

Obtusifol has previously [1] been isolated from the epigeal part of *Haplophyllum obtusifolium* Ledeb. (Rutaceae), and on the basis of chemical and spectral characteristics structure (I) was suggested for it. Later [2], in a study of the coumarin composition of *Haplophyllum schelkovnikovii*, in addition to other coumarin derivatives, we isolated a substance (II) with the composition $C_{15}H_{14}O_6$, mp 151-152°C, M^+ 292 corresponding in its physicochemical constants to obtusifol (I), but the chemical and spectral characteristics that we found did not agree with the structure (I) put forward previously. This follows primarily from an analysis of

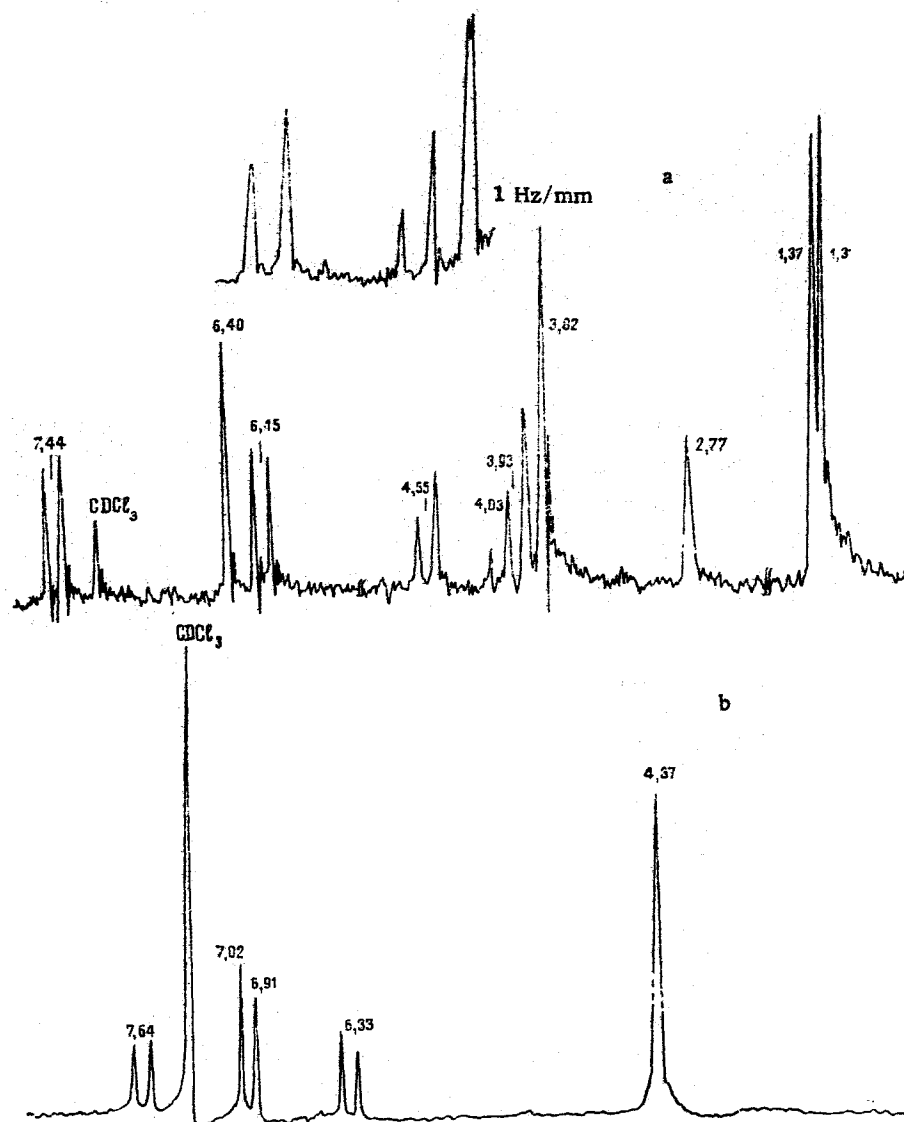


Fig. 1. PMR spectra of obtusifol (a) and of 1',4'-dioxano-[5',6':6,7]coumarin (b).

