

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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TABLE 2. Chemical Shifts of the ^{13}C Nuclei (δ , ppm)

Ketone	C-1	C-2	C-3	C-4	C-5	C-7	C-8, 9	C-10
I	200,8 s	169,9 s	150,5 d	134,5 d	123,1 d	51,1 t	21,8 q 26,9 q	33,4 q
II	200 s	150,4 d	169 s	130,2 d	127 d	54,5 t	27,5 q 21,8 q	33,2 q

Tables 1 and 2 give the chemical shifts of the protons and ^{13}C nuclei in the compounds isolated.

Thus, the results that we have obtained show the presence in industrial turpentine from Pinus sylvestris L. of oxygen-containing monoterpenoids with 7-membered rings.

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CHEMICAL COMPOSITION OF ESSENTIAL OILS OF PLANTS OF THE GENUS

Schizonepeta

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The genus Schizonepeta Briq. is represented in the USSR by two species: S. annua (Pall.) Schischk. and S. multifida (L.) Briq., growing in Western and Eastern Siberia and in the Far East [1]. The essential oils of these species, which differ sharply in anti-fungal activity, have served as a basis for a detailed chemical study, and this all the more since their component compositions vary greatly according to the ecological conditions of growth [2-5].

We have investigated the chemical compositions of the essential oils of S. annua and S. multifida growing in the Gorno-Altai. The plant material was gathered in 1986 in the flowering phase: S. annua in the Ongudai region of the rocky wastes at the confluence of the rivers Chui and Katuni, and S. multifida in the Kosh-Agach region in the environs of the village of Kurai on a southern meadow slope at a height of 1800 m.

The essential oils were obtained from the epigeal parts of these species by the steam distillation of the comminuted air-dry raw material. The amounts of essential oils and their physicochemical constants were determined by the methods usually adopted [6, 7]. For analytical GLC we used a Chrom-41 instrument with a flame-ionization detector, the carrier gas being nitrogen at a rate of 2 ml/min, and the stationary phase polymethylsiloxane (PMS). Capillary column 0.2 mm \times 50 m, temperature of the evaporator 160°C and of the column 60°C. The components were identified from their relative retention times and from the increase in the volume of the peaks on the addition of authentic samples.

As a result of the investigation, the following indices were established for the essential oil of S. annua: yield 1.11% on the air-dry raw material, d_{20}^{20} 0.8313; n_D^{20} 1.4975; $[\alpha]_D^{20}$ +0.72°; acid No. 2.8; ester No. 14.9. A considerable amount of phenols was detected: