

# MONO- AND SESQUITERPENOIDS OF THE OLEORESINS OF

*Larix dahurica* and *L. amurensis*

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The present paper gives the results of an investigation of the mono- and sesquiterpenoids of the oleoresins of *L. dahurica* Turcz., obtained by tapping, in the upper reaches of the Bureya (Khabarovsk territory) in 1972 and the oleoresin of *L. amurensis* Kolosn., collected in 1971 in the region of lake Kizi in the lower reaches of the Amur. According to Bobrov [1], *L. dahurica* is an independent species, and *L. amurensis* is a hybrid of *L. dahurica* Turcz. *L. kamtschatica* Carr., and *L. olgensis* A. Henry.

The fractions of monoterpenes and of sesquiterpene hydrocarbons isolated after preliminary treatment [2] from the oleoresin of *L. dahurica* amounted to 11 and 1.05%, and those from *L. amurensis* to 12.6 and 1.47%, respectively.

The qualitative and quantitative compositions of the monoterpene hydrocarbons of the two oleoresins were determined by GLC (TCEP, 2.5 m × 3 mm, 74°C). Twelve monoterpene hydrocarbons were found in the oleoresin, their percentage being given below:

Component	<i>L. dahurica</i>	<i>L. amurensis</i>
$\alpha$ -pinene	54.9	70.6
fenchene	Tr.	Tr.
camphene	1.1	0.6
$\beta$ -pinene	19.2	12.7
$\Delta^3$ -carene	8.0	8.5
sabinene	8.5	—
myrcene	2.0	0.6
limonene	2.0	1.1
$\beta$ -phellandrene	2.8	1.3
$\gamma$ -terpinene	Tr.	0.6
terpinolene	1.2	2.4
p-cymene	0.5	1.7

In a study of the sesquiterpene fraction of the oleoresin of *L. dahurica* we used the methods described in a previous paper [3]. Thirteen sesquiterpene hydrocarbons were isolated: longifolene, longicyclene,  $\gamma$ -elemene,  $\alpha$ -amorphene,  $\alpha$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -cadinenes,  $\alpha$ -,  $\gamma$ -, and  $\epsilon$ -murolenes, calamenene, and  $\alpha$ -calacorene and a number of monoterpene ethers, esters, and ketones, of which we identified thymol methyl ether, bornyl acetate,  $\alpha$ -terpinyl acetate,  $\alpha$ -neryl acetate, and menthyl acetate. By analytical GLC in two capillary columns (Tween-60, Apiezon L, 50 m × 0.2 mm), in addition to the hydrocarbons isolated we detected the presence of  $\beta$ -ylangene,  $\alpha$ -selinene,  $\alpha$ -curcumene,  $\beta$ -bisabolene,  $\alpha$ -humulene,  $\beta$ -elemene,  $\alpha$ -longipinene, sibirene, and cyclosativene.

The composition of the sesquiterpene hydrocarbon fraction of the oleoresin of *L. amurensis*, according to the results of GLC, proved to be similar to that of the sesquiterpene hydrocarbon fraction of the oleoresin of *L. dahurica*. All the sesquiterpene hydrocarbons mentioned were found in it on the basis of their relative retention times and the two-capillary column. Among the monoterpene derivatives we identified thymol methyl

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ether,  $\alpha$ -terpinyl acetate, and bornyl acetate. To confirm the results obtained, we isolated the main components from the sesquiterpenoid fraction of the oleoresin of L. amurensis by preparative GLC (Tween-60, 5 m  $\times$  6 mm): longifolene, thymol methyl ether, bornyl acetate, and  $\alpha$ -terpinyl acetate, which were identified from their IR spectra. The main component of both oleoresins is longifolene (30-35%).

In their chemical compositions, the mono- and sesquiterpenoids of the oleoresins of L. dahurica and L. amurensis are very similar. In their sesquiterpene fractions a large number of oxidized monoterpenoids was found. In addition, by GLC two labile sesquiterpene compounds were detected in both oleoresins the amounts of which fell when the oleoresins were stored. Attempts to isolate them by column chromatography were unsuccessful, since on the sorbents used ( $\text{SiO}_2$ ,  $\text{SiO}_2 + \text{AgNO}_3$ ) these compounds were converted into a complex mixture of sesquiterpene hydrocarbons from which we succeeded in isolating  $\alpha$ -amorphene and  $\alpha$ -muroloene.

In the compositions of their mono- and sesquiterpenoids, the oleoresins studied differed considerably from the oleoresin of L. sibirica L. [3]. Thus, in contrast to far-eastern species of larch, in oleoresin of L. sibirica we found only a small number of oxidized monoterpenoids. The main component of the sesquiterpene fraction was not longifolene but  $\gamma$ -elemene.

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#### SESQUITERPENE LACTONES OF Handelia trichophylla

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We have continued a study of the lactones of the inflorescences of Handelia trichophylla Heimerl [1]. The fraction of a chloroform extract that was soluble in 60% ethanol was separated on a column of type KSK silica gel. The components were eluted with mixtures of benzene and methyl ethyl ketone with increasing proportions of the latter.

The first fractions of the eluate yielded cumambrin A, and from the eluates germacranolide with mp 191°C crystallized.

The recrystallization from ethyl acetate of fraction 17 yielded colorless rhombic crystals (I) with the composition  $\text{C}_{15}\text{H}_{20}\text{O}_4$ , mp 224°C (preheated metal block),  $[\alpha]_D^{22} +46^\circ$  (c 0.4; chloroform). IR spectrum ( $\text{cm}^{-1}$ ):  $\nu_{\text{max}}^{\text{KBr}}$  3500 (OH), 1750 (carbonyl of an  $\alpha$ -methylene- $\gamma$ -lactone ring), 1700 ( $\text{C}=\text{O}$  in a six-membered ring).

This compound formed an adduct with dimethylamine (according to Michael) with mp 127°C and  $M^+$  309 (mass spectrometry), which confirms the presence of an exomethylene group in the lactone ring and the composition of (I).

The hydroxy group is readily acetylated by acetic anhydride in pyridine. The acetate of (I) has the composition  $\text{C}_{17}\text{H}_{22}\text{O}_5$  with mp 210°C (acetone).

The NMR spectrum of (I) (JNM-H-4, H-100 MHz instrument, in deuteropyridine,  $\delta$  scale, internal standard

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