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# AN INVESTIGATION OF THE XANTHONES OF *Gentiana algida* AND *G. karelinii*

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Continuing a study of the xanthones of plants of the genus *Gentiana* L. [1, 2], from a chloroform fraction of an alcoholic extract of the epigeal part of *G. algida* Päll. by column chromatography on silica gel in a chloroform–hexane gradient system we have additionally isolated xanthones (I-III).

Xanthones (I), composition $C_{14}H_{10}O_6$ ($M^+$ 274) with mp 258-260°C, and (II), composition $C_{15}H_{12}O_6$ ($M^+$ 288), mp 185-186°C, were identified as isobellidifolin and swerchirin, respectively, by a study of spectral characteristics and by direct comparison with authentic samples.

Xanthone (III), composition $C_{15}H_{12}O_6$ ($M^+$ 304), mp 264-266, $\lambda_{max}^{ethanol}$ 254, 278, 345 nm. The PMR spectrum (Py-$d_5$) of the compound under consideration exhbited the signals of two $-OCH_3$ groups (3.75 and 3.88 ppm, each s), three aromatic protons (6.60 ppm, s, H-2; 6.73 ppm, d, 9 Hz, H-7; 7.18 ppm, d, 9 Hz, H-6) and of a chelate hydroxy group (11.45 and 11.62 ppm, each br.s).

On acetylation with acetic anhydride in pyridine, compound (III) formd a triacetyl derivative with mp 197-198°C. The mass spectrum of substance (III) was characteristic for xanthones containing a methoxy group in the C-4 or C-5 position, and had the peaks of ions with m/z 304 ($M^+$), 289 ($M - CH_3$, 100%), 261 (289 − CO) and others [3].

By a study of spectral characteristics and comparison with the literature, compound (III) was identified as 1,5,8-trihydroxy-3,4-dimethoxyxanthone [3, 4].

The xanthone glycoside (IV), composition $C_{25}H_{28}O_{15}$, mp 246-247°C, $\lambda_{max}^{ethanol}$ 237, 263, 316, 381 nm was isolated from the butanol fraction of the alcoholic extract of the epigeal aprt of *G. karelinii* Griseb by column chromatography on silica gel in the chloroform–methanol (8.1:1.5) system.

The hydrolytic cleavage of glycoside (IV) with 5% hydrochloric acid led to the formation of gentiakochianin (1,7,8-trihydroxy-3-methoxyxanthone) [2] and the monosaccharides D-glucose and D-xylose. The PMR spectrum of xanthone (IV) in Py-$d_5$ contained the signals of protons at (ppm) 3.57 (s, $-OCH_3$), 3.70-4.25 (protons of the carbohydrate moiety, 4.77 (d, 7 Hz, H-1″), 5.26 (d, 6.5 Hz, H-1′), 6.30 (d, 2 Hz, H-2), 6.35 (d, 2 Hz, H-4), 7.02 (d, 9 Hz, H-5), 7.36 (d, 9 Hz, H-6) and 13.13 (br.s, 1-OH).

Acetylation of glycoside (IV) gave an octaacetyl derivative with mp 112-114°C. The mass spectrum of the latter contained, in addition to the weak peak of the molecular ion with m/z 904, intense peaks of fragmentary ions: of the aglycon with m/z 274 and of the residues of a diglycoside acetate with m/z 547 and of triacetylxylose with m/z 259, 199, and 139. Consequently, compound (IV) was a bioside in which D-xylose was the terminal sugar.

The partial acid hydrolysis of glycoside (IV) with 0.5% $H_2SO_4$ solution gave the known compound gentiakochianin 8-O-β-D-glucopyranoside with the composition $C_{20}H_{20}O_{11}$, mp 271-219°C [4, 5].

The physicochemical properties of glycoside (IV) differed from those of the known gentiakochianin 8-O-primeveroside [4]. In order to establish the structure of its carbohydrate moiety, the glycoside under consideration was methylated by Hakomori's method. In a hydrolysate of the methylation product 3,4,6-tri-O-methyl-D-glucopyranose and 2,3,4-tri-O-methyl-D-xylopyranose were identified by GLC and TLC.

Thus, in the glycoside (IV) molecule the terminal D-xylose was attached to the D-glucose by a 1→2 bond, and it had the structure of 1,7-dihydroxy-3-methoxy-8-[β-D-xylopyranosyl-(1→2)-β-D-glucopyranosyloxy]xanthone. This compound is a new glycoside of gentiakochianin.

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