Semenov's fir belongs to the *Sibiricae* series of species of the section Piceaster, like the Siberian fir (*Abies sibirica* Ledeb.) [3], but the compositions of the terpenoids of the oleoresins of these species differ considerably. The oleoresin of Semenov's fir contains an unusually large amount of 3-carene, which is possibly connected with the conditions of growth of the species (2500-3000 m above sea level). Compounds of the bisabolane series predominate among the sesquiterpenes of this fir, which is due to the 1,6-cyclization of an acyclic precursor — trans,cis-farnesyl pyrophosphate, while the biosynthesis of the sesquiterpenoids in the Siberian fir takes place in two main directions — by 1,6- and 1,11-cyclizations with the formation of caryophyllene and α-humulene, as well as bisabolane compounds. In the composition of its diterpenoids, the oleoresin of Semenov's fir is very similar to that of Far-Eastern species of fir [4], where a high content of cis-abienol has also been found.

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TERPENOIDS OF THE OLEORESIN OF *Pinus pallasiana*

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UDC 547.913.2

Continuing an investigation of the oleoresin of conifers of the family Pinaceae growing in the USSR, we have studied the composition of the terpenoids of the oleoresin of *Pinus pallasiana* D. Don. (Crimean pine) collected in 1982 in the Crimean reservation-hunting area from trees 100-130 years old.

The neutral part was separated from the acids by treatment with a 1% solution of caustic soda, and it amounted to 33% of the weight of the oleoresin. By chromatography on air-dry SiO_2 is was separated into hydrocarbons (71%) and oxygen-containing compounds (26%). Vacuum distillation of the hydrocarbons gave mono-, sesqui-, and diterpenoid fractions.

The monoterpenoids (62.7% of the neutral fraction) consisted mainly of α-pinene — 9.18%. Camphene (3.1%), β-pinene (2.6%), and β-phellandrene (2.5%) were also detected in this fraction by their relative retention times (GLC). Among the sesquiterpene hydrocarbons (5.4% of the neutral fraction), germacrene D, identified by its spectral characteristics (IR and PMR), predominated (90.3%). Of the minor components, δ-cadinene (4.6%), β-bisabolene (2.0%), longifolene (1.0%), longicyclene, α-copaene, and α-ylangene (traces) were determined by GLC (OV-101, 50 m).

Germacrene D has been found previously only in the oleoresins of three species of pines — *Pinus monophylla*, *Pinus edulis* [1], and *Pinus kohiana* [2]. It is possible that such a marked accumulation of germacrene D in conifers of the family Pinaceae is connected with its lability, since, according to [6], it is an intermediate in the biosynthesis of widely distributed sesquiterpenoids of the cadalene series.

From the diterpene fraction (1.2% of the neutral part), pimaradiene with n_D^{20} 1.5238, $[\alpha]_D^{20}$ +31.3°, and isopimaradiene with n_D^{20} 1.5217, $[\alpha]_D^{20}$ −35.3°, identified by their spectral characteristics, were isolated by chromatography on SiO_2 + 5% of $AgNO_3$.

Oxygen-containing compounds were chromatographed by the rapid method on SiO_2 [4]. Gradient elution led to the isolation of diterpene aldehydes (∿40%) — pimarinal (mp 43-45°C, $[\alpha]_D^{20}$ +94°) and isopimarinal (n_D^{20} 1.5290) — and diterpene alcohols (∿30%) — pimarinol (n_D^{20}

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 116-117, January-February, 1984. Original article submitted July 11, 1983.

0009-3130/84/2001-0116$08.50

1.5259, $[\alpha]_D^{20}$ +60.5°) and isopimarinol (n_D^{20} 1.5250, $[\alpha]_D^{20}$ −40.1°). All the compounds isolated were identified by TLC with markers. Alcohols have not previously been found in the oleoresin of the Crimean pine [5].

In the most polar fraction (∿5%) hydroxy esters were detected — methyl 15-hydroxyabietate and methyl 15-hydroxydehydroabietate, present in a ratio of 1:8 (GLC) — and they were identified by additions of authentic samples.

The extremely small amount of oxygen-containing mono- and sesquiterpenoids in the oleoresin of the Crimean pine must be mentioned. 5,8-Germacra-1E,6E-5-ol,* cubebol, epicubebol, δ-cadinol, methyleugenol, and 2,4-dimethoxyallylbenzene were isolated in trace amounts. These components were identified from their PMR spectra.

The acids of the oleoresin were analyzed by GLC in the form of their methyl esters. Pimaric (4.5%), palustric/levopalustric (37%), isopimaric (14%), dehydroabietic (11%), abietic (29.5%), and neoabietic (4%) acids were identified. The quantitative composition of the acids of the oleoresin of the Crimean pine that we studied differs from the figures published previously [6].

In the composition of the terpenoids of its oleoresin the Crimean pine differs from a species close to it — the Scotch pine — by the high content of germacrene D and of diterpene aldehydes.

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BIOMIMETIC CYCLIZATION OF CARYOPHYLLENE TO β-PANASINSENE

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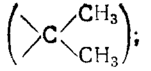
UDC 547.91

One of the components of the essential oil of ginseng (*Panax ginseng* C. A. Mayer) — β-panasinsene — is biogenetically linked with neoclovene and, apparently, with caryophyllene. This is shown by the common presence of all these hydrocarbons in the oil mentioned [1]. Although a suggested scheme of the conversion of caryophyllene into neoclovene also includes the intermediate formation of a carbocation with the 1,5,5,8-tetramethyltricyclo$[5.4.0.0^{4,7}]$-undecane skeleton, no hydrocarbons corresponding to this particle were detected among the products of the acid-catalyzed cyclization of caryophyllene [2].

On studying the products of the mercuration-demercuration of caryophyllene under the action of mercury(II) acetate in acetic acid, we found that an 8% yield was formed of a hydrocarbon having the following characteristics: $[\alpha]_D^{23}$ −27.4° (c 3.28; $CHCl_3$); IR spectrum (CCl_4, cm^{-1}): 3092, 1639 and 894 ($>C=CH_2$), 1382 and 1369  $\left(>C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$; PMR spectrum (60 MHz, CCl_4, δ scale, ppm): 0.73, 0.85, and 1.07 (singlets, 3H each); 4.79 and 4.87 (doublets, 1H each, J = 2 Hz); ^{13}C NMR spectrum (50.323 MHz, $CDCl_3$, δ_{TMS}, ppm): quartets at 18.14, 24.78, and 30.56; triplets at 24.65, 25.03, 33.72, 35.62, 35.95, 41.02, and 108.27; doublet at 52.53; singlets at 30.46, 45.53, 52.70, and 153.20; mass spectrum: 204 (M^+, 37%), 189

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 117-118, January-February, 1984. Original article submitted July 21, 1983.

0009-3130/84/2001-0117$08.50