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RESIN ACIDS OF THE OLEORESINS OF CONIFERS GROWING IN TRANSCARPATHIA

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The chemical composition of the resin acids of the oleoresins of five species of the conifers of Transcarpathia has been studied. The oleoresins contain eight resin acids. $\Delta^{8,9}$-Isopimaric and anticopalic acids have been found in the acid part of the oleoresin of the Weymouth pine.

Continuing a systematic investigation of oleoresins of conifers of the USSR [1], we have studied the compositions of the resin acids of several species having small areas in Transcarpathia with a chemical composition of which there is no information in the literature.

In the present communication we give the results of a study of the acid fractions of the oleoresins of *Abies alba* Mill. (silver fir), *Larix decidua* Mill. (European larch), *Pinus mugo* T. (Swiss mountain pine), *Pinus strobus* Ladb. (Weymouth pine), and *Picea excelsa* L.* and *Picea abies* K. (Norway spruce†), growing in Transcarpathia. The Swiss stone pine, having a limited area in Transcarpathia, belongs to the peculiar species series *Montanae* [2].

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*The oleoresin of the Norway spruce *Picea excelsa* was collected in Chelyabinsk province.

†The Russian text gives for *P. excelsa* L. a name translating as "common spruce" and for *P. abies* K. "European spruce." According to all the reference works consulted the Latin names are synonymous and apply to the Norway spruce [Translator].

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TABLE 1. Amounts and Composition of the Resin Acids in the Oleoresin

Species	Acids in the oleoresin, %	Composition of the acid fraction, %		Composition of the resin acid fractions, %								
		resin acids	hydroxy acids	abietic	dehydroabietic	neoabietic	isopimaric	palustric and levopimaric	pimaric	sandaracopimaric	anticopalic	$\Delta^{8,9}$ isopimaric
Pinus mugo	82,5	47,3	51,5	15,7	33,1	14,0	12,2	24,6	7,5	2,0	—	0,6
Pinus strobus	71,4	73,5	25,7	29,1	1,8	18,6	26,3	16,3	0,4	1,6	12,7	0,5
Picea abies	65	71,4	21,4	10,6	13,0	10,8	11,3	47,4	1,9	5,1	—	—
Picea excelsa	47	65	35	17,8	25,6	6,4	13,2	31,7	1,0	3,6	—	—
Larix decidua	44	71,4	22,8	14,4	6,4	7,3	44,9	24,9	Сл.	2,1	—	—
Abies alba	39	47,3	51,8	40,9	16,7	10,9	6,0	23,4	—	2,1	—	—

The physicochemical characteristics of the oleoresins of the other-mentioned species are given below:

Species	Refractive index, n_D^{22}	Specific rotation, $[\alpha]_D^{21}$, degrees	Acid No.
Pinus mugo	1,5240	—16 6	150—153
Pinus strobus	1 5227	+2,6	129—131
Picea abies	1,5248	+28,8	112—113
Picea excelsa	1,5238	—38,4	94—95
Larix decidua	1,5215	+18,8	92 -94
Abies alba	1,5160	+26,0	86—89

The low acid numbers in the oleoresins of the fir, larch, and spruce permit the assumption of a considerable amount of neutral components in them. The largest amount of acids (about 82.5%) was present in the oleoresin of the Swiss stone pine, the smallest amount in the oleoresins of the fir (39%).

The separate the acid components, the oleoresins were treated by the method described in [3]. The compositions of the resin acids of the oleoresins of all the species were analyzed by gas-liquid and adsorption chromatography.

It was found that the component compositions of the acids of the species investigated scarcely differed from one another but there were distinct quantitative differences (Table 1).

For the Swiss stone pine, the Weymouth pine, and the Norway spruces (*P. excelsa* and *P. abies*) the predominance of dehydroabietic and palustric and/or mesopimaric acids was characteristic, while in the acid fraction of the oleoresin of the larch the main component was isopimaric acid (45%) and in the oleoresin of the silver fir it was abietic acid (41%) while pimaric acid was absent.

