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COMPOSITION OF THE ESSENTIAL OIL OF *Larix sibirica*

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The composition of the essential oil isolated under production conditions from the woody verdure of *Larix sibirica* Ldb. growing in the Krasnoyarsk district has been studied. The bulk of the essential oil is composed of monoterpenes (84.95%). Among the sesquiterpene hydrocarbons α -murolene, β -humulene, and caryophyllene are present in considerable amounts. The sesquiterpene alcohol δ -cadinol has been detected. α -Murolene, γ -murolene, and longifolene have been isolated from the essential oil in the chromatographically pure state by column and preparative thin-layer chromatography.

The essential oil of *Larix sibirica* Ldb has been studied for the first time by the GLC method [1]. The raw material used was Siberian larch litter collected in July in the Tuva ASSR. The main components of the monoterpenes proved to be Δ^3 -carene and α -pinene (42 and 40%, respectively).

The oil from the needles of the Siberian larch growing in Pribaikal' contained 50.4% of Δ^3 -carene [2].

We have studied the essential oil of young shoots (winter) [3] and of the litter (July) [4] of a different species of larch taken in the experimental forest farm of the Voronezh Institute of Wood Technology. A paper by Kolesnikova et al. [4] is the only one which gives the composition of the sesquiterpenes of the needle oil from the Siberian larch.

All the information available in the literature related to the essential oils from the needles or from the litter of *Larix sibirica* isolated under laboratory conditions. For practical use, great interest is undoubtedly presented by the oil from the woody verdure obtained under industrial conditions.

We give the results of an investigation of the essential oil isolated by steam distillation in an industrial apparatus of the western Siberian type from the woody verdure of *Larix sibirica* growing in the Uibatskii lespromkhoz [timber industry farm], Krasnoyarsk district.

The essential oil was separated into groups of substances similar in chemical nature (acids, phenols, monoterpenes, sesquiterpenes, oxygen-containing terpene derivatives), and these were investigated further with the aid of various chromatographic and spectrometric methods.

For the general characterization of the essential oil we determined some generally adopted indices: density 0.8793 g/cm³; refractive index, n_D^{20} 1.4730; acid No. 2.01 mg/g; saponification No. 53.27 mg/g; ester No. 51.26 mg/g.

The low values of the density and of the refractive index of the essential oil of the Siberian larch as compared with other oils indicate that the bulk of it is represented by monoterpene hydrocarbons.

The composition of the essential oil of *Larix sibirica* is given in Table 1.

The monoterpene hydrocarbons made up 84.95% of the essential oil. The predominating component — Δ^3 -carene — amounted to 53.11%. The main components of the sesquiterpene hydrocarbons were α -murolene, β -humulene, and caryophyllene. The amount of bornyl acetate in the

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TABLE 1. Composition of the Essential Oil of *Larix sibirica*

Component	Amount, % on the fraction
Acids	0.41
Phenols	0.27
Monoterpenes	84.95
including	
α -pinene	12.59
camphene	Tr.
β -pinene	8.58
myrcene	0.51
Δ^3 -carene	53.11
limonene	5.00
β -phellandrene	3.03
γ -terpinene	0.36
terpinolene	1.77
Sesquiterpenes	5.86
including	
α -longipinene	
ylangene	0.13
isolongifolene	0.11
sibirene	Tr.
longifolin	0.33
X ₁	Tr.
X ₂	0.13
caryophyllene	1.02
X ₃	0.60
α -murolene	0.83
α -murolene + β -humulene	2.55
bisabolene	Tr.
not identified	0.78
Oxygen-containing terpene derivatives	9.26
including:	
camphor	0.11
isoborneol	1.79
borneol	2.10
α -terpineol	Tr.
bornyl acetate	4.68
δ -cadinol	Tr.
unidentified	0.51

essential oil of the Siberian larch was relatively low (4.68%). Among the oxygen-containing compounds the sesquiterpene alcohol δ -cadinol was detected. The sesquiterpene hydrocarbons α -murolene, γ -murolene, and longifolene were isolated from the essential oil in the chromatographically pure form.

The sesquiterpene hydrocarbons of the essential oil of the Siberian larch, freed from oxygen-containing compounds on alumina, were separated by column chromatography on silica gel impregnated with 12% of silver nitrate. This gave three fractions (Table 2) analytical chromatograms of which on "argentized" plates each had a single spot.

It was established by analytical GLC that fractions 1 and 2 were individual compounds, and these were identified by the method of additives and from their retention times as α -murolene and longifolene, respectively.

The IR spectrum of the α -murolene was identical with the published IR spectrum of this compound that we isolated from the needle oil of the Scotch pine.