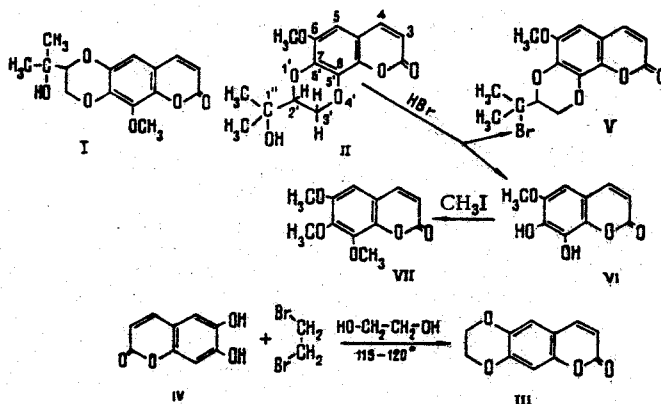
the PMR spectra of (II) and of 1',4'-dioxano[5',6':6,7]coumarin (III), $C_{11}H_8O_4$, mp 219–220°C, M^+ 204 which we synthesized from esculetin (IV) and from the results of the treatment of (II) with hydrobromic acid.

In the PMR spectrum of (II) (Fig. 1a), in the weak-field region, together with other signals, one singlet is observed at 6.40 ppm (1 H) which was previously assigned [1] to the H_5 proton, although the cause of such a strong diamagnetic shift of the signal was not explained. The same signal in the PMR spectrum of (III) (Fig. 1b), which has a linear structure, appears at 7.02 ppm (1 H). On the basis of these facts it may be concluded that (II) obviously has an angular structure and in it the 1',4'-dioxane nucleus occupies the 7,8 position (the presence of this ring in the 5,6 position is not considered, since in this case the signal from H_4 should be observed in a weaker field at 8.0–8.30 ppm [3, 4], which is not the case in the spectrum of (II)), and the methoxy group is present in position 5 or 6. We have seen that when the signal of the $-OCH_3$ protons is suppressed, the integral intensity of the H_4 signal does not change, i.e., there is no intramolecular nuclear Overhauser effect between these protons [5], which is usually observed when the methoxy group is present in position 5 [6]. Consequently, the $-OCH_3$ occupies position 6 and the detection of the signals H_5 in the spectrum of (II) in a weaker field than usual is due to the diamagnetic effect of the methoxy group in the ortho position.

The facts given above are in complete harmony with the results of the treatment of (II) with concentrated hydrobromic acid. This formed two substances: (V) with the composition $C_{15}H_{15}O_5Br$, mp 171–173°C, M^+ 354, and (VI) with the composition $C_{10}H_8O_5$, mp 229–230°C, M^+ 208.

The IR spectrum of (V) lacked the absorption band of a hydroxy group, and its PMR spectrum was analogous to that of (II) with the exception of the signals of the protons of the methyl groups, which were observed in the form of singlets at 1.82 and 1.93 ppm (3 H each). These facts correspond to the structure of obtusifol bromide (V). Consequently, the observation of the signals of the methyl group protons in a weaker field than in the initial compound (II) is due to the inductive effect of the bromine, i.e., the latter and the methyl group are on the same quaternary carbon atom in the 1'' position.

In its physicochemical constants and the features of its IR and PMR spectra, substance (VI) corresponds to the known coumarin fraxetin (7,8-dihydroxy-6-methoxycoumarin) [7], which, on methylation with methyl iodide, formed 6,7,8-trimethoxycoumarin [7] with the composition $C_{12}H_{12}O_5$, mp 104–105°C, M^+ 236 [8]. Thus, the position of the 1',4'-dioxane ring and that of the methoxy group in the obtusifol molecule have been determined unambiguously and the angular structure (II) is correct for it.



