, 3.89 ppm, 3 H), of an alcoholic hydroxy group (broadened singlet, 2.84 ppm, 1 H) and of a  $CH\langle^{CH_3}_{CH_3}$ grouping (1.24 and 1.30 ppm, 3 H each) in which the signals of the protons of the methyl groups are separated into two components with the constant J = 6.5 Hz because of coupling with the methine proton (multiplet, 1.58 ppm, 1 H).

The signal of the phenolic hydroxy group appears at 8.0 ppm (1 H). The positions of the substituents in the molecule of (I) were determined in the basis of the results of its treatment with hydrogen bromide, as a result of which fraxetin (II), $C_{10}H_8O_5$, mp 229-231°C [1] was formed. Consequently, the methoxy group occupies position 6 and the signal at 6.85 ppm in the PMR spectrum of (I) must be assigned to H-5. In view of the fact that an OH group in position 7 has a more acidic nature and its signal in a PMR spectrum is generally found in the weaker field at 12-14 ppm [2, 3] (which is not the case in the spectrum of (I)), it may be assumed that the side chain in (I) is in position 7. Consequently, the following structure is suggested for (I):



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

1. S. Carboni, V. Malaguzzi, and A. Marsili, Tetrahedron Lett., 2783 (1964).
2. L. Crombie, D. E. Games, H. J. Haskins et al., J. Chem. Soc., Perkin Trans., No. 1, 2241 (1972).
3. B. S. Joshi and V. N. Kamat, Tetrahedron Lett., 5767 (1966).

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