Thus, the compositions of the diterpene acids of the species investigated are characteristic for conifer resins [4, 5] and only in the oleoresin of the Weymouth pine (*Haploxylon* subgenus) did we find anticopalic acid which has previously been isolated in considerable amounts (50%) from the oleoresin of *Pinus pumila* [6, 7]. It must be mentioned that we did not detect strobic acid in the acid fraction of the oleoresin of *Pinus strobus* L. although it has been found in the extractive substances of the bark and needles of this species [8].

EXPERIMENTAL

The oleoresins of the Swiss stone pine, the Weymouth pine, the European larch, and the silver fir were collected on the territory of the Ust'-Chernyanka forestry combine (Transcarpathia) in July, 1985, and the oleoresin of the Norway spruce *Picea excelsa* in the Chelyabinsk province (Katav-Ivanovsk region) at the same time.

IR spectra were recorded on a UR-20 instrument in CCl_4 solution, UV spectra for solutions in ethanol on a Specord UV-VIS instrument, and NMR spectra for solutions in CCl_4 on a Varian A 56/60 A instrument, δ scale. Specific rotations were measured on a Zeiss polarimeter for solutions in chloroform.

Isolation of the Acids. The oleoresins were saponified with 1% aqueous caustic soda. The neutral compounds were separated by extraction with diethyl ether. The solution of the sodium salts of the resin acids was treated with 10% hydrochloric acid and the combined acids were isolated and were then treated with an ethereal solution of diazomethane and were investigated in the form of their methyl esters.

The adsorption chromatography of the mixtures of methyl esters was performed on silica gel with silver nitrate by the method of flash chromatography [9] with elution by mixtures of petroleum ether and diethyl ether.

Analysis of the Methyl Esters of the Resin Acids. The analysis of the mixtures of methyl esters was carried out by the GLC method on a Chrom-41 instrument using a glass capillary column (0.3 mm × 50 m) with the stationary phase XE-60 at a column temperature of 200°C and an evaporator temperature of 240°C, with nitrogen as the carrier gas.

Chromatography of the Methyl Esters of the Acid from the Weymouth Pine. The combined methyl esters (1.8 g) were chromatographed on type L silica gel (Czechoslovakia) with a grain size of 0.40-0.100 mm impregnated with silver nitrate (5%). Petroleum ether—diethyl ether (99:1) led to the isolation of 0.3 g of methyl anticopalate with $[\alpha]_D^{21}$ +40° (c 4.5; chloroform), n_D^{22} —1.5067; according to the literature [7]: $[\alpha]_D^{24}$ +44.5 (c 2.02; chloroform); n_D^{23} —1.5150. The MR, IR, and UV spectra of the methyl anticopalate corresponded to those given in the literature [7].

A combined fraction (0.41 g) containing, according to its NMR spectrum, methylabietate, methyldehydroabietate, and methyl neoabietate (3:1:2) was isolated by means of the same mixture. Petroleum ether—diethyl ether (97:3) yielded methyl neoabietate (0.15 g) with n_D^{21} 1.5340; methyl palustrate (0.14 g) with n_D^{21} 1.5352; and methyl isopimarate (0.15 g) with mp 57-58°C; according to the literature [10]: mp 62°C. The IR, UV, and NMR spectra of the compounds isolated agreed completely with those of authentic samples.

The amounts of resin acids and hydroxy acids in the oleoresins studied and the component compositions of the acid fractions are given in Table 1.

SUMMARY

1. The chemical compositions of the resin acids of the oleoresins of five species of conifers growing in Transcarpathia have been studied. It has been established that the oleoresins contain eight resin acids that are characteristic for conifers. The quantitative composition of the acids differs according to the species of conifer.

2. $\Delta^{8,9}$-Isopimaric and anticopalic acids have been detected in the acid fraction of the oleoresin of the Weymouth pine, the amount of the latter acid being about 13% of the total resin acids.

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