The IR spectra were recorded on a UR-20 spectrometer (in paraffin oil), the PMR spectra on a Brüker HX-90 spectrometer [(II), (III), (V), and (VII) in $CDCl_3$ and (VI) in CD_3OD , 0 – TMS], and the mass spectra on a Hewlett-Packard 5890 A chromatomass spectrometer. The melting points were determined on a Kofler block.

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OBTUSIN — A NEW COUMARIN FROM *Haplophyllum obtusifolium*

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In a study of the coumarin composition of *Haplophyllum obtusifolium*, one of us has previously [1] isolated a new coumarin — obtusifol (I). Continuing the investigation of this plant, we have isolated a substance (II) with the composition $C_{15}H_{14}O_5$, mp 109–110°C, $[\alpha]_D^{20} +48.6^\circ$ (c 1.48; ethanol), M^+ 274. Compound (II) possesses the properties characteristic for coumarins and does not correspond to any of the known derivatives of 5,6-benzo- α -pyrone. We have called it obtusin.

The IR spectrum of (II) has absorption bands at 1725 cm^{-1} (C=O of an α -pyrone), and 1620, 1580, and 1510 cm^{-1} (—CH=CH bonds in an aromatic nucleus), which are characteristic for 6,7,8-trisubstituted coumarins, as is confirmed by the PMR spectrum of (II) (Fig. 1), in which the region of aromatic protons contains only the signals of the H₃, H₄, and H₅ protons (doublets at 6.25 and 7.65 ppm, J = 10 Hz, and singlet at 6.50 ppm; 1 H each). In the region of aliphatic protons are observed the signals of the protons of a methylene group on a double bond (singlets at 5.10 and 5.22 ppm, 1 H each) of a methyl group on a double bond (singlet at 1.86 ppm, 3H), of a methoxy group (singlet at 3.87 ppm, 3H), and of the fragment O—CH—CH₂—O (multiplet at 3.95–4.75 ppm, 3 H). The facts given show that (II), just like (I),

is a 6,7,8-trisubstituted coumarin and has the angular structure (II) as was shown by its formation from (I) on dehydration with 20% sulfuric acid. The IR, PMR, and mass spectra of the synthetic sample of (II) coincided completely with the corresponding characteristics of natural obtusin,

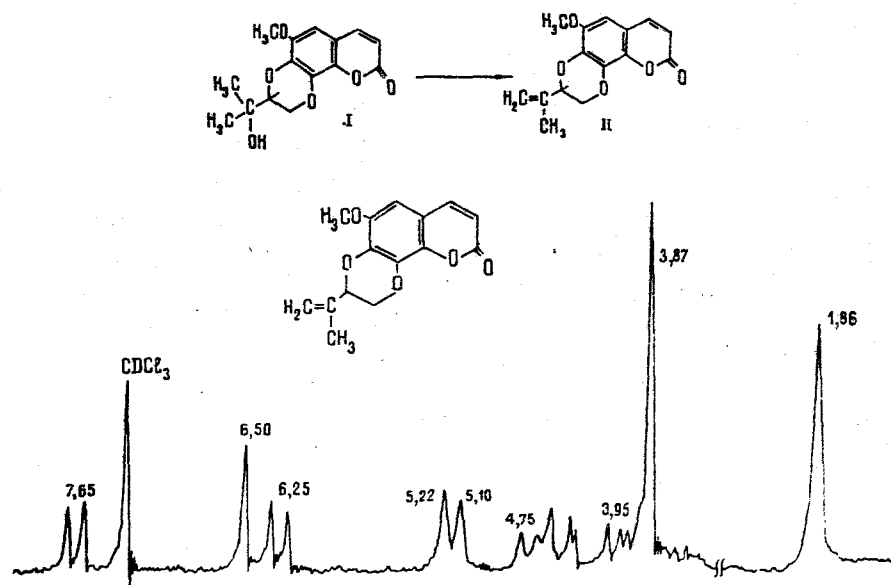


Fig. 1. PMR spectrum of obtusin in $CDCl_3$, 0 — TMS.

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