7-methoxycoumarin), $C_{10}H_8O_4$, mp 184-187°C [6]; esculetin (6,7-dihydroxocoumarin), $C_9H_6O_4$, mp 267-270°C [7]; esculin (VII, 6,7-dihydroxycoumarin 6-O-β-D-glucopyranoside), $C_{15}H_{16}O_9$, mp 202-205°C, $[\alpha]_D^{20}$ −143° (c 0.5; CH_3OH) [6, 7]; cichorin (VIII, 6,7-dihydroxycoumarin 7-O-β-D-glucopyranoside), $C_{15}H_{16}O_9$, mp 212-214°C, $[\alpha]_D^{21}$ −103° (c 0.5; dioxane); scopolin (IX, 7-glucopyranosylox-6-methoxycoumarin), $C_{16}H_{18}O_9$, mp 217-219°C, $[\alpha]_D^{21}$ −89° (c 0.6, CH_3OH).

In a comparative chromatographic analysis of alcoholic extracts of the epigeal parts and the roots of *A. armenica* and *A. officinalis* in the solvent systems given above it was established that their coumarin compositions were similar. This is first time that any of the compounds obtained have been isolated from the species investigated.

LITERATURE CITED

1. Plant Resources of the USSR: Flowering Plants, Their Chemical Composition and Use; *Paeoniaceae—Thymelaceae* families [in Russian], Nauka, Leningrad (1985), p. 336.
2. L. A. Gumenyuk, N. F. Komissarenko, V. S. Batyuk, and P. A. Gnedkov, Khim. Prir. Soedin., 396 (1970).
3. N. F. Komissarenko, Khim. Prir. Soedin., 624 (1970).
4. N. F. Komissarenko, Khim. Prir. Soedin., 142 (1969).
5. É. D. Giorgobiani and N. F. Komissarenko, Soobshch. Akad. Nauk SSSR, GSSR, 33, No. 2, 365 (1969).
6. V. I. Dikhtyarev, V. N. Kovalev, and N. F. Komissarenko, Khim. Prir. Soedin., 384 (1969).
7. N. F. Komissarenko and M. A. Baimukhametov, Khim. Prir. Soedin., 722 (1989).

XANTHONES AND FLAVONOIDS OF *Gentiana algida* AND *G. karelinii*

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Some plant species of the genus *Gentiana* L. are used in medical practice for digestive disorders and diseases of the liver and of the gallbladder. They are rich sources of xanthones, flavonoids, iridoids, and alkaloids [1].

We have studied the phenolic compounds of *G. algida* Pall. and *G. karelinii* Griseb. Flavone C-glycosides have previously been isolated from *G. algida* [1], but *G. karelinii* has not been investigated phytochemically.

The air-dry comminuted epigeal part of *G. algida* gathered in the flowering period on the territory of Kyrgystan was extracted with ethanol at room temperature. The concentrated extract was diluted with water and was re-extracted with chloroform, ethyl acetate, and butanol. The fractions so obtained were separated by column chromatography on silica gel in a chloroform—methanol gradient system. The ethyl acetate fraction yielded compound (I), and the butanol fraction compounds (II) and (III). Substance (IV) was isolated from an alcoholic extract of the epigeal part of *G. karelinii*. To identify the compounds isolated we used UV, mass, and (^1H and ^{13}C) NMR spectroscopies, and also some chemical transformations.

Bellidifolin (I) – yellow crystals with the composition $C_{14}H_{10}O_6$ (M^+ 274), mp 273-274°C, λ_{max} 254, 276, 330 nm. The PMR spectrum showed the signals of four aromatic protons (6.06 ppm, d, 2.5 Hz, H-2; 6.34 ppm, d, 2.5 Hz, H-4; 6.68 ppm, d, 8.5 Hz, H-6); 7.34 ppm, d, 8.5 Hz, H-7), and of one CH_3O group (3.50 ppm) and two chelate hydroxy groups (singlets at 11.30 and 12.05 ppm).

