TERPENOIDS OF THE OLEORESIN OF *Larix olgensis*

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UDC 547.595.9

In the systematics of Far Eastern species of larches there is a number of obscure questions, but the Korean Dahurian larch (*Larix olgensis* A. Henry) is recognized by all botanists as an individual species [1]. In the present paper we give information on the composition of the terpenoids of the oleoresin of the Korean Dahurian larch, a sample of which was taken directly from the site where this species was described (village of Ol'ga, Maritime Territory). As compared with other larches, the resin productivity of this species is extremely low.

After the group separation of the oleoresin (40 g) by a method described previously [2], 5 g of monoterpene hydrocarbons, 0.3 g of sesquiterpenes, 7.2 g of diterpene hydrocarbons and aldehydes, 5.4 g of diterpene alcohols, and 13 g of resin acids were obtained.

The qualitative and quantitative analysis of the monoterpenes was carried out by the GLC method [3]. It was established that the monoterpene fraction contained: α-pinene (20.5%), camphene (0.3%), β-pinene (23.2%), 3-carene (49.8%), myrcene (0.3%), limonene (1.1%), and β-phellandrene (2.3%).

In the sesquiterpenoid fraction we identified by the GLC method 16 compounds: cyclosativene, longicyclene, α-longipinene, sibirene, longifolene, γ-elemene, α-, γ-, and ε-murolenes, β-selinene, δ-, γ-, and ε-cadinenes, α-humulene, calamenene, and the methyl ether of thymol, the main components being δ- and γ-cadinenes and longifolene. From the fraction of diterpene hydrocarbons and aldehydes (0.25 g), by chromatography on $SiO_2 + AgNO_3$ we isolated dehydroabietane (0.09 g), a mixture of dehydroabietinal and abietinal (0.07 g; 4 : 1 according to the PMR spectrum), and palustral (0.04 g, mp 51-54°C, $[\alpha]_D^{20} + 55°$).

By chromatography of the diterpene alcohols (3 g) on SiO_2, we isolated epimanool (0.4 g), larixyl acetate (0.39 g, mp 80°C), and larixol (1.65 g, mp 96-98°C).

The diterpene acids were methylated with diazomethane, and the methyl esters (7 g) were chromatographed on SiO_2 to separate the hydroxy acids (1.0 g). Rechromatography of the methyl esters of the hydroxy acids led to the isolation of methyl 7-oxodehydroabietate (0.02 g), methyl 15-hydroxyabietate (0.06 g), and methyl 15-hydroxydehydroabietate (0.08 g). All the diterpenoids isolated were identified from their PMR spectra.

The analytical GLC of the mixture of resin acid methyl esters showed the presence in them of the esters of the acids palustric and (or) levopimaric (7.2%), isopimaric (86.2%), dehydroabietic (2.0%), abietic (4.6%), and neoabietic (traces).

The results of the investigation given above showed that the chemical composition of the oleoresin of the Korean Dahurian larch is close to that of the terpenoids of the oleoresin of other Far Eastern species of larch: *Larix gmelinii* (Rupr.) Rupr., and *Larix cajanderi* Mayr. [2-4]. Appreciable differences are observed only in the amounts of individual monoterpenes and resin acids. Among the monoterpenes in the Korean Dahurian larch 3-carene predominates, which may be due to the severe conditions of growth on the slopes of coastal mountains with the constant action of cold winds. In the acid part, the main component was isopimaric acid, and the acids of the abietane series were present in considerably smaller amounts than for other species of larch [2, 4].

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SYNTHESIS OF DEUTERATED (–)-LIMONENE

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UDC 547.596.7

Studying the isomerization transformations of limonene, we have synthesized for the first time [3,3-$^2H_1$]- and [3-$^2H_1$]limonenes (ratio 3 : 1) by the dehydration of a mixture of deuterated stereoisomeric dihydrocarveols obtained by the reduction of deuterated dihydrocarbone.

According to our results (GLC and ^{13}C NMR spectrum), (–)-dihydrocarvone obtained from carvone [1] contains the cis and trans isomers in a ratio of 1 : 5.

The deuteration of the dihydrocarvone was performed by the method of Reich et al. [2]. A reaction product was obtained with a yield of 81% containing, according to GLC, the cis and trans isomers in a ratio of 1 : 5, bp 70-72°C (2 mm), $[\alpha]_D^{20} -16°$, α_4^{20}0.9427, n_D^{20} 1.4708. IR spectrum (ν, in a thin layer), cm^{-1}: 895, 1640 ($CH_2{=}CH$), 1715 (C=O), 2140, 2235, 2375 (C–D). Mass spectrum: M$^+$ 155, 154, 152; isotopic composition: 81% of [1,3,3-$^2H_3$]dihydrocarvone (I), 15% of [3,3-$^2H_2$]dihydrocarvone, and 4% of undeuterated dihydrocarvone. ^{13}C NMR spectrum of the trans isomer (I) ($CDCl_3$, 0 – TMS; δ, isotope shift, ppm) 44.2, –0.5 (C^1); 46.2, –0.7 (C^3).

A mixture of 38 g of the deuterated dihydrocarvone, 10 g of sodium tetrahydroborate, and 300 ml of dioxane was stirred at room temperature for 10 h. After the usual working up and vacuum distillation, 32 g (85%) of a product was obtained which, according to GLC, contained the four stereoisomeric dihydrocarveols in a ratio of 1 : 4 : 10 : 15, bp 83-85°C (3-5 mm), $[\alpha]_D^{20} + 3°$, d_4^{20} 0.9415, n_D^{20} 1.4781. IR spectrum (ν, in a thin layer, cm^{-1}): 890, 1640 ($CH_2{=}CH$), 2120, 2200 (C–D), 3360 (O–H).

At 110°C, 32 g of dihydrocarveol was added to a solution of 150 g of p-toluenesulfonyl chloride in 740 ml of pyridine, and the mixture was stirred for 5 h. After the usual working up of the reaction mixture and vacuum distillation, 9.0 g (32%) of a hydrocarbon fraction (bp 51-52°C/5-6 mm, $[\alpha]_D^{20} -106°$, d_4^{20}0.8546, n_D^{20}1.4716) was isolated, which, according to GLC, contained 96% of limonene, 3.4% of trans-isolimonene, and 0.6% of an unknown hydrocarbon, probably cis-isolimonene. IR spectrum (ν, in a thin layer), cm^{-1}: 870, 1640 ($CH_2{=}CH$), 2059, 2155 (C–D). Mass spectrum: M$^+$ 138, 137, 136; isotopic composition: 70% of [3,3-$^2H_2$] limonene (II), 21.5% of [3-$^2H_1$]limonene, and 8.5% of undeuterated limonene. ^{13}C spectrum of the limonene (II) (C_6D_6, 0 – TMS; δ, isotopic shift, ppm): 33.39, 0.110 (C^1), 122.11–0.126 (C^2), 31.98 –0.280 (C^3), 41.40, –1.180 (C^4) 28.34 –0.039 (C^5), 30.98, 0.004 (C^6), 23.57, 0.006 (C^7), 149.67, –0.006 (C^8), 108.90, 0.019 (C^9), 20.85, 0.008 (C^{10}).

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0009-3130/83/1901-0111$07.50