XANTHONES OF *Gentiana lutea*

G. G. Nikolaeva, V. I. Glyzin,
M. S. Mladentseva, V. I. Sheichenko,
and A. V. Patudin

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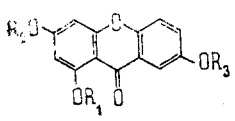
Continuing a study of domestic species of the genus *Gentiana* we have made a chemical investigation of *Gentiana lutea* (yellow gentian) — a perennial herbaceous plant introduced into the botanical garden of VILR (All-Union Scientific-Research Institute of Medicinal Plants) and widely used in officinal and traditional medicine.

The first natural xanthone, gentisin, was isolated from yellow gentian in 1821 [1] and was described as a monomethyl ether of 1,3,7-trihydroxyxanthone. However, as a result of more accurate investigations [2, 3], its structure was established as 1,7-dihydroxy-3-methoxyxanthone, and this was later confirmed by synthesis [4]. In 1955, an isomer of gentisin — isogentisin (1,3-dihydroxy-7-methoxyxanthone) and a glycoside of it — gentioside (1,3-dihydroxy-7-methoxyxanthone 3-O-primveroside) — were isolated.

In a study of a methanolic extract from the roots of yellow gentian collected in the fruit-bearing phase in 1979, we have isolated four compounds belonging to the xanthone group (I-IV), two of which are new (III and IV).

Compound (I) has the composition $C_{14}H_{10}O_5$, M^+ 258, mp 266-270°C, λ_{max}^{MeOH} 237, 259, 307, 374 nm. PMR spectrum (TPC, 0 — TMS, ppm); 7.84 (tr, H-8) and 7.72 (d, H-5 and H-6); 6.90 and 6.78 (d, J = 2.5 Hz, 1 H each, H-2 and H-4); 4.12 (methoxy group in position 3). The presence of the methoxy group in position 3 was confirmed from UV spectra (absence of a bathochromic shift with NaOAc) and PMR spectra (Overhauser effect). When the signal of the methoxy group was irradiated, the intensities of the H-2 and H-4 signals increased by 20% [6, 7]. Thus, compound (I) had the structure of 1,7-dihydroxy-3-methoxyxanthone and was identical with gentisin [5].

Compound (II) had the composition $C_{25}H_{28}O_{14}$, mp 267-270°C and according to its UV, IR, and PMR spectra and the products of acid hydrolysis corresponded to gentioside — 1,3-dihydroxy-7-methoxyxanthone 3-O-primveroside [5].



I. $R_1=R_3=H$; $R_2=CH_3$
II. $R_1=H$; $R_3=CH_3$; $R_2=$ primverose
III. $R_1=H$; $R_2=CH_3$; $R_3=$ primverose
IV. $R_3=H$; $R_2=CH_3$; $R_1=$ primverose

Compound (III) formed yellow crystals, R_f in 15% CH_3COOH, 0.40 (in UV light, brown, and after treatment with 3% ethanolic $AlCl_3$, yellow); $C_{25}H_{28}O_{14}$, mp 214-218°C; λ_{max}^{MeOH} 237, 257, 306, 365 nm; + NaOAc 257, 306, 365 nm; + $AlCl_3$ 223, 257, 273, 315, 330, 424 nm. The PMR spectrum of the acetate of the compound ($CDCl_3$, 0 — TMS, ppm) contained the signals (ppm) 7.82 (tr, H-8) and 7.70 (d, H-5 and H-6), and two one-proton doublets at 6.92 and 6.78 (d, J = 2.5 Hz; H-2 and H-4). A signal at 2.5 ppm (s, 3 H) represented an acetyl group in the α position to a carbonyl. The presence of the signals of six aliphatic acetyl groups in the 1.90-2.06 ppm region showed the presence of two carbohydrate substituents, as was confirmed by acid hydrolysis. Hydrolysis with 2% HCl gave glucose and xylose, which were identified by paper chromatography (butan-1-ol—pyridine—water (6 : 4 : 3); aniline phthalate), and an aglycone with the composition $C_{14}H_{10}O_5$, which was identified by its mass, UV, and PMR spectra, and also by chromatographic comparison with an authentic sample, as gentisin. In compound (III), the primverose residue was attached to the aglycone in position 7, as is shown by the bathochromic shift with $AlCl_3$, the PMR spectrum of the acetyl derivative, and

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the absence of a bathochromic shift with NaOAc in the UV spectrum of the aglycone. Compound (III) had the structure of 1,7-dihydroxy-3-methoxyxanthone 7-O-primveroside.

Compound (IV) formed white crystals with R_f in 15% CH_3COOH 0.32 (blue in UV light; after treatment with $AlCl_3$, yellow), $C_{25}H_{28}O_{14}$, mp 250-253°C, λ_{max}^{MeOH} 240, 252, 306, 362 nm; + NaOAc 240, 253, 306, 362 nm, + NaOAc 240, 252, 306, 362 nm. The PMR spectrum of the acetate of compound (IV) corresponded to the spectrum of the acetate of compound (III), apart from the signal at 2.32 ppm, which was shifted upfield, as is characteristic for an acetyl group in position 3 or 7. The carbohydrate moiety of the glycoside consisted of primverose, and on hydrolysis with 2% HCl glucose, xylose, and an aglycone identified as gentisin were obtained. On the basis of the characteristics of the UV and PMR spectra and the products of acid hydrolysis, it was established that the primverose was present in position 1 of the xanthone and the compound had the structure of 1,7-dihydroxy-3-methoxyxanthone 1-O-primveroside.

In view of the fact that in papers published previously [5, 8], gentioside and its aglycone isogentisin were shown as the predominating component, and in the population of yellow gentian that we have investigated it was mainly glycosides of gentisin that were isolated, we performed the preparative isolation of the aglycone after enzymatic hydrolysis of the glycosides in the plant material with the enzyme preparation Pektofoetidin.

The roots subjected to fermentation yielded mainly gentisin.

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