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TERPENOIDS OF THE OLEORESIN OF *Abies semenovii*

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The oleoresin of *Abies semenovii* B. Fedtsch. (Semenov's fir) (1000 g), collected in the Aflatun gorge in the Tian-Shan was separated into neutral (520 g) and acidic (400 g) components by treatment with an 80% solution of caustic soda. Fractional distillation of the neutral part of the oleoresin yielded 196 g of monoterpenes (bp 60-100°C/10 mm Hg), 53 g of mono- and sesquiterpenoids (bp 70-130°C/0.1 mm Hg), and 248 g of diterpenoids.

The following hydrocarbons were identified in the monoterpene fraction by GLC [1]: α-pinene (7.2%), camphene (3.6%), β-pinene (10.1%), 3-carene (55.7%), β-phellandrene (21.2%), limonene (2.5%), myrcene (1.0%), and γ-terpinene (traces). The mono- and sesquiterpene fractions were separated by chromatography on Al_2O_3 (neutral, activity grade II) into sesquiterpene hydrocarbons (16 g) and oxygen-containing compounds (35 g). The hydrocarbons were analyzed by GLC (Biokhrom-01; glass capillary column 52 m long, OV-101); the following were determined from their relative retention times and by the method of additives: sibirene (11.2%), β-bisabolene (45.6%), γ-bisabolene (11.5%), α-bisabolene (3.0%), δ-cadinene (7.0%), β-selinene (2.5%), caryophyllene (0.9%), and an unidentified hydrocarbon (9.5%), and, in very small amounts, α-longipinene, longicyclene, α-copaene, α-ylangene, and α-humulene. Isolated by column chromatography on SiO_2 and SiO_2 + 20% $AgNO_3$, and identified by their PMR spectra, were α-ylangene, sibirene, β-selinene, δ-cadinene, and β- and γ-bisabolenes. The unidentified hydrocarbon was also isolated: it had $[\alpha]_D^{20}$ −9.1°. PMR ($CDCL_3$, ppm): 0.84 (3H, doublet, J = 7 Hz); 1.60, 1.63, and 1.70 (singlets, 3H each); 5.38 (1H, multiplets); 1.21 (1H, multiplet); 1.43 (1H, multiplet); 1.75-2.42 (9H). ^{13}C NMR spectrum (ppm): singlets at 143.3, 133.1, 122.2, and 45.5; doublets at 121.8 and 44.4; triplets at 33.0, 31.7, 31.1, 30.3, and 28.4; and quartets at 23.8 (two), 20.7, and 17.6. The mass spectrum had the peak of M^+ at 204 and strong peaks corresponding to ions with masses of 121 and 136. Of the sesquiterpenes described in the literature, the hydrocarbon isolated is closest, in relation to these properties, to β-alaskene [2].

By chromatography of the oxygen-containing mono- and sesquiterpenes on SiO_2 and SiO_2 + 20% of $AgNO_3$ we isolated bisabolol (∿30% fraction), bornyl acetate, geranyl acetate, geraniol, borneol, cubebol, epicubebol, and nerolidol.

The diterpenoids were represented mainly by the bicylic labdane alcohol cis-abienol (mp 40-41°C, 90% fraction), identical with an authentic sample according to melting point and spectral characteristics. Not only cis-abienol, but also palustral, abietinal, and abietinol were isolated chromatographically and identified.

The acids of the oleoresin of Semenov's fir were studied in the form of the methyl esters by the GLC method [1]. The main components were abietic acid (64.5%) and neoabietic acid (25%), with smaller amounts of sandaracopimaric acid (1.2%), dehydroabietic acid (1.1%), palustric or levopimaric acid (8%), and isopimaric acid (traces).

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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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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 ($\sim$40%) — pimarinal (mp 43-45°C, $[\alpha]_D^{20}$ +94°) and isopimarinal (n_D^{20} 1.5290) — and diterpene alcohols ($\sim$30%) — pimarinol (n_D^{20}

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