As can be seen from Table 1, the bulk of the ash in the samples investigated was made up of magnesium and calcium, which are bound in complex form through oxygen atoms with the galacturonic acid present in the material.

It was established by Lowry's method [5] that 6-7% of the weight of the dry polysaccharide preparation consisted of protein impurities. The high content of protein permits the assumption that it was strongly bound to the polysaccharides and was isolated together with them.

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FLAVONOIDS OF *Caragana pygmaea*

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The epigeal part of the shrub *Caragana pygmaea* (L.) D. C. (pigmy peashrub), collected in the flowering period in June, 1982 close to the village of Inya, Gorno-Altai autonomous province, has been studied for the presence of flavonoids.

To obtain the total flavonoids, 0.6 kg of the dried and comminuted raw material was extracted successively with 40, 70, and 96% ethanol. The ethanolic extracts were evaporated in vacuum to an aqueous residue, and this was treated with chloroform to eliminate ballast substances. The flavonoids were extracted from the purified aqueous extract with ethyl acetate, which was evaporated in vacuum. After cooling, the combined flavonoids that had deposited were separated from ethyl acetate residues by centrifugation, dried, and deposited on a column of polyamide sorbent. Then the flavonoids were eluted successively with water and with ethanol in various concentrations.

Five individual substances were isolated: three glycosides (substances (I), (II),and (III)), and two aglycones ((IV) and (V)).

Substance (I) (eluted by 5-10% ethanol) was identified as narcissin (isorhamnetin 3-O-rutinoside), $C_{28}H_{32}O_{16}$, mp 175-178°C (aqueous ethanol), $[\alpha]_D^{20}$ −35.5° (c 0.4; methanol). $\lambda_{max}^{C_2H_5OH}$ 359, 255 nm [1, 2].

Substance (II) (eluted by 30% ethanol) was rutin (quercetin 3-O-rutinoside), $C_{27}H_{30}O_{16}$, mp 185-189°C (aqueous ethanol), $[\alpha]_D^{20}$ − 32.2° (c 0.3; methanol). $\lambda_{max}^{C_2H_5OH}$ 365, 259, nm [1, 2].

Substance (III) (eluted by 40% ethanol) was quercetin 3'-glucoside, $C_{21}H_{21}O_{12}$, mp 177-179°C (aqueous ethanol), $[\alpha]_D^{20}$ − 63.5° (c 0.33; methanol). $\lambda_{max}^{C_2H_5OH}$ 370, 252 nm [1].

Substance (IV) (eluted by 50% ethanol) was 3-methylquercetin, $C_{16}H_{12}O_7$, mp 258-262°C (aqueous ethanol). $\lambda_{max}^{C_2H_5OH}$ 360, 257 nm [1].

Substance (V) (eluted by 70% ethanol) was quercetin, $C_{15}H_{10}O_7$, mp 309-312°C (ethanol), $\lambda_{max}^{C_2H_5OH}$ 373, 255 nm [1, 2].

The structures of all the compounds isolated were confirmed by the results of UV and IR spectroscopy and a study of the products of acid hydrolysis, and also by comparison with authentic samples.

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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 ± 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.

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