

(continued)

Component	Stems	Bark	Wood
Terpinen-4-ol	7.0	6.8	8.4
$\beta$ -Caryophyllene	0.4	0.7	0.7
$\alpha$ -Terpineol	0.5	0.3	1.9
$\alpha$ -Terpinyl acetate	20.5	17.3	44.8
Methyleugenol	3.2	3.1	3.8
Eugenol	2.2	1.7	5.0

The essential oils of the bark and wood differed considerably from one another with respect to the amounts of the components.

In the wood, as compared with the bark, the biosynthesis of terpenes is directed toward a sharp increase in the amount of  $\alpha$ -terpinyl acetate, sabinene, eugenol, and  $\alpha$ -terpineol and to a fall in the amount of 1,8-cineole,  $\alpha$ - and  $\beta$ -pinenes, camphene,  $\alpha$ - and  $\beta$ -phellandrenes,  $\gamma$ -terpinene, p-cynene, mycrene, and terpinolene. Linalool,  $\beta$ -caryophyllene, and terpinen-4-ol were present in equal amounts in the essential oil.

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#### MONO- AND SESQUITERPENOIDS OF THE OLEORESIN OF *Picea schrenkiana*

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Continuing a systematic study of the chemical composition of the oleoresins of conifers of the family Pinaceae, we have determined the composition of the volatile components of the oleoresin of *Picea schrenkiana* Fisch. (Schrenk spruce) gathered in July, 1980 in the Aflatun gorge (Western Tien-Shan) at a height of 2000-2500 m above sea level.

The neutral part of the oleoresin of this species contains ~40% of hydrocarbons and ~60% of oxygen-containing compounds. The following composition of the hydrocarbon fraction (%) was found by the method of internal normalization (GLC, OV-17, 50 m, 80°C):  $\alpha$ -pinene, 11.7;  $\beta$ -pinene, 3.1; 3-carene, 46.5; dipentene, 19.9;  $\beta$ -phellandrene, 1.3; terpinolene, 3.1; camphene, sabinene, and p-cynene, 0.2% each; cis- $\alpha$ -bisabolene, 1.3; and diterpenes, 13. The high amount of 3-carene, as also in Semenov's fir [1] growing in the same region, is apparently due to the severe high-mountain conditions, as has also been reported for other mountain species [2].

The neutral oxygen-containing compounds of the oleoresin consisted mainly of diterpenoids, monoterpene compounds making up 2% of this fraction and oxygen-containing sesquiterpenoids not being detected in the oleoresin even in trace amounts. Among the monoterpene compounds the following were identified by GLC (OV-101, 50 m, 80-180°C/3°C per minute) and also by adsorption chromatography and spectral methods (%): linalool, 45; geraniol, 21.2;  $\alpha$ -terpineol, 13.8; geranyl acetate, 9; sabinene hydrate, 4.6; and, in very small amounts (less than 1%), methylchavicol, borneol, terpineol-4, and thymol methyl ether.

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Thus, in the oleoresin of Schrenk's spruce we have identified and determined quantitatively 18 monoterpene compounds making up 35.3% of the weight of the neutral fraction.

Of sesquiterpene compounds we found in this oleoresin only (+)-cis- $\alpha$ -bisabolene, which we have detected previously in the oleoresin of *Pinus pumila* Pall. Rgl. [3]. It must be mentioned that sesquiterpenes of the bisabolane series are not characteristic for spruce oleoresins and have been detected in other species only in trace amounts [3]. At the same time, they are dominant among the sesquiterpenoids of the oleoresin of Semenov's fir [1]. It is possible that the formation of terpenoids of this group in conifers of the family Pinaceae is a feature of this region.

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#### OXYGEN-CONTAINING MONO- AND SESQUITERPENOIDS OF THE OLEORESIN OF *Abies sibirica*

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Gas-chromatographic investigations of the mono- and sesquiterpenoids of the oleoresin of *Abies sibirica* Ledeb. (Siberian fir) [1] and also of the resin acid [2] and of the neutral diterpenoids [3] have been reported previously.

The oleoresins of the Siberian fir collected in Novosibirsk province in 1980 contained 43.4% of neutral compounds, which, by chromatography followed by fractional vacuum distillation, were separated into monoterpenes (22.2%), sesquiterpene hydrocarbons (4.6%), oxygen-containing monoterpenes (5.8%), and sesquiterpene compounds (0.7%). The compositions of the fractions of mono- and sesquiterpene hydrocarbons differed insignificantly from those given previously [1].

In the fraction of oxygen-containing monoterpenoids, the predominating component was borneol, a large proportion of which was separated by crystallization. By adsorption chromatography on silica gel impregnated with 20% silver nitrate we isolated, in addition to borneol  $[\alpha]_D^{20} - 34^\circ$ , thymol methyl ether, bornyl acetate,  $\alpha$ -terpenyl acetate, a mixture of geranyl acetate and citronellyl acetate (3:1, PMR), terpineol-4, citronellol,  $\alpha$ -terpineol geraniol, and sabinene hydrate, which were identified by their spectral characteristics.

We may note that the bulk of the borneol was formed on alkaline saponification of the oleoresin (1% NaOH, 24 h) from bornyl acetate. Thus, GLC analysis (XE-60, 50 m, 80-180°C/3°C per minute) of the fraction of neutral oxygen-containing compounds obtained on the rapid saponification of a small sample of the oleoresin (1% NaOH, 5 min) showed a high amount of bornyl acetate - 93% of the monoterpenoids - while the amount of borneol was only 0.8%. Apart from these compounds, 3.8% of thymol methyl ether, 1.3% of geranyl acetate, acetate, and 0.5% of citronellyl acetate were determined in the fraction. The amount of other monoterpenoids isolated by adsorption chromatography did not exceed 0.1%.

In the same fraction we found the following composition of the sesquiterpenoids (%):  $\alpha$ -bisabolol, 67.0; nerolidol, 14.1; caryophylla-4(12),8(13)-dien-5 $\alpha$ -ol, 9.0;  $\beta$ -eudesmol, 5.8; caryophellene  $\alpha$ -oxide; humulene oxide, and  $\beta$ -cedrol, each ~0.3%). All these components were isolated by adsorption chromatography and were identified from their PMR spectra.  $\alpha$ -Bisabolol ( $[\alpha]_D^{20} + 62^\circ$ ) - the main component of the sesquiterpenoids - was, according to

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