THE STRUCTURE OF HAPLOPEROSIDE B — AN ACYLATED COUMARIN GLYCOSIDE FROM *Haplophyllum perforatum*

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By chemical and spectral methods using INDOR the structure of an acylated coumarin glycoside, haploperoside B, isolated from *Haplophyllum perforatum* has been established as 7-[2-O-[4-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranosyloxy]-6-methoxycoumarin.

We have previously [1] reported the isolation from *Haplophyllum perforatum* (MB.) Kar. et Kir. of a new coumarin glycoside — haploperoside B (I). The acid hydrolysis of (I). The acid hydrolysis of (I) formed the aglycone scopoletin and the monosaccharides glucose and rhamnose. According to its IR spectrum (1725 cm^{-1}) and its PMR spectrum (δ 1.93 ppm, 3H, s), compound (I) contained one acetyl group. The alkaline hydrolysis of (I) with a 0.5% solution of NaOH at room temperature led to the formation of acetic acid and haploperoside A (scopoletin 7-O-neohesperiodoside (II)) [2]. The acetylation of (I) with acetic anhydride in the presence of pyridine gave a hexaacetate identical with the acetate of (II).

Thus, haploperoside B is a natural monoacetyl derivative of scopoletin 7-O-neohesperidoside.

The position of attachment of the acetyl group was established on the basis of an analysis of PMR spectra. In the spectrum of (I) taken in Py-d_5, the signal of the hemiacyl proton is masked by the signals of the protons of hydroxy groups (Fig. 1). Consequently, we obtained the TMS ether of (I) and recorded its PMR spectrum in CCl_4 and C_6D_6. In the spectrum taken in deuterobenzene, the signal of the proton geminal to the acetoxy group appears in the form of a triplet with δ 5.37 ppm ($J_1 = J_2 = 9.5$ Hz). Consequently, both neighboring protons are axial. However, the two coupling constants of 9.5 Hz do not permit an unambiguous assignment of this signals to the protons of rhamnose or glucose. To prove the position of attachment of the acetyl group it was necessary to investigate the structure of the signals of the protons vicinal to the hemiacyl proton, for which purpose we made use of the INDOR method. In the INDOR spectrum obtained on the first and third lines of the triplet, the signal of one of these protons appeared in the form of a quartet with constants of 9.5 and 6.8 Hz. The structure of the signal of the second vicinal proton could not be determined apparently because it contains a series of lines of low intensity some of which are lost in the noise.

In glucose, all the protons are axial, and therefore large values (8.6-11.5 Hz) of the coupling constants correspond to them [3-6]. The 6.8 Hz value of one of the constants of the quartet indicates the presence in the vicinal position to this proton of an equatorial proton, which can be only the proton in the C_2 position of rhamnose. Thus, the only possible position of the acetoxy group is the C_4 position of the rhamnose residue, and haploperoside B has structure (I) (see scheme on following page).

The values of the chemical shifts and spin—spin coupling constants of the anomeric protons of the glucose (5.02 ppm, d, 7.5 Hz) and of the rhamnose (4.39 ppm, broadened singlet) residues agree well with the suggested structure [7, 8]. The difference in the values of the chemical shifts of the methoxy group ($\delta_{CCl_4} - \delta_{C_6D_6} = +0.51$ ppm) confirms its position at C_6 [9].

Thus, haploperoside B has the structure of 7-[2-O-(4-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranosyloxy]-6-methoxycoumarin.

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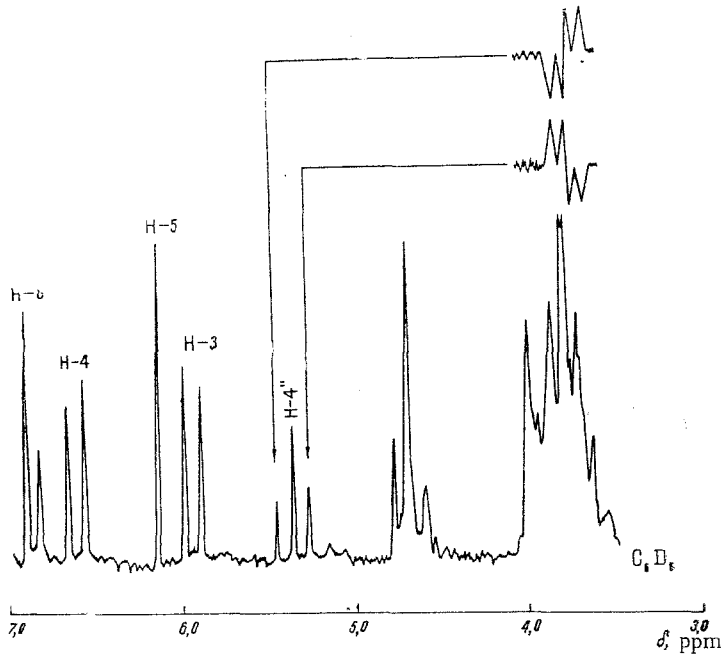
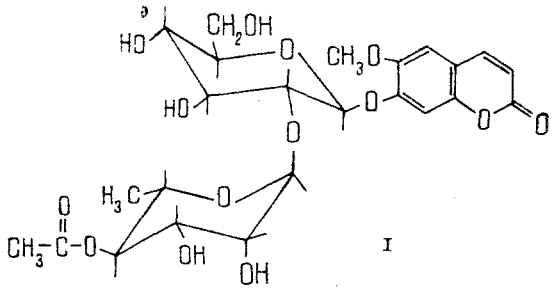


Fig. 1. INDOR spectrum of haploperoside B in C_6D_6.



I

EXPERIMENTAL

The PMR spectrum were taken on JNM-4H-100 (0 — HMDS) and Varian-HA-100 (δ scale, 0 — TMS) instruments. The conditions for recording the other spectra have been given previously [2].

Isolation. After extraction with butanol [2], the aqueous-ethanolic solution continued to show qualitative reactions for coumarins and flavonoids. In order to separate the flavonoids, the solution was passed through a column filled with polyamide sorbent. After evaporation of the eluates in vacuum, 98.0 g of combined water-soluble substances was obtained, 68 g of which was subjected to chromatographic separation in a column of type KSK silica gel (1:25, 6 × 110 cm). Elution was performed with ethyl acetate–ethanol with a gradually increasing concentration of the latter. At a 95:5 composition of the mixture, 0.47 g of (I) issued from the column, and it was purified by rechromatography on silica gel.

Haploperoside B: $C_{24}H_{30}O_{14}$, mp 89-90°C, $[\alpha]_D^{22} - 45^\circ$ (s 0.2; CH_3OH), $\lambda_{max}^{C_2H_5OH}$ 228, 252 sh., 291 336 (log ε 4.20; 3.67; 3.80; 3.91).

PMR spectrum of the TMS ether in CCl_4 (ppm): 2.07 (s, $-COCH_3$), 3.82 (s, $-OCH_3$), 3.28-4.02 (m, 9H of the sugar moiety), 4.39 (br.s, H-1"), 5.02 (d, 7.5 Hz, H-1'), 5.02 (t, H-4"), 6.57 (d, 9.5 Hz, H-3), 6.79 (s, H-5), 6.96 (s, H-8), 7.45 (d, 9.5 Hz, H-4).

PMR spectrum of the TMS ether in C_6D_6 (ppm): 1.92 (s, $-COCH_3$), 3.31 (s, $-OCH_3$), 3.04-4.16 (m, 9H of the sugar moiety), 4.72 (br.s, H-1"), 4.76 (d, 8 Hz, H-1'), 5.37 (t, 9.5 Hz, H-4"), 5.96 (d, 10 Hz, H-3), 6.16 (s, H-5), 6.65 (d, 10 Hz, H-4), 6.92 (s, H-8).

Acid Hydrolysis of (I). The hydrolysis of 30 mg of (I) was carried out with 5% sulfuric acid as described previously [2]. From the hydrolysis products scopoletin and also D-glucose and L-rhamnose were isolated and identified (PC, GLC).

Acetylation of (I). A mixture of 50 mg of (I), 0.5 ml of pyridine, 2 ml of acetic anhydride was kept at room temperature for 48 h. Then the acetyl derivative was isolated in the usual way. mp 83-84°C (ethanol); yield 42 mg. A mixture with the hexaacetate of (II) gave no depression of the melting point, and their IR spectra were identical.

Alkaline Hydrolysis of (I). A solution of 30 mg of (I) in 4 ml of 0.5% NaOH was left at room temperature for 30 min. Then it was neutralized with 5% hydrochloric acid and was extracted with diethyl ether. The solvent was distilled off and the residue was made alkaline with diethylamine. Diethylammonium acetate was detected by the PC method in the butanol—diethylamine—water (50:0.5:7.5) system. Haploperoside A was isolated from the evaporated aqueous solution after purification on a column of silica gel [2].

SUMMARY

It has been established that haploperoside B isolated from *Haplophyllum perforatum* has the structure of 7-[2-O-(4-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranosyloxyl]-6-methoxycoumarin.

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FLAVANONES OF *Tanacetum sibiricum*

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Six flavanones have been isolated for the first time from Siberian tansy, and two of them have proved to be new compounds.

We have already reported the isolation from Siberian tansy, *Tanacetum sibiricum*, of a flavone and of two flavonols (compounds I-III) [1]. From the same fraction we have now isolated six flavanones (compounds IV-IX), two of which have not been described in the literature.

All the substances isolated formed yellow crystals soluble in acetone and ethanol and gave a pink coloration with sodium tetrahydroborate.

In the IR spectra of the compounds the absorption band of a carbonyl group appears in the 1640-1635 cm^{-1} region, which is somewhat lower than in the corresponding flavones. The main UV absorption maximum of methanolic solutions of the flavanones isolated is at about 290 nm. In the PMR spectra (in CCl_4, $(CD_3)_2CO$, and C_5D_5N), there are the signals of a proton at C_2 and of two protons at C_3, H-2 appearing in the form of a quartet at 5.3-5.6 ppm,

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