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COMPOSITION OF THE RESINOUS SUBSTANCES OF CONIFER NEEDLES.

I. GROUP COMPOSITION OF THE RESINOUS SUBSTANCES OF THE NEEDLES

OF THE PINE *Pinus silvestris*

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UDC 634.0.866.1:647.0.32.475.4

A system of solvents has been selected for the successive extraction of pine needles (benzene, isopropanol, and isopropanol + chloroform). Extraction was carried out by the steeping method at room temperature, and the yield of resinous substances was 19.4%. The extractive substances isolated consisted of neutral compounds, glycolipids, and phospholipids. The group compositions of the neutral substances have been determined by column chromatography. The predominating components in them are hydrocarbons (15.9%), diglycerides (10.7%), and waxy substances (27.6%).

The chemical composition of conifer needles is extremely complex and diverse, and it depends on many conditions; specific features of the plants, age of the plant and of the needles themselves, the environmental conditions, the type of soil, etc. [1-3]. The composition of the resinous substances may also change with the solvent with which extraction is performed, and also with a change in the conditions of extraction [4]. There is information in the literature on the chemical composition of pine needles, but this information characterizes the resinous substances of trees growing mainly in the European part of the USSR [3]. