QUANTITATIVE COMPOSITION OF THE RESIN ACIDS PRODUCED BY THE CONIFEROUS SPECIES OF THE USSR

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The approximate quantitative composition of the mixtures of resin acids of conifers of the USSR was established previously by partition chromatography and UV spectroscopy [1]. However, it is impossible by these methods to determine the amount in mixtures of those acids which issue from the column simultaneously and which have no characteristic absorption bands in their UV spectra (pimaric, isopimaric, and sandaracopimaric acids [2]).

For this reason, in the preceding papers [1], only the total content of these acids in the mixtures were shown.

In the present paper we give the quantitative compositions of mixtures of resin acids of balsams of the most important coniferous species of the USSR determined by gas-liquid chromatography (GLC): Pinus silvestris L. ssp. silvestris L. (P. silvestris) (Scotch pine, timber pine); P. pallasiana Lamb. (P. pallasiana) (Crimean pine); P. pityusa Stev. (P. pityusa); P. silvestris L. ssp. hamata (Stev.) Fomin (P. hamata); Picea excelsa Link (P. excelsa) (Norway spruce); Larix sibirica Ldb. (L. sibirica) (Siberian larch); and Pinus sibirica (Rupr.) Mayr. (P. sibirica) (Siberian pine).

EXPERIMENTAL

The average samples of resin acids consisted of balsams taken from 50 or more trees of each species of conifer (aged 70-100 years).

A 0.5-ml sample of a 10% solution of the resin acids in methanol was neutralized with a 0.1 N benzene solution of anhydrous tetramethylammonium hydroxide (in the presence of one drop of 0.1% methanolic phenolphthalein). The solution was evaporated almost to dryness and diluted with methanol (1:1) [3]. The resulting solution (0.5-1.0 μliter) was introduced into the evaporator block of an LKhM-8M chromatograph. The column was filled with Chromosorb G (60-80 mesh) impregnated with polyethylene glycol phthalate (5%). The temperature of the column was 200°C, the carrier gas was nitrogen (0.45 atm at the inlet); when a flame-ionization detector was used, the consumption of hydrogen and air did not exceed 20 ml/min.

The acids were identified by the GLC method with the injection of authentic pure substances. The sandaracopimarate, palustrate, and isopimarate were identified by comparing their relative retention times (RRT) with those given in the literature [4].

The composition of the mixtures of resin acids on the chromatograms was calculated by internal normalization of the areas of the peaks, which were determined provisionally as the products of the heights of the peaks and their bases (the mean square error for the main components of the mixture of resin acids of the balsams with three recordings was 2.8%).

The amount of levopimaric acid in the mixtures of resin acids was determined chemically [5].

All the species of conifers produce resin acids of similar qualitative but different quantitative compositions (Table 1).

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TABLE 1. Relative Retention Times of the Methyl Esters of the Resin Acids and Their Composition for Different Conifer Balsams (tr. means less than 0.1%)

Acid	RRT	Mixtures of acids, contents, %						
		P. silvestris	P. palasiona	P. pityusa	P. hamata	P. excelsa	L. sibirica	P. sibirica
Fatty acids (mixture)	—	0,4	0,1	0,1	0,1	5,2	0,4	0,3
X_1	0,33	0,3	0,4	0,5	0,4	1,0	0,1	0,1
X_2	0,38	0,2	0,4	0,4	0,3	0,7	2,4	0,5
Pimaric	0,43	9,0	6,1	0,1	11,5	1,2	2,8	tr.
Sandaracopimaric	0,50	1,6	2,1	2,1	2,0	2,4	3,0	1,2
Dihydroabietic	0,54	0,3	5,1	tr.	2,4	tr.	tr.	tr.
Levopimaric	0,62	27,0	17,3	12,6	36,0	28,2	1,0	1,0
Palustric	0,62	20,8	27,4	16,0	14,8	15,6	7,6	4,0
Isopimaric	0,68	6,0	11,5	9,5	6,5	12,0	25,3	25,4
X_3	0,76	1,9	0,5	сл.	0,6	2,1	1,3	сл.
Abietic	1,00	13,3	9,2	38,0	8,0	8,5	42,0	32,4
Dehydroabietic	1,08	5,7	6,1	14,1	5,2	15,6	10,6	4,5
Neoabietic	1,20	13,5	13,8	6,1	12,2	7,5	3,5	4,0
New resin acid (X_4)	1,25	tr.	tr.	0,5	tr.	tr.	tr.	26,6

The composition of the resin acids of the Siberian larch and pine is distinguished by the small amount (not more than 5% each) of pimaric, sandaracopimaric, levopimaric, and neoabietic acids and the large amount of isopimaric and abietic acids. The resin acids of the Siberian pine are distinguished from the resin acids of the Siberian larch, and also from other conifers, by their large content (about 27%) of the so-called new resin acid ($C_{20}H_{30}O_3$) (X_4) of undetermined chemical structure [6].

The quantitative compositions of the resin acids of Norway spruce and various species of pines, especially Scotch pine and P. hamata, are similar to one another. In the balsams of P. hamata, Scotch pine, and Norway spruce there are large amounts of levopimaric, palustric, and abietic acids. There is a particularly large amount of abietic acid in the mixture of resin acids from the balsam of P. pityusa.

Compared with all the other conifers, the balsam of Norway spruce contains a large amount of higher fatty acids. As our investigations have shown [7], the chemical composition of the fatty acids produced by various conifers are similar. They contain saturated and unsaturated fatty acids (a total of about 30 acids). Among the saturated fatty acids the main one is palmitic (6-14%), and the main unsaturated acids are oleic and linoleic (11-27%).

The similar qualitative acid composition of the balsams of the various species of conifers shows that the mechanism for the biogenesis of the resin acids is the same.

The difference in the quantitative composition of the balsams shows that particular groups of resin acids are formed in various species of conifers as a result of biogenesis.

CONCLUSIONS

1. The chemical composition of mixtures of resin acids isolated from the balsams of native conifer species, Scotch, Crimean, and Siberian pines and P. hamota and P. pityusa, Norway spruce, and Siberian larch, has been studied by the GLC method.

2. The following resin acids are present in the balsams: pimaric, sandaracopimaric, levopimaric, palustric, isopimaric, abietic, dehydro- and dihydroabietic, neoabietic, four acids of undetermined chemical structure, and fatty acids. The balsams differ in the quantitative composition of the resin acids that they contain.

LITERATURE CITED

1. Kh. A. Cherches and I. I. Bardyshev, in: Synthetic Products from Rosin and Turpentine [in Russian], Minsk (1964), p. 267.
2. I. I. Bardyshev, A. L. Pertsovskii, A. N. Bulgakov, and V. G. Kazushchik, DAN BSSR, No. 12, 636 (1968).
3. I. N. Mason and R. V. Lawrence, J. Chem., Eng. Data, 12, 279 (1967).
4. G. Valkanas and N. Iconomou, Pharmac. Acta Helv., 41, 209 (1966).

5. A. G. Sokolov, Tr. TsNILKhI, No. 13, 119 (1959).
6. I. I. Bardyshev, Kh. A. Cherches, and Zh. F. Kokhanskaya, ZhPKh, 34, 1147 (1961).
7. I. I. Bardyshev, S. I. Kryuk, and A. L. Pertsovskii, KhPS [Chemistry of Natural Compounds], 361 (1970).