DITERPENOIDS OF THE OLEORESIN OF Picea koraiensis, P. glehnii, AND P. excelsa

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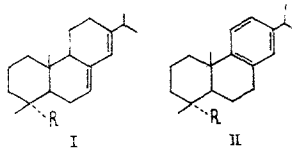
The diterpenoids of the oleoresin of the genus Picea A. Dietr. (spruce) have been little studied chemically. There is information on the composition of the neutral diterpenoids of only three species: the Siberian spruce [1], the Jeddo spruce [2], and the Norway spruce [3].

We give the results of a study of the neutral diterpenoids of the Korean spruce (Picea koraiensis Nak, Maritime Territory), the Sakhalin spruce [Pices glehnii (Fr. Schmidt) Mast, Sekhalin oblast], and the common spruce [Picea abies (L.) Karst., Leningrad oblast].

The high-boiling neutral compounds of these oleoresins were obtained as described previously [2]. The mixture of diterpenoids was separated by chromatography on alumina into hydrocarbons and oxygen-containing compounds. The composition of the mixture of hydrocarbons was determined by adsorption chromatography.

Abietadiene (Ia) and dehydroabietane (IIa) were found and identified in the oleoresin of the Korean spruce.



I II

a. R = CH_3
b. R = CH_2OH
c. R = CHO
d. R = $COOCH_3$

In the oleoresins of the Sakhalin spruce and the common spruce the main hydrocarbon is cembrene, and compounds (Ia) and (IIa) are present with it in minor amounts. The amount of hydrocarbons in the oleoresins of the spruces are very small, the bulk of the diterpenoids consisting of oxygen-containing compounds represented by acyclic and mono-, bi-, and tricyclic diterpenoids. Geranyllinalool – an acyclic diterpenoid – was detected in the oleoresin of the Korean spruce and the common spruce but did not appear in the oleoresin of the Sakhalin spruce.

The monocyclic diterpene alcohol isocembrol predominates in the oleoresins of the Sakhalin spruce and the common spruce. It has been shown previously that isocembrol is readily dehydrated to cembrene [4], and this may explain the variability of the amount of cembrene in the hydrocarbon fractions of the oleresins.

The bicyclic alcohol cis-abienol is one of the main components of the oleresins of the species mentioned. We directed our attention to the fact that where vacuum distillation is used the amount of cis-abienol falls and the amount of cis-neoabienol rises, which is due to the thermal isomerization of cis-abienol [5, 6]. These facts and the instability of the diterpenoids impose the necessity for taking particular care in the choice of a procedure for treating the oleoresins when deciding the question of whether a particular component is present in the native state.

The tricyclic diterpenoids of the oleoresins of the spruces are represented by abietane and dehydrobietane derivatives. Abietinol (Ib) predominates in the oleoresin of the Korean spruce, and dehydroabietinol (IIb) in the oleoresin of the Sakhalin spruce. The methyl esters of resin acids (Id, IId) and aldehydes (Ic, IIc) are also found in the oleoresin.

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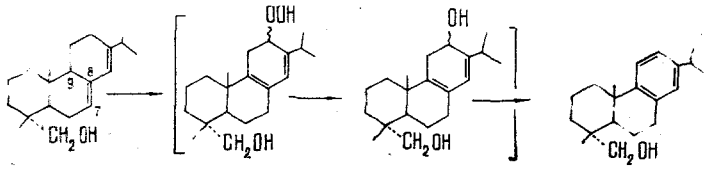
TABLE 1. Distribution of the Neutral Diterpenoids in Various Species of the Genus Picea Dietr.

Species of spruce	Individual diterpenoids												
	cembrene	abietadiene	dehydroabietane	phyllocladene	isophyllocladene	abietinal	dehydroabietinal	palustral	isopimarinal	methyl abietate	methyl dehydroabietate	geranyllinalol
The section Morinda												
Siberian	++*	+	+	−	−	+	+	+	+	−	−	+
Korean	−	++	++	−	−	+	+	+	+	+	+	+
Common	+	+	+	−	−	+	+	−	−	+	+	+
Sakhalin	++	+	+	−	−	−	+	−	−	++	++	−
Norway	++	−	−	−	−	−	+	−	+	−	−	+
The section Casicta												
Jeddo	+	−	−	+	+	−	−	−	−	−	−	+

Species of spruce	Individual diterpenoids										Literature
	manoyl oxide	epimanoyl oxide	manool	epimanool	cis abienol	neoabienol	phylloladanol	abietinol	dehydroabietinol	isocembrol	
The section Morinda											
Siberian	−	+	−	−	−	+	−	+	−+	+	[1]
Korean	−	−	−	−	+	−	−	+	+	−	
Common	−	−	−	−	+	−	−	+	+	+	
Sakhalin	−	−	−	−	+	−	−	−	−	−	
Norway	+	+	−	−	−	−	−	+	+	+	[3]
The section Casicta											
Jeddo	+	+	+	+	+	+	++	−	−	−	[2]

*High content of the component.

