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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° (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 H_3, H_4, and H_5 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–CH_2–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,

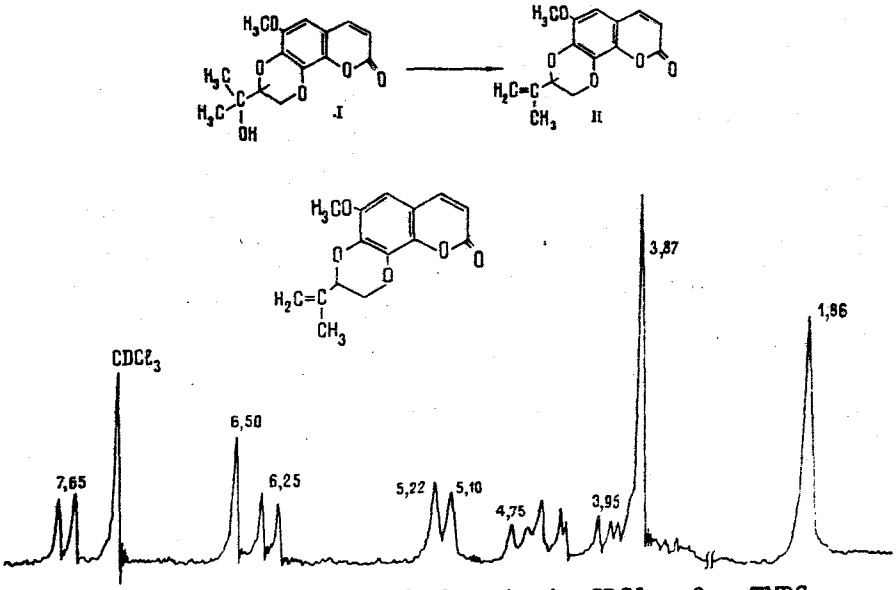

Fig. 1. PMR spectrum of obtusin in $CDCl_3$, 0 — TMDS.

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The IR spectra were taken on a UR-10 spectrometer (in paraffin oil) the PMR spectra on a Brüker HX-90 spectrometer, and the mass spectra on a Hewlett-Packard-5980 A chromato-mass spectrometer. The melting points were determined on a Kofler block.

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NEW FLAVONOL GLYCOSIDES OF *Rhodiola algida*

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In a course of the study of the components of *Rhodiola algida* (Ledeb.) (Fisch. et Mey.), family Crassulaceae, collected in the Gorno-Altai Autonomous Oblast at the end of flowering, we have found flavonoids not previously described. For their isolation, the comminuted air-dry rhizomes were extracted three times with 95% ethanol, and the combined extracts were concentrated in vacuum, diluted with hot water, and extracted with chloroform, ether, ethyl acetate, and butanol.

The ethereal extract yielded lemon-yellow acicular crystals (I). After their removal, the residue was separated by chromatography on columns of polyamide. On elution with chloroform containing 5 and 7% of ethanol (by volume) and after fractional crystallization, three new flavonoid compounds were isolated (II)-(IV). From its physicochemical properties, compound (I) was similar to acetylrhodalgin. The PMR spectrum of the TMS ether of the acylglycoside, obtained by I. P. Kovalev (Kharkov Scientific-Research Institute of Pharmaceutical Chemistry), proved to be identical with the latter [1].

Substance (II), $C_{25}H_{24}O_{14}$, mp 182-183°C, $[\alpha]_D^{20}$ −68° (c 0.15; CH_3OH), $\lambda_{max}^{CH_3OH}$ 274, 329, 379 nm, R_f 0.27 and 0.66 (PC on FN-4; here and below in the 15 and 60% CH_3COOH systems).

Substance (III), $C_{25}H_{24}O_{14}$, mp 196-197°C, $[\alpha]_D^{20}$ −120° (c 0.1; CH_3OH), $\lambda_{max}^{CH_3OH}$ 275, 328, 385 nm, R_f 0.19 and 0.61.

The hydrolysis of these compounds with 2% HCl (100°C, 1 h) gave herbacetin with mp 295-297°C, D-glucose, and acetic acid. The latter was identified by paper chromatography in the presence of a marker, and also by the production of acethydroxamate. UV spectra with diagnostic reagents [2] showed the presence of free hydroxy groups in positions 3, 5, and 7; $\Delta\lambda^{+MeONa}$ 84 and 77 nm, respectively, but after 10 min the long-wave maximum disappeared, which shows the presence of a 4'-hydroxy group. A negative reaction with p-benzoquinone under the conditions of the gossypetone test, in contrast to the behavior of the aglycone, gave grounds for concluding that the carbohydrate components were attached to the C_8 atom of herbacetin. On chromatograms of the substances, a bright yellow fluorescence appeared in UV light, which showed the presence of a free hydroxy group at C_3 in each of them.

The IR spectra were very close: 3470-3280 cm^{-1} (OH), 1745 cm^{-1} (ester C=O), 1007 m^{-1} (O–C–O of a glycosidic bond), and 888 cm^{-1} (β linkage). The only difference appeared in the 1010-1110 cm^{-1} region: in the case of substance (II) three absorption bands were observed (1045, 1080, and 1090 cm^{-1} – the pyranose ring of glucose) and in the case of substance (III) only two absorption bands (1053 and 1080 cm^{-1}), which is characteristic for furanosides. The difference in the sizes of the oxide rings of the carbohydrate components of the flavonol glycosides was confirmed by the polarimetric method [3]. The results of the hydroxamic reaction with the glucosides and their aglycones and the comparison of the IR spectra confirms that the two acetoxy groups were present in the carbohydrate moiety.

Consequently, substances (II) and (III) are new compounds, not previously described in the literature, with the structures of 3,4',5,7,8-pentahydroxyflavone 8-O-(di-O-acetyl-β-D-glucopyranoside), which we have called rhodalgisin and 3,4',5,7,8-pentahydroxyflavone 8-O-(di-O-acetyl-β-D-glucofuranoside), for which we propose the name rhodalgiside.

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