TERPENOIDS OF THE OLEORESIN OF *Larix leptolepis*

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We have studied the composition of the oleoresin of the Japanese larch, *Larix leptolepis* (Siebold et Zucc.) Gord., collected in July, 1983, in the southern part of the island of Sakhalin.

The oleoresin (460 g) was separated into individual fractions by the usual method [1]. The compositions of the terpene hydrocarbons (62 g), oxygen-containing compounds (153 g), and resin acids (244 g) obtained from it were investigated by a group of chromatographic and spectral methods [1].

The monoterpenes (56 g) were analyzed by the GLC method. Seven compounds were identified from their relative retention times, α-pinene (1.5%), β-pinene (1.7%), 3-carene (85.6%), myrcene (0.5%), β-phellandrene (4.7), limonene (1.0%), and γ-terpinene (1.4%). As in a botanically close species, the Kamchatkan larch, 3-carene predominated in this oleoresin, but a considerably smaller amount of α- and β-pinenes was found.

The composition of the sesquiterpene fraction (2.6 g) was studied with the aid of spectral methods and GLC. In this fraction, 20 hydrocarbons were found, the main components being: longifolene (23.7%), δ-cadinene (20%), α-cadinene (8.2%), and α-calacorene (6.2%). The other compounds – β-farnesene, α- and γ-muurolenes, γ-cadinene, β-bisabolene, γ-elemene, ar-curcumene, β-selinene, sibirene, α-longipinene, longicyclene, α-ylangene, α- and β-copaenenes, α-humulene, and carophyllene – were present in only small amounts (1-5%). Compounds of the cadalene and longifolane types predominated in this fraction (∿50% and ∿25%, respectively), which is characteristic for the oleoresin of Far Eastern species of larch. The main difference of the Japanese larch sesquiterpenes from the Kamchatkan larch sesquiterpenes studied previously [2] was the insignificant amount of germacrene D and γ-elemene and the greater amount of δ-cadinene. No oxygen-containing sesquiterpenes were found in the oleoresin studied.

Particularly appreciable differences between the oleoresins of the Japanese and the Kamchatkan larch were found in the composition of the diterpenoids. While the diterpene hydrocarbons (4.2 g) were likewise represented by abietadiene (24.3%), dehydroabietadiene (35.5%), and isopimaradiene (25.0%), the oleoresin of the Japanese larch also contained diterpene aldehydes (7.6 g): dehydroabietinal (6.6%), abietinal (8.0%), neoabietinal (20.6%), palustral (14.6%), and isopimarinal (13.3%). These compounds were completely absent from the oleoresin of the Kamchatkan larch [2].

The oxygen-containing diterpenoids also contained epimanool (13%; here and below the amounts are given as percentages of the fraction of oxygen-containing compounds), larixyl acetate (29%), larixol (42%) and a group of primary alcohols (8%). The primary alcohols were converted into their acetates. These were analyzed by the GLC method [2]. The following primary alcohols were identified: palustrol (11.6%), isopimarinol (19.4%), dehydroabietinol (18.1%), abietinol (32.1%), and neoabietinol (10.7%). In the oleoresin of the Kamchatkan larch the main component of the oxygen-containing diterpenoids is larixyl acetate (57%).

In the oleoresin of the Japanese larch, unlike that of the Kamchatkan larch, a considerable amount of α-terpenyl acetate (1.2 g) was found.

The resin acids of the oleoresin were investigated in the form of their methyl esters by GLC and adsorption chromatography. Sandaracopimaric (8.5%), palustric (10.0%), isopimaric (34.2%), dehydroabietic (5.6%), abietic (27.4%), neoabietic (8.2%), 15-hydroxydehydroabietic (1.9%), and 15-hydroxyabietic (3.3%) acids were found. Thus, in the oleoresin of the Japanese larch the amount of abietic acid was greater than in the oleoresin of the Kamchatkan

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larch but the main acid for the oleoresins of both species was isopimaric.

The facts given above show that the oleoresin of Japanese larch differs qualitatively from the oleoresin of the Kamchatkan larch, although these species are botanically close. In its diterpenoid composition, the oleoresin of the Japanese larch is close to the oleoresin of the Dahurian larch growing on Kamchatka [3].

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CHEMICAL COMPOSITION OF THE ESSENTIAL OILS OF *Thymus pastoralis* AND *Th. dagestanicus*

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The genus *Thymus* L. – one of the largest genera of the family of Labiatae – is widely distributed in the flora of the Caucasus. It includes 38 species which are promising for chemical study and use in the national economy.

The raw material and essential oil of wild thyme and common thyme are used in the food and perfumery-cum-cosmetics industry and also in medicine [1-4]. The compositions of the essential oils of individual species of thyme have been studied inadequately or have not been investigated at all. The compositions of the essential oils of some species of thyme have been reported previously [5, 6].

We have studied the chemical compositions of the essential oils of the thymes *Th. dagestanicus* Klok. et Schost and *Th. pastoralis* Iljin. For the analysis we used material collected in various vegetation phases in the Baksan region of the Kabardino-Balkarsk ASSR, in the environs of the Tyrnauz on the glassy slopes of the south western exposure of the Baksal gorge, at a height of 1000-2300 m above sea level. These species are distributed in the foothills and low and medium mountain zones there are considerable natural reserves of them. The amounts of essential oils in the epigeal parts of *Th. dagestanicus* and *Th. pastoralis* in the phase of mass flowering range between 0.33 and 0.90% and between 0.28 and 0.87%, respectively, on the absolutely dry weight.

To determine the best period for collecting the raw material we studied the dynamics of the accumulation of the essential oils in these species. It was found that the largest amount of essential oils in the epigeal parts of both species accumulated in the phase of budding and mass vegetation: 9.27-0.35, 0.93-1.0, 0.38-0.46, and 0.55-0.86%, respectively on the air-dry weight of the plant.

The essential oil of *Th. dagestanicus* consisted of a mobile pale yellow liquid with a sharp thyme odor, caustic properties, and a sharp taste. Physicochemical constants of the oil: d_{20}^{20} 0.8587; n_D^{20} 1.4955; acid No. 3.27; ester No. 23.14; ester number after acetylation 126.15.

The essential oil of *Th. pastoralis* was a yellow liquid with a thyme odor and caustic properties which crystallized at −7°C. The physicochemical constants of the oil were: d_{20}^{20} 0.9094; n_D^{20} 1.5020; acid No. 3.31; ester No. 37.20; ester number after acetylation 137.20.

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