We have studied the products of the oxidation of abietinol both on its storage in the air and with the addition of an initiator (cobalt acetate) to the reaction mixture. Under these conditions a complex mixture of hydroxy and oxo derivatives and of polymeric products is formed. From this mixture we isolated dehydroabietinol (IIb), the formation of which can be represented by the following scheme:



It has been shown previously that the action of various oxidizing agents on derivatives of abietic acid forms compounds of the dehydroabietin type [7, 8]. This direction of the reaction can probably explained by the ease of migration of the C_7-C_8 bond to the $\Delta^{8,9}$ position with the subsequent oxidation and dehydration of the compound formed.

Literature information and the results of our own investigations on the oleoresins of spruces make it possible to trace the development of the neutral diterpenoids in various species of spruce (Table 1).

EXPERIMENTAL

The sample of the oleoresin of the Korean spruce was collected in July, 1973, that of the Sakhalin spruce in July, 1974, and that of the common spruce in July, 1974. The oleoresins were treated as described previously [2], and the neutral diterpenoids were isolated by the same method.

The IR spectra were recorded for solutions in carbon tetrachloride on a UR-20 instrument, the UV spectra for solutions in ethanol on a Specord UV-Vis, and the NMR spectra were obtained on Varian HA-100

and Varian A56/60A instruments for solutions in CCl_4 with HMDS as the internal standard, δ scale. The specific rotations were determined on a Zeiss polarimeter for solutions in chloroform.

For adsorption chromatography we used air-dry silica gel and silica gel impregnated with silver nitrate (5%). In all cases mixtures of petroleum ether with increasing amounts of diethyl ether were used as the eluents.

Separation of the Neutral Diterpenoids. The neutral diterpenoids were chromatographed on alkaline alumina (activity grade I-II; ratio of 1:15). Petroleum ether eluted the hydrocarbons, and ethanol the oxygen-containing compounds, which were distributed in the following way:

Species of spruce	Weight of Neutral Diterpenoids, g	Yield of Hydrocarbons, g	Yield of Oxygen-containing Compounds, g
Korean	124	1,1	109
Sakhalin	50	0,45	48,3
Common	2,5	0,15	2,2

Abietadiene and Dehydroabietane. The hydrocarbons from the oleoresin of the Korean spruce (0.5 g) were chromatographed on silica gel impregnated with silver nitrate (ratio 1:30). This led to the isolation of dehydroabietane (0.1 g) – n_D^{20} 1.5280, $[\alpha]_D^{20}$ + 52° (c 3.0); UV spectrum: λ_{max} 269, 272 nm (log ε 2.12); literature data [9]: $[\alpha]_D^{25}$ + 53.8° (c 10, $CHCl_3$); and abietadiene (0.15 g) – n_D^{20} 1.5310, $[\alpha]_D^{20}$ – 79.5° (c 2.3); UV spectrum: λ_{max} 241 nm (log ε 3.97): literature data [10]: n_D^{20} 1.5311, $[\alpha]_D^{20}$ – 79.6°.

The IR, NMR, and UV spectra of the hydrocarbons were identical with those of authentic samples. Abietadiene and dehydroabietane were also found in the hydrocarbon fraction of the oleoresin of the Sakhalin spruce (0.02 g and 0.01 g, respectively). These hydrocarbons were detected by thin-layer chromatography in the oleoresin of the common spruce.

Cembrene. The mixture of hydrocarbons from the oleoresin of the Sakhalin spruce (0.45 g) was chromatographed under the conditions described above. Petroleum ether–diethyl ether (99:1) yielded cembrene (0.35 g) with mp 60–61°C, $[\alpha]_D^{20}$ + 230° (c 3.0), literature information [11]: mp 59–60°C, $[\alpha]_D^{20}$ + 234° (c 3.0). The IR, UV, and NMR spectra were identical with those of an authentic sample of cembrene.

