MONO- AND SESQUITERPENOIDS OF THE OLEORESIN OF *Picea glehnii*

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We have studied the composition of the mono- and sesquiterpenoids of the oleoresin of the Sakhalin spruce (*Picea glehnii*, Mast.) collected in 1974 in the Korsakov leskhoz [Forestry farm] (Sakhalin). After the working up of the oleoresin (1.75 kg), fractions of monoterpene hydrocarbons (137 g), monoterpene alcohols (8.4 g), sesquiterpene hydrocarbons (10.5 g), and sequiterpene alcohols (4.1 g) were isolated.

The qualitative and quantitative compositions of the monoterpene hydrocarbon fraction were determined by the GLC method (TCEP, 2.5 m × 3 mm, 74°C). The results of an analysis of this fraction coincided with the results obtained in a study of the composition of the monoterpene hydrocarbons of the oleoresin turpentine from the Sakhalin spruce [1]. The total amount of the main components α-pinene and β-pinene was 90-93%, which is comparable with their amount in the oleoresins of other species of spruce of this geographical region [1, 2], but as compared with that of other spruces the oleoresin of the Sakhalin spruce contained 1.5-2 times as much α-pinene (about 82%) and only one third as much β-pinene (about 10%). The other monoterpene hydrocarbons were present in small amounts (β-phellandrene — 3.5%; limonene — 1.4%; thujene, camphene, Δ^3-carene, myrcene, γ-terpinene, terpinolene, and p-cymene — less than 1% each).

The monoterpene alcohols consisted of two monocyclic compounds — α-terpineol and 4-terpineol.

The composition of the sesquiterpene hydrocarbon fraction was studied with the aid of various chromatographic and spectral methods. Column chromatography (Al_2O_3, SiO_2 + 3.5% of $AgNO_3$) and micropreparative GLC permitted the isolation and identification by means of their IR and PMR specta of β-farnesene, β-bisabolene, α-selinene, selina-4,11-diene, (+)-eremophilene, (+)-δ-cadinene, (+)-α-copaene, (+)-α-ylangene, (+)-sibirene, (+)-longifolene, longicyclene, and cyclosativene. According to analytical GLC in two capillary columns, the sesquiterpene hydrocarbon fraction contained 21 components. In addition to the hydrocarbons mentioned, from their relative retention times we also identified γ-cadinene, α-cadinene, and α-calacorene. The main components of this fraction were sibirene (16.7%), longifolene (12%), δ-cadinene (16.3%), and eremophilene (6.9%).

The mixture of sesquiterpene alcohols was chromatographed on SiO_2. Hexane with increasing amounts of diethyl ether eluted six fractions: A (0.1 g), B (0.52 g), C (0.1 g), D (0.97 g), E (0.43 g), and F (4.51 g). Fractions A, B, C, and E consisted of individual compounds, while fraction D contained two components and fraction F consisted of a complex mixture of highly oxidized compounds and was not investigated further.

Compounds C and E were identified as 4-terpineol and α-terpineol, respectively.

Compound A had $[\alpha]_D^{20}$ +10° ($CHCl_3$), and the mp of its p-nitrobenzoate was 85°C. It follows from its IR, PMR, and ^{13}C NMR spectra that this alcohol contains three methyl groups on saturated carbon atoms, a methyl group on a double bond, a triply substituted double bond, and a secondary hydroxy group. The spectral characteristics of alcohol A did not coincide with those of known sesquiterpene alcohols. The study of the structure of alcohol A is continuing.

Alcohol B, with $[\alpha]_D^{20}$ +80.4° ($CHCl_3$) showed spectra very similar to those of epicubenol, which was first isolated from cubeb oil [3]. The absolute value of the specific rotation of the alcohol isolated by us differs slightly from the value given in the literature (—95.6° [3]). When dehydrating alcohol B ($POCl_3$, pyridine, 0°), we obtained cubenene, the PMR spectra of which coincided with the spectra of cubenene obtained from epicubenol [3]. Consequently alcohol B is an enantiomer of epicubenol.

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Fraction D consisted of a mixture of related compounds. By crystallizing it was possible to isolate only one compound in the individual state — a saturated tricyclic tertiary alcohol with mp 64-65°C and $[\alpha]_D^{20}$ +70.4° ($CHCl_3$). In its physicochemical constants and spectral characteristics, this alcohol proved to be identical with cubebol and differed from it only in the sign of the optical rotation. The residue after crystallization consisted of a mixture of cubebol and an oily alcohol in a ratio of 1:1. It may be assumed that the second alcohol of fraction D is epicubebol, since cubebol is found in natural raw material together with its epimer. This also agrees with the PMR spectrum of fraction D. To confirm the structure of both alcohols we performed the dehydration of the mixture of compounds of fraction D ($POCl_3$, pyridine, 0°C), which led to a mixture of hydrocarbons the main one of which was (—)-δ-cadinene. This result agrees well with the result of the acid isomerization of α-cubebene into δ-cadinene [5].

Thus, in the oleoresin of the Sakhalin spruce eleven monoterpene hydrocarbons, two monoterpene alcohols, 15 sesquiterpene hydrocarbons, and three sesquiterpene alcohols have been identified. This is the first time that eremophilene, cubenol, and cubebol have been isolated from oleoresins of the family *Pinaceae*.

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REGIOSELECTIVE AND STEREOSELECTIVE OXIDATION OF CEMBRENE BY SELENIUM DIOXIDE

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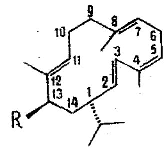
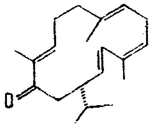
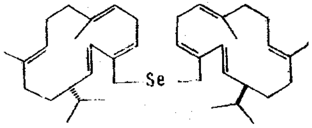
According to the mechanism of the allyl oxidations of olefins by selenium dioxide [1] and the characteristics of this reaction that have been found [2], the diterpene hydrocarbon cembrene (I) [3] should be oxidized primarily at the two methylene groups present in similar environments at C_9 and C_{13}. In fact, it was found that cembrene is oxidized predominantly at the C_{13} methylene group, forming the alcohol (II) [n_D^{22} 1.5180, $[\alpha]_D^{24}$ +188.5° (chloroform)] and its acetate (III) [n_D^{22} 1.5188, $[\alpha]_D^{20}$ +183° (chloroform)] with total yield of 55% on the cembrene that reacted. The oxidation was carried out by stirring for two hours at 60-70°C a mixture of 4 g of cembrene, 0.59 g of selenium dioxide, 5 ml of acetic anhydride, and 50 ml of acetic acid, followed by pouring onto ice and extraction of the total reaction products with petroleum ether.



I. R = H
II. R = OH
III. R = $OCOCH_3$



IV



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