The isorhamnetin and quercetin were identified by their physicochemical constants and by a comparison with markers [1]. The presence of the sugars in the glycosides at C_3 and C_7 was established by a spectral investigation in the UV region.

The products of stepwise acid hydrolysis (0.1% hydrochloric acid) were 7-monosides identical with compounds isolated previously: isorhamnetin 7-O-β-D-glucopyranoside, $C_{22}H_{23}O_{12}$, mp 250-252°C, $[\alpha]_D^{20}-40.5°$, and quercetin 7-O-β-D-glucopyranoside, $C_{21}H_{20}O_{12}$, mp 247-248°C $[\alpha]_D^{20}-52°$ [2]. Alkaline hydrolysis [3] (0.5% KOH) yielded isorhamnetin 3-galactoside, $C_{22}H_{23}O_{12}$, mp 198-200°C, $[\alpha]_D^{20}-120°$ (c 0.1; methanol) and quercetin 3-galactoside, $C_{21}H_{20}O_{12}$, mp 237-239°C, $[\alpha]_D^{20}-128°$ (c 0.12; methanol), respectively. The results of a calculation of molecular rotations according to Klyne [4] showed the β-linkage and the furanose form of the galactose, and this was confirmed by the results of differential spectroscopy in the UV region (890, 1030, 1070 cm^{-1}) and the rapid acid hydrolysis [5]. The NMR spectrum of the TMS ether in CCl_4 showed that the carbohydrates are attached by β-linkages at the C_3 and C_7 of the aglycone: d, 5.80 ppm (1H, J = 7 Hz), d 4.80 ppm (1H, J = 7 Hz) [6] (Fig. 1). On the basis of the results obtained, the flavonoids isolated can be characterized as 3,4',5,7-tetrahydroxy-3'methoxyflavone 3-O-β-D-galactofuranoside-7-O-β-D-glucopyranoside (I) and 3,3'4',5,6-pentahydroxyflavone 3-O-β-D-galacofuranoside-7-O-β-D-glucopyranoside.

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FLAVONOIDS OF THE NEEDLES OF *Picea ajanensis*

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From a fraction of the methanolis extract of the needles of Picea ajanenis (Yeddo spruce) [1] by preparative chromatography on polyamide sorbent (with chloroform–methanol as the eluent) we have isolated the total flavonoid components. GLC analysis of the TMS ethers in comparison with the authentic samples showed the presence of naringenin (RT 7.12 min, taken as 1.0), aromadendrin (RRT 1.15), kaempferol (RRT 1.86), spigenin (RRT 1.91), and quercetin (RRT 2.56). For identification by the GLC method, we used additions of authentic samples.

The analysis was performed on a Tsvet-4 chromatograph with a flame-ionization detector. The column, 300 × 0.3 cm, was filled with 5% of SE-30 on Chromaton N-AW-HMDS, carrier gas helium, column temperature 284°C, evaporator temperature 350°C.

The naringenin and apigenin, which were present in the fraction in sufficient amount, were obtained by column chromatography on silica gel (with chloroform–methanol as the eluent). Naringenin – mp 249-251°C (CH_3OH), λ_{max} 288 nm (log ε 4.20), mol. wt. 272 (mass spectrometrically).

Apigenin – mp 346-348°C (CH_3OH), λ_{max} 268, 336 nm (log ε 4.39, 4.42), mol. wt. 270 (mass spectrometrically).

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The PMR spectrum of the TMS ether of naringenin showed doublets at δ 7.19 ppm (1H) and 6.7 ppm (2H), and the spectrum of the TMS ether of apigenin had doublets at δ 7.83 ppm (2H) and 6.83 ppm (2H) with J = 8 Hz, belonging to the 2.6', and 3',5', protons, respectively.

Protons 6 and 8 of ring B in the spectrum of naringenin are shown by doublets at about δ 5.92 ppm (1H) and 6.14 ppm (1H) with J = 2 Hz, and in the spectrum of apigenin the signals of these protons are observed at δ 6.08 ppm (1H) and 6.48 ppm (1H) with J = 2 Hz. The spectrum of apigenin has the signal of the H-3 proton in the form of a singlet at δ 6.23 ppm. In the spectrum of naringenin, the H-3 protons of the hydrogenated C_{2-3} bond are represented by a multiplet signal at δ 2.7 ppm (2H) in the strong field as typical aliphatic protons; the H-2 protons appear in the form of a doublet of doublets with its center at δ 5.21 ppm (1H), J = 8 Hz and J = 14 Hz, which shows the coupling of the H-2 proton with the H-3 protons in the trans and cis positions with respect to the H-2 proton [2]. The PMR spectra were taken on a Varian 100 instrument with CCl_4 as the solvent and HMDS as internal standard, and the chemical shifts are given in the δ scale.

The flavonoid compounds of the needles of the genus Picea have not been studied hitherto. All that was known is the presence of kaempferol in the needles of Picea maximoviczii Regel. [3].

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FLAVONOIDS OF SOME SPECIES OF Cephalaria

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We have studied the flavonoid composition of the flowers of two species of Cephalaria – Cephalaria kotschyi Boiss. et Hoh. and C. nachiczevanica Bobr. family Dipsacaceae – collected in the environs of Bata-Bat, Nakhichevan ASSR.

The comminuted and previously defatted raw material was extracted with methanol. The combined extracts were evaporated in vacuum. The resulting viscous product was dissolved in water and the solution was filtered. Then it was purified with chloroform, and the polyphenolic compounds were extracted with ethyl acetate. After the elimination of the solvent and drying, residues of 7.2 and 3.6%, respectively (calculated on the air-dry weight of the raw material) were obtained.

Paper chromatography in systems 1) 30% CH_3COOH and 2) butan-1-ol–CH_3COOH–water (4 : 1 : 5) followed by inspection in UV light showed that the composition of the two species of Cephalaria were identical, and each included eight substances. On the basis of color reactions on the paper, six of them were assigned to the flavonoids and the others to the phenolic acids [1]. Then the flavonoids of Cephalaria kotschyi were investigated. By column chromatography on polyamide sorbents [2] with elution by chloroform–methanol at increasing concentrations of the latter we obtained three compounds in the individual state. On the basis of qualitative reactions, IR and UV spectra with ionizing and complex-forming reagents [3], physicochemical properties, the results of comparative chromatographic analyses, and mixed melting points with authentic samples, the substances were identified as hyperoside, cynaroside [4], and quercimeritrin, respectively.

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