Aldehydes and Methyl Esters. The mixtures of carbonyl compounds from the oleoresin of the Korean spruce (0.9 g) was stirred with 1.5 g of sodium sodium tetrahydroborate in aqueous methanol at room temperature for 1 h. After the usual working up of the reaction mixture [12], 0.8 g of a mixture of alcohols, as the products of the reduction of aldehydes, and of unchanged methyl esters of resin acids was obtained. Chromatography on silica gel yielded methyl dehydroabietate (0.05 g), methyl abietate (0.08 g), dehydroabietinol (0.1 g), abietinol (0.5 g), and isopimarinol (0.03 g). All the compounds isolated were identified by direct comparison with authentic samples.

The similar treatment of the fraction of the carbonyl compounds from the oleoresin of the Sakhalin spruce (0.5 g) showed a predominance of esters (80%, determined from the integral intensity of the signals of methoxycarbonyl and aldehyde groups in the NMR spectra of the initial mixture). Dehydroabietinol (0.08 g) and abietinol (0.1 g) were identified in the mixture of alcohols formed by the reduction of the aldehydes.

In the oleoresin of the common spruce, the above-mentioned aldehydes and esters were detected by TLC and their presence was confirmed by the NMR spectra of the mixture of carbonyl compounds.

cis-Neoabienol and cis-Abienol. The oxygen-containing compounds of the oleoresin of the Korean spruce (2.0 g) were chromatographed on silica gel (100 μ, ratio 1:40). A mixture of petroleum ether and diethyl ether (95:5) yielded Δ^{13}-cis-neoabienol (0.8 g), n_D^{20} 1.5238, $[\alpha]_D^{20}$ + 12° (c 3.0), λ_{max} 239 nm (log ε 4.3), literature information [6]: n_D^{20} 1.5260, $[\alpha]_D^{20}$ + 10.8° (c 5.4).

The IR, UV, and NMR spectra were identical with those of an authentic sample. The same mixture eluted 0.1 g of cis-abienol, which was identified by direct comparison with an authentic sample.

The part of the oleoresin not subjected to distillation (3.0 g), after chromatography, yielded cis-abienol (1.5 g), mp 40–41°C $[\alpha]_D^{20}$ + 14.2° (c 3.0); literature information [6]: mp 39–41°C.

The IR, UV, and NMR spectra and a mixed melting point showed the identity of the alcohol isolated and an authentic sample. The presence of cis-abienol in the oleoresins of the Sakhalin spruce and the common spruce was established by TLC and by comparison of IR, UV, and NMR spectra.

Abietinol and Dehydroabietinol. By chromatography on silica gel (140 μ, ratio 1 : 30), the mixture of polar alcohols from the oleoresin of the Korean spruce (4.0 g) yielded abietinol (2.5 g), mp 83-84°C, $[\alpha]_D^{20}$ − 120° (c 3.0), λ_{max} 234, 241 nm (log ε 4.2); according to the literature [13]: mp 85.5-87°C, $[\alpha]_D^{20}$ − 130° (c 2.0); and dehydroabietinol (1.3 g), n_D^{20} 1.5390, $[\alpha]_D^{20}$ + 53° (c 3.0).

The IR, UV, and NMR spectra of the alcohols isolated were identical with the spectra of authentic samples.

The monohydric alcohols were isolated from the oleoresin of the Sakhalin spruce similarly, the ratio of abietinol and dehydroabietinol in this oleoresin being 1 : 1.5. These alcohols were detected by thin-layer chromatography in the oleoresin of the common spruce.

Oxidation of Abietinol by Atmospheric Oxygen. Abietinol (2 g) was dissolved in 5 ml of benzene, 0.1 g of cobalt acetate was added as an initiator, and the mixture was left at room temperature for 5 days. A TLC check of the reaction mixture showed the presence of five components. After the elimination of the cobalt acetate and the benzene, the polymeric products (0.8 g) were separated by treating the mixture with petroleum ether. The IR spectrum of the compounds soluble in petroleum ether (1 g) showed the presence of carbonyl (1680 cm^{-1}) and hydroxy (3620 cm^{-1}) groups. Dehydroabietinol (0.15 g), identical in its constants and spectral characteristics with an authentic sample, was isolated from this fraction by chromatography on silica gel.

SUMMARY

1. The composition of the neutral diterpenoids of the oleoreins of three species of spruce have been studied: Korean spruce, common spruce, and Sakhalin spruce.

2. The distribution of diterpenoids over the species in the genus Picea has been shown. In the oleoresins of spruces of the section Morinda, tricyclic diterpenoids with the abietane skeleton predominate.

3. It has been established that when abietinol is oxidized by atmospheric oxygen, aromatization of the ring takes place with the formation of dehydroabietinol.

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