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The mass spectrum of compound (I) was characteristic for xanthones containing a methoxy group in the C-3 position and had the peaks of ions with m/z 274 (M^+, 100%), 254, 231, 169, and 119, and others [2]. Consequently, substance (I) contained three hydroxy groups, in the C-1,5,8 positions, and one CH_3O group in the C-3 position of the xanthone nucleus and was 1,5,8-trihydroxy-3-methoxyxanthone [2, 3].

Swertianolin (II) – yellow acicular crystals with the composition $C_{20}H_{20}O_{11}$, mp 216-217°C, λ_{max} 255, 266, 277, 327 nm. Substance (II) was a glycoside, and its PMR spectrum showed the signals of an anomeric proton at 5.30 ppm (d, 6 Hz) and the signals of other protons of the carbohydrate moiety in the 3.90-4.60 ppm region. On acid hydrolysis, glycoside (II) formed bellidifolin and glucose.

A comparison of the PMR spectra of compounds (I) and (II) showed that on passing from bellidifolin to swertianolin the signals of the H-7 proton underwent a paramagnetic shift by 0.52 ppm. This showed that the hydroxy group at C-8 had been glycosylated [3]. Thus, compound (II) was bellidifolin 8-O-β-D-glucopyranoside [2-4].

Swertisin (III) – light yellow crystals with the composition $C_{22}H_{22}O_{10}$, mp 246-247°C, λ_{max} 273, 337 nm. According to its PMR spectrum and its UV spectra with diagnostic additives, substance (III) was a flavone glycoside and contained a methoxy group in the C-7 position and hydroxy groups at C-5 and C-4'.

^{13}C NMR spectrum (DMSO-d_6): 163.3 (C-2), 102.5 (C-3), 181.6 (C-4), 159.8 (C-5), 109.2 (C-6), 164.3 (C-7), 90.5 (C-8), 156.3 (C-9), 104.0 (C-10), 120.5 (C-1'), 128.0 (C-2',6'), 115.5 (C-3',5'), 160.7 (C-4'), 72.2 (C-1"), 70.3 (C-2"), 78.6 (C-3"), 69.6 (C-4"), 81.0 (C-5"), 61.2 (C-6"). The chemical shifts of the carbon atoms of the carbohydrate moiety showed that compound (III) was a flavone C-glycoside. The hydrolysis of glycoside (III) with Kiliani's mixture led to 7-O-methylapigenin (genkwanin) and glucose.

Substance (III) was identified as 4',5-dihydroxy-7-methoxyflavone 6-C-β-D-glucopyranoside [5].

Swerchrysin (IV) – yellow acicular crystals with the composition $C_{15}H_{12}O_6$ (M^+ 288), mp 186-187°C, λ_{max} 255, 280, 338 nm. In its PMR spectrum there were the signals of the resonance of the protons of two chelate phenolic hydroxy groups (11.3 and 11.9 ppm) and of two CH_3O groups (3.80 and 3.86 ppm), and also of four aromatic protons.

According to its PMR and mass spectra, hydroxy groups occupied the C-1 and C-8 positions and methoxy groups the C-3 and C-5 positions, and compound (IV) was 1,8-dihydroxy-3,5-methoxyxanthone. In actual fact, xanthone (IV) was identical with the methylbellidifolin obtained by methylating bellidifolin with an ethereal solution of diazomethane [2, 3, 6].

This is the first time that compounds (I-IV) have been isolated from the given Gentiana species.

LITERATURE CITED

1. Plant Resources of the USSR. Flowering Plants, Their Chemical Composition and Use. The Caprifoliaceae—Plantaginaceae Families [in Russian], Nauka, Leningrad (1990), p. 50.
2. V. I. Glyzin, G. G. Nikolaeva, and T. D. Dargaeva, Natural Xanthones [in Russian], Nauka, Novosibirsk (1986), p. 174.
3. K. S. Khetwal and R. S. Bisht, Phytochemistry, 27, 1910 (1988).
4. I. Sakamoto, T. Tanaka, O. Tanaka, and T. Tomimori, Chem. Pharm. Bull., 30, 4088 (1982).
5. M. Kaldas, K. Hostettmann, and A. Jacot-Guillarmod, Helv. Chim. Acta, 58, 2188 (1975).
6. I. Ishimaru, H. Sudo, M. Satake, et al., Phytochemistry, 29, 1563 (1990).