The IR spectrum of the compound identified as longifolene had an absorption band corresponding to the stretching vibrations of an exomethylene double bond on a five-membered ring

TABLE 2. Characteristics of the Fractions of Sesquiterpene Hydrocarbons Isolated by Chromatography in a Column ($\text{SiO}_2 + 12\% \text{AgNO}_3$)

Practice (in order of elution from the column)	Eluent	Analytical TLC	
		color of the spot	R_f
1	Hexane	Green	0.72
2	80% of hexane + 20% of diethyl ether	Bordeau	0.51
3	50% of hexane + 50% of diethyl ether	Blue-green	0.35

(1657 cm^{-1}). The presence of an exomethylene double bond was confirmed by the nonplanar deformation vibrations of C-H bonds at 885 cm^{-1} .

Analysis of fraction 3 by analytical GLC showed that it consisted of a mixture of compounds. By preparative thin-layer chromatography on a plate with a fixed layer of silica gel impregnated with silver nitrate in the solvent system hexane-diethyl ether (50:50), γ -muroloene was isolated from this fraction; it was identified by GLC and IR spectroscopy. Its IR spectrum coincided with that given in the literature and with the spectrum of γ -muroloene which we have isolated from pine essential oil.

Of the three hydrocarbons isolated, α -muroloene was eluted first from a column of silica gel impregnated with silver nitrate, since both its double bonds are located in the ring. Longifolene, forming a strong π -complex thanks to the exomethylene double bond is eluted from a column with a more polar solvent (Table 2); γ -muroloene, having in its structure two double bonds one of which is terminal while the other is in a ring, probably possesses an even greater capacity for complex-formation with silver ions (Ag^+) and is eluted from the column after the other compounds considered.

EXPERIMENTAL

The essential oil was isolated in an industrial apparatus of the western Siberian type by steam distillation from the woody verdure (litter more than 35 cm long and not more than 8 mm thick) collected from 30-40 growing trees in the Uibatskii lespromkhoz, Krasnoyarsk district.

The composition of the monoterpenes was determined by gas-liquid chromatography using methods described previously [5].

The high-boiling fraction of the coniferous essential oils was separated into hydrocarbons and oxygen-containing compounds by column chromatography on alkaline alumin (Brockmann activity II). The ratio of the substance to be separated and the sorbent was 1:20. The hydrocarbons were eluted with petroleum ether (fraction having bp $40-70^\circ\text{C}$) and the oxygen-containing substances with ethanol. The separation was monitored from the refractive index of the solvent leaving the column and by thin-layer chromatography on Silufol plates.

The GLC analysis of the sesquiterpenes was performed on an LKhM-72 chromatograph with a flame-ionization detector using a $6000 \times 4 \text{ mm}$ column. The stationary liquid phase was 1,2,3-tris(cyanoethoxy)propane, deposited in an amount of 16% on Chromaton N-AW (grain size 0.20-0.25 mm). Programmed heating from 100 to 150°C at the rate of 0.5 deg/min . Evaporator temperature 250°C . Rate of flow of carrier gas (helium) 70 ml/min . The components were identified by the method of adding the appropriate pure substances and from literature figures in accordance with the retention characteristics. The quantitative amounts of the individual components were determined by the method of internal normalization with respect to the areas of the peaks.

The separation of the fraction of sesquiterpene hydrocarbons by absorption column chromatography was carried out on silica gel impregnated with silver nitrate (12% of silver nitrate on the weight of the sorbent). The ratio of the substance being separated and the sorbent was 1:40. The eluents used were petroleum ether and petroleum ether with increasing concentrations of diethyl ether. The separation was monitored by analytical thin-layer chromatography in the same system of solvents on plates prepared by ourselves with a fixed layer

of silica gel impregnated with silver nitrate (12% on the weight of the sorbent). Concentrated sulfuric acid was used to reveal the spots on the analytical plates.

For preparative thin-layer chromatography we used glass plates with dimensions of 25 × 25 cm with a fixed layer of silica gel. The solvent system was hexane-diethyl ether (1:1). The spots on the plates were revealed in UV light.

The analytical GLC of the sesquiterpene hydrocarbon fractions isolated by column chromatography was carried out on an LKhM-72 chromatograph using a thermal conductivity detector and programmed heating from 85 to 240°C at the rate of 2.5 deg/min. Separation was carried out in a steel column 3 m long and 4 mm in internal diameter filled with Apiezon L, deposited in an amount of 15% on Chromosorb W. The temperature of the evaporator was 285°C and that of the detector 250°C. Helium was fed at the rate of 75 ml/min.

The IR spectra of the sesquiterpenes were recorded on a UR-20 spectrophotometer in carbon tetrachloride in the 700-4000 cm⁻¹ region.

SUMMARY

1. The composition of the essential oil from the woody verdure of the Siberian larch isolated under industrial conditions has been studied.

2. The sesquiterpene hydrocarbons α -murolene, γ -murolene, and longifolene have been isolated in the chromatographically pure form from the essential oil of *Larix sibirica* L.

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