# XANTHONES AND FLAVONOIDS OF *Gentiana karelinii*

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Continuing an investigation of the phenolic components of plants of the genus *Gentiana* L. [1], we have studied the epigeal part of *Gentiana karelinii* Griseb. The plant was gathered in the flowering period (August, 1989) on the territory of the Kalai–Kumbskii region, Gorno–Badakhshan Autonomous Oblast. The comminuted air-dry raw material (1.3 kg) was extracted five times with methanol at room temperature. The concentrated extract was diluted with water and was extracted successively with chloroform, ethyl acetate, and butanol. The fractions obtained were separated further by chromatography on silica gel. Elution of the chloroform fraction with a benzene–chloroform gradient led to the isolation of compounds (I)-(IV). Chromatography of the ethyl acetate fraction in the chloroform–methanol system gave compounds (V) and (VI).

To identify the substances isolated we used UV, PMR, and mass spectra and also a comparison of physicochemical constants with literature information.

The positions of the free phenolic hydroxy groups in compounds (I)-(VI) were established by UV spectroscopy with diagnostic additives [2].

**Swertsiaperennin (1,8-dihydroxy-3,7-dimethoxyxanthone) (I)** — yellow crystalline substance with the composition $C_{15}H_{12}O_6$ ($M^+$ 288), mp 188-189°C, $\lambda_{max}^{ethanol}$ 240, 265, 310*, 332, 380 nm. The PMR spectrum (Py–$d_5$) showed signals of the protons of two methoxy groups (3.62 and 3.72 ppm, s, each) and also of H-2 (6.33 ppm, d, 2.5 Hz), H-4 (6.37 ppm, d, 2.5 Hz), H-5 (6.72 ppm, d, 8.5 Hz), and H-6 (7.20 ppm, d, 8.5 Hz) [2, 3].

**Gentiacaulein (1,7-dihydroxy-3,8-dimethoxyxanthone) (II)** — substance with mp 192-193°C, composition $C_{15}H_{12}O_6$, $\lambda_{max}^{ethanol}$ 239, 262, 311, 372 nm. Its mass spectrum contained the peaks of ions with m/z 288 ($M^+$), 273 $(M-CH_3)^+$, 270 $(M - H_2O)^+$, 259 $(M - CHO)^+$, 245 $(M - CH_3-CO)^+$ and others PMR spectrum (Py-$d_5$): 3.67 (s, 3-$OCH_3$), 3.99 (s, 8-$OCH_3$), 6.37 (d, 2.5 Hz, H-2), 6.47 (d, 2.5 Hz, H-4), 7.12 (d, 9.0 Hz, H-5), 7.52 (d, 9.0 Hz. H-6), 11.74 (7-OH), 13.77 ppm (br.s, 1-OH) [2, 3].

**Gentiakochianin (1,7,8-trihydroxy-3-methoxyxanthone) (III)** — mp 222-224°C, composition $C_{14}H_{10}O_6$ ($M^+$ 274), $\lambda_{max}^{ethanol}$ 242, 270, 323,* 332, 388 nm. The PMR spectrum (in Py-$d_5$) contained the signals of the protons of Ar–$OCH_3$ (3.60 ppm, s), H-2 (6.31 ppm, d, 2.0 Hz), H-4 (6.35 ppm, d, 2.0 Hz), H-5 (6.75 ppm, d, 9.0 Hz), H-6 (7.37 ppm., d, 9.0 Hz) and of a chelated OH group (12.11 ppm) [2, 3].

**Isobellidifolin (1,3,8-trihydroxy-5-methoxyxanthone) (IV)** — composition $C_{14}H_{10}O_6$ ($M^+$ 274) with mp 259-261°C, $\lambda_{max}^{ethanol}$ 254, 278, 278, 338 nm. PMR spectrum (Py-$d_5$): 3.75 (s, $-OCH_3$), 6.37 (d, 2.5 Hz, H-2), 6.40 (d, 2.5 Hz, H-4), 6.51 (d, 9.0 Hz, H-7), 7.39 ppm (d, 9.0 Hz, H-6). The mass spectrum of this xanthone, unlike that of bellidifolin [1], contained an intense peak of an ion with m/z 259 $(M - CH_3)^+$ due to the presence of a methoxy group in position 5 [2].

**Mangiferin (2-C-β-D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone (V)** — mp 258-260°C (decomp.), composition $C_{19}H_{18}O_{11}$, $\lambda_{max}^{ethanol}$ 241, 258, 317, 369 nm. PMR spectrum (DMSO-$d_6$): 3.83-4.62 (m, H-3′; 6′), 4.97 (t, 9.5 Hz), H-2′), 5.68 (d, 9.5 Hz, H-1′), 6.43 (s, H-4), 6.99 (s, H-5), 7.44 (s, H-8). The SSCC value of the anomeric proton (J = 9.5 Hz) and the resistance of the substance to acid hydrolysis showed that compound (V) was a xanthone C-glycoside [4, 5]. The oxidation of the substance with ferric chloride solution gave glucose.

**Isoorientin (6-C-β-D-glucopyranosyl-3′,4′,5,7-tetrahydroxyflavone) (VI)** — mp 233-235°C, composition $C_{21}H_{20}O_{11}$, $\lambda_{max}^{ethanol}$ 258, 271, 352 nm. The PMR spectrum of (VI) showed the signals of protons at 3.92-4.55 (m, H-3″, 6″), 5.04 (t,

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9.0 Hz, H-2″), 5.72 (d, 9.0 Hz, H-1″), 6.54 (s, H-3), 6.76 (s, H-8), 7.13 (d, 8.5 Hz, H-5′), 7.39 (dd, 8.5 and 2.0 Hz, H-6′), 7.75 (d, 2.0 Hz, H-2′) and 14.24 ppm (s, 5-OH).

According to its UV and PMR spectra, substance (VI) contained phenolic hydroxy groups in positions 3′, 4′, 5, and 7 of the flavone nucleus. The oxidation of glycoside (VI) with ferric chloride solution gave luteolin and glucose.

This is the first time that the above-mentioned compounds have been isolated from *G. karelinii*.

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