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MONOTERPENES OF THE ESSENTIAL OIL OF *Larix sukaczewii*

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An analytical separation has been performed of the essential oil of the bark of one-year winter shoots of L. sukaczewii *and* L. sibirica. *Out of the 37 terpenes detected, 13 monoterpenes have been identified. The two species have identical sets of monoterpenes with significant differences in their relative amounts.*

The aim of the present work was a study of the monoterpenes of Sukachev's larch *Larix sukaczewii* Dyl. growing in the South Urals in order to determine their applicability in chemotaxonomic investigations of this species.

As a result of GLC analysis we detected 33 terpenes in the bark of one-year shoots of *L. sukaczewii*, of which 13 were monterpenes; in the bark of the closely related specied *L. sibirica* Ldb. we found 37 terpenes including the same 13 monoterpenes. These monoterpenes, in the order of their issuance from a column, were: santene, tricyclene, α-pinene, fenchene, camphene, β-pinene, Δ^3-carene, α-terpinene, limonene (dipentene), β-phellandrene, γ-terpinene, *p*-cymene, and terpinolene. No identification was made of the high-boiling fractions.

Other workers have reported other terpenes, as well, for the species under study [1, 2], which is explained by their use of different phases and conditions of GLC analysis.

The qualitative compositions of the monoterpene fractions of all the samples were identical (Table 1). α- and β-Pinenes, Δ^3-carene, and camphene predominated, making up 90% of the total. A high percentage of Δ^3-carene can be seen — 36-45% and, in individual trees up to 60%, which is a distinguishing characteristic of *L. sukaczewii* [2]. The constancy of the quantitative ratio of the amounts of α-pinene and Δ^3-carene first reported in [2, 3] disappears in our case. According to the literature, for *L. sukaczewii* this ratio, α-pinene/Δ^3-carene, is 1.0:5.0, and for *L. sibirica* var. *sajansis* it is 1.0:2.0 [2, 3]. In our investigation, the α-pinene/Δ^3-carene ratio averaged over four samples of *L. sukaczewii* was 1.0:3.4, while in the Krasnoyarsk sample it was 1.0:1.7. We are unable to suggest a reliable explanation of this difference in ratios for *L. sukaczewii*.

The variation in the relative content of the monoterpenes over the samples averaged 15-40%. With a low fenchene content (0.4-1.0%), the coefficient of variation of this component amounted to 88.4-165.7%.

A calculation of Student's *t* criterion between the samples of *L. sukaczewii* (average over four samples) and *L. sibirica* showed that with respect to the mean relative content of monoterpenes $t_f = 2.81$, with respect to the coefficients of variation $t_f = 14.31$ (at $P_{95\%}$ of the criterion, the tabular value of $t_{st} = 1.96$), i.e. for both indices the differences are significant.

EXPERIMENTAL

The one-year shoots were collected in January-February, 1990, in natural populations of *L. sukaczewii* in the Southern Urals and of *L. sibirica* in Krasnoyarsk territory. A total of four samples of *L. sukaczewii* and one of *L. sibirica* were taken — from 70 model trees 90-100 years old in each.

The procedures for extraction and the determination of the monoterpenes had been tested previously on *Pinus sylvestris* L. [4].

Samples (15 g) of the shoots from each tree were comminuted to 3-5 mm and were covered with 15 ml of *n*-pentane with the addition of 0.01% of the antioxidant Ionol. After two days, the extract was filtered through a layer of silica gel (LS

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TABLE 1. Mean Relative Contents (X, %) of the Monoterpenes of the Bark of One-year Shoots of *Larix sukaczewii* and *L. sibirica*

Samples	Indices	α-Pinene	Fenchene	Camphene	β-Pinene	Δ^3-Carene	α-Terpinene	Limonene	β-Phellandrene	Terpinene	*p*-Cymene	Terpinolene
Central region	X	10.60	0.58	8.95	25.54	45.13	1.07	1.22	2.40	0.44	1.17	3.01
	C_v*	24.43	165.67	33.59	28.59	15.72	33.34	23.90	31.97	32.82	28.94	23.51
High-mountain region	X	13.23	0.42	11.27	19.91	45.31	0.80	1.11	3.16	0.94	0.59	3.25
	C_v	26.53	137.55	32.34	25.53	14.94	39.76	33.16	30.68	69.75	62.78	38.20
cis-Urals region	X	14.22	12.00	8.39	26.09	38.63	1.44	1.81	3.08	1.48	0.95	2.73
	C_v	27.21	88.40	32.85	29.67	23.39	40.59	25.96	31.03	59.90	42.45	33.69
Marginal region	X	11.66	0.79	12.04	29.97	36.57	0.91	1.58	2.56	0.36	1.15	2.30
	C_v	28.32	149.91	26.73	17.98	16.81	31.18	35.25	41.39	30.70	24.77	31.18
Mean of the four samples	X	12.43	0.70	10.16	25.38	42.41	1.06	1.43	2.80	0.81	0.97	2.82
L. sukaczewii	C_v	26.62	135.38	31.38	25.44	17.71	35.27	29.57	33.77	48.29	34.74	31.65
Krasnoyarsk territory	X	20.68	1.74	14.91	17.04	34.28	1.08	1.75	5.10	1.00	0.57	1.78
L. sibirica	C_v	26.20	77.79	27.78	43.56	21.20	29.96	25.75	30.03	64.83	43.99	38.76

*C_v is the coefficient of variation (%); santene and tricyclene were present in trace amounts.

5/40) to free it from pigments. The purified extracted was concentrated by evaporating the *n*-pentane with a current of argon, and it was then cooled with liquid nitrogen and was stored, until analyzed, in sealed ampuls at −4°C.

The monoterpenes were determined on a LKhM-8MD chromatograph with a flame-ionization detector, a 3 × 5000 mm stainless-steel column containing the stationary phase Chromaton N-AW-HMDS with 15% of Carbowax 20 M (grain size 0.200-0.250); programming of the column temperature from 80 to 200°C at a rate of rise of 1.5°C per minute, the temperature of the evaporator being 175°C. Rate of flow of air 300, of hydrogen 50, and of carrier gas (helium) 50 ml/min. Sensitivity threshold 5×10^{-9} mg/s, sample volume 1 μl.

The monoterpenes were identified by the graphical correlation of known and the measured values of the relative retention times and by the method of adding pure substances. The GLC chromatograms for each tree were calculated separately by the area normalization method.

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