LITERATURE CITED

1. L. K. Klyshev, V. A. Bandyukova, and L. S. Alyukina, Plant Flavonoids [in Russian], Alma-Ata (1978).
2. T. J. Mabry, K. R. Markham and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).

FLAVONOIDS OF *Haplophyllum perforatum*.

STRUCTURE OF HAPLOSIDE F

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We have isolated a number of flavonoids from an ethanolic extract of the epigeal part of *Haplophyllum perforatum* (M. B.) Kar. et Kir. In the present communication we give a proof of the structure of the most polar glycoside, haploside F, with the composition of $C_{28}H_{30}O_7$, mp 277-279°C, $[\alpha]_D^{22} - 58.7 \pm 2°$ (c 0.15; dimethylformamide), ν_{max}^{KBr} (cm^{-1}); 3600-3200 (OH group), 1660 (γ-pyrone C=O), 1615, 1568 (aromatic C=C bonds), 1107-1000 (C–O vibrations of a glycoside).

From its UV spectrum (λ_{max}^{MeOH}, nm 261, 279 sh., 344 sh., 391) and its qualitative reactions, haploside F was assigned to the flavonal glycosides [1]. This conclusion was confirmed by the formation on acid hydrolysis of an aglycone which was identified as haplogenin [2], and also the monosaccharides D-glucose and L-rhamnose (GLC and TLC).

Haploside F gave a positive gossypetin test (free OH groups at C-5 and C-8) and, according to UV spectra taken with the addition of diagnostic reagents, it contained hydroxy groups at C-3 and C-4'. The compound was readily acetylated with acetic anhydride in pyridine to form a decaacetate with mp 129-131°C. The mass spectrum of the latter had the peak of an ion with m/z 1018 (M − 42) and strong peaks of the following fragmentary ions: of the aglycone with m/z 332 (54.5%), of the residues of a disaccharide acetate with m/z 561 (45.5%) and of triacetylrhamnose with m/z 273 (100%), 213 (12), and 153 (91). Consequently, haploside F is a bioside in which L-rhamnose is the terminal sugar. The PMR spectrum of the compound contained the signals of the protons of the CH_3 group of a rhamnose residue (1.37 ppm, 3 H, d, 6 Hz), of a methoxy group (3.86 ppm, 3 H, s), of the protons of the sugar moiety (3.58-4.97 ppm), and of the anomeric proton of β-D-glucopyranose (5.40 ppm, 1 H, d, 6.5 Hz).

The signals of the protons of the aglycone appeared in the weak-field region of the spectrum at (ppm) at 6.83 (1 H, s, H-6); 7.10 (1 H, d, 8 Hz, H-5'); 8.10 (1 H, q, 8 and 2 Hz, H-6'); and 8.15 (1 H, d, 2 Hz, H-2').

With the aim of determining the structure of the carbohydrate moiety, haploside F was methylated by Hakomori's method [3]. The hydrolystate of the methylation production was found by TLC and GLC to contain 2,3,4-tri-O-methyl-L-rhamnose and 3,4,6-tri-O-methyl-D-glucose. Thus, the L-rhamnose residue is attached to the D-glucose residue by a 1 → 2 bond, and haploside F has the structure of 3,4',5,8-tetrahydroxy-3'-methoxy-7-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyloxy]flavone. This compound has been obtained previously by the alkaline hydrolysis of haploside D [4]. According to its IR spectrum and a mixed melting point, the acetate of haploside F was identical with the acetate of haploside D.

LITERATURE CITED

1. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer, New York (1970).
2. É. Kh. Batirov and V. M. Malikov, Khim. Prir. Soedin., 330 (1980).
3. S. Hakomori, J. Biochem. (Tokyo), 55, 205 (1964).
4. É. Kh. Batirov, V. M. Malikov, and M. E. Perel'son, Khim, Prir. Soedin., 304 (1981).

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