MONOTERPENOIDS AND SESQUITERPENOIDS OF THE OLEORESIN OF *Larix sibirica*

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The oleoresin of *Larix sibirica* L. that we have investigated was obtained by tapping the trees in the Tuva ASSR in 1971. After preliminary treatment of the oleoresin (3 kg), fractions of monoterpene hydrocarbons (480 g), monoterpene alcohols (12 g), and sesquiterpene hydrocarbons (13.2 g) were isolated. This resin contains only small amounts of oxygen-containing sesquiterpene compounds, and we have not studied them.

The qualitative and quantitative compositions of the monoterpene hydrocarbons were determined by the GLC method (β,β'-oxydipropionitrile, 55°C). In the oleoresin of *Larix sibirica* L. we found 11 hydrocarbons: α-pinene (5.8%), camphene (0.5%), β-pinene (19.4%), Δ^3-carene (22.3%), α-phellandrene (0.2%), myrcene (12.4%), limonene (10.0%), β-phellandrene (20.4%), γ-terpinene (1.0%), terpinolene (6.9%), and p-cymene (0.9%).

From the monoterpene alcohol fraction we isolated seven individual compounds by column chromatography (SiO_2, SiO_2 + 10% $AgNO_3$). α-Terpineol (∿50%), 4-terpineol, borneol, and the methyl ether of thymol were identified by spectral methods.

The sesquiterpene fraction, which had a complex composition, was separated by various chromatographic methods (column and thin-layer chromatography on Al_2O_3, SiO_2, and SiO_2 + $AgNO_3$). Fractions with less complex compositions were obtained, individual compounds from which were isolated by micropreparative GLC (Reoplex-400, 120°C). To collect individual components, we used V-shaped capillary traps the lower ends of which were cooled to 0°C. The compounds collected were transferred with a small amount of CCl_4 (30 μl) directly into microcells for recording their IR spectra. The samples of hydrocarbons (0.2-0.5 mg) gave readily distinguishable IR spectra; the NMR spectra were taken of samples amounting to 7-10 mg. The sesquiterpene hydrocarbons were identified by their IR and NMR spectra.

From the sesquiterpene hydrocarbon fraction we isolated 30 compounds, and 23 of them have been identified. In the oleoresin of *Larix sibirica* L. in terms of the number of compounds hydrocarbons with a cadalene carbon skeleton predominated: α- and β-copaenes; α- and β-ylangenes; α-, γ-, β-, and ε-cadinenes; α-, γ-, and ε-murolenes; α- and γ-amorphenes; ε-bulgarene; calamenene; and α-calacorene. Of compounds of other types, γ- and δ-elemenes, longifolene, caryophyllene, α-humulene, cyclosativene, and the hydrocarbons described by Vlahov et al. [1] were identified.

Longifolene has been isolated previously [2] from the oleoresins of the internal resin vessels of the Siberian larch (Irkutsk oblast). Later [3], by the GLC method nine sesquiterpene hydrocarbons were identified in the same oleoresin from trees growing in the Krasnoyarsk territory. The main components of this oleoresin were longifoline, caryophyllene, and humulene. The results that we have obtained differ substantially from those given above. The main hydrocarbon of the oleoresin studied is γ-elemene (∿30%). We have isolated a large group of compounds which have not so far been identified, but no longicyclene, isolongifolene, or sibirene have been found in the oleoresin.

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