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FLAVONE C-GLYCOSIDES FROM *Gentiana macrophylla*

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We have investigated the epigeal part of large-leaved gentian, *Gentiana macrophylla* Pall., family Gentianaceae, gathered in the flowering period in August, 1985, in various regions of the Altai.

No less than four flavonoids were detected in alcoholic extracts from the epigeal part of the species under investigation by paper chromatography in 15% acetic acid, butanol-acetic acid-water (4:1:2), and ethyl acetate-formic acid-water (10:2:3) systems.

To isolate the substances detected, the air-dried comminuted herbage of large-leaved gentian was extracted with 80% methanol. The alcohol was distilled off and the aqueous residue was treated successively with chloroform, ethyl acetate, and n-butanol.

In the present communication we give the results of an investigation of the ethyl acetate fraction.

The total flavonoids from the ethyl acetate fraction were deposited on a column of polyamide and were eluted successively with chloroform and mixtures of chloroform and methanol (with gradientwise increasing concentrations of methanol). As a result, two individual substances were isolated which have been designated as compounds (I) and (II).

Both substances were resistant to acid hydrolysis. They were cleaved to an aglycon and a carbohydrate residue by hydriodic acid in liquid phenol and acetic anhydride [1], which showed the C-glycosidic nature of the substances isolated, and they were identified by comparison with authentic samples.

Substance (I), $C_{21}H_{20}O_{10}$, mp 193-194°C (methanol), $[\alpha]_D^{20} +46^\circ$ (methanol), $[\alpha]_{\max}^{CH_3OH}$ 271.333 nm.

Under the action of hydriodic acid, substance (I) was cleaved into apigenin and D-glucose; it was isomerized by 5% HCl into apigenin 8-C- β -D-glucopyranoside (vitexin) [2]. On the basis of the results of UV spectroscopy and also from the products of cleavage and isomerization, compound (I) was identified as saponaretin [3].

Substance (II) had the general formula $C_{21}H_{20}O_{11}$, mp 227-231°C (methanol), $[\alpha]_D^{20} +22^\circ$ (methanol), $\lambda_{\max}^{CH_3OH}$ 257 sh., 272, 350 nm. It was cleaved by hydriodic acid into luteolin and D-glucose. It was isomerized by 5% HCl into luteolin 8-C- β -D-glucopyranoside [2, 3]. Thus, the results obtained permitted the conclusion that substance (III) was homoorientin (isoorientin) - 6-C- β -D-glucopyranosyl-3',4',5,7-tetrahydroxyflavone.

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The flavone C-glycosides saponaretin and homoorientin have been isolated previously from gentians belonging to the sections Coelanthe and Cyclostigma [4, 5]. This is the first time that these flavonoids have been isolated in the herbage of large-leaved gentian.

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2,6,6-TRIMETHYLCYCLOHEPTA-2,4-DIENONE AND 3,6,6-TRIMETHYLCYCLOHEPTA-2,4-DIENONE - COMPONENTS OF THE TURPENTINE FROM *Pinus sylvestris*

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The oxygen-containing part of pine oleoresin turpentine contains more than 32 compounds, among which only 15 have been identified [1]. These are mainly alcohols, esters, and ketones having p- and m-menthane and bicyclo[3.1.1]- and bicyclo[2.2.1]heptane skeletons. In the present paper we give the results of the isolation and the determination of the structures of two previously unknown components present in the oxygen-containing fraction of pine oleoresin turpentine from the Borisov wood-chemical factory in amounts of 1.2-1.4% [component (I)] and 1.5-1.7% [component (II)].

From the saponified fraction, OH-containing components were removed by boiling with H_3BO_3 . The organic part (47% of the total weight of the fraction) was treated with $NaHSO_3$. After the separation of the bisulfite derivative and its decomposition, the carbonyl-containing concentrate (24%) was subjected to fractional distillation (column of 100 theoretical plates, reflux No. 100). Two fractions were obtained, one of which contained 18.4% of component (I) and the second 24.7% of component (II). The individual components (I) and (II) were isolated from the fractions by PGLC [2]. Component (I), with a purity of 99.4% and the composition $C_{10}H_{14}O$ had: n_D^{20} 1.5060, d_4^{20} 0.9700. Its physicochemical properties and UV spectrum corresponded to those of 2,6,6-trimethylcyclohepta-2,4-dienone (eucarvone) [3]. Component (II), with a purity of 99.7% and the composition $C_{10}H_{14}O$, had: n_D^{20} 1.5101, d_4^{20} 0.9680. Its physicochemical properties corresponded to those of 3,6,6-trimethylcyclohepta-2,4-dienone [4]. The structures of the ketones isolated, (I) and (II), were confirmed by their PMR and ^{13}C spectra (WN-360 instrument, in $CDCl_3$, with HMDS as internal standard).

TABLE 1. Chemical Shifts of the Protons at C-n (δ , ppm)

Ketone	C-2	C-3	C-4	C-5	C-7	C-8	C-9 and C-10
I	—	6,44 d	5,75 dd	5,93 d	2,49 s	1,87 s	1,01 s
II	5,97 s	—	6,02 d	5,68 d	2,54 s	1,95 s	1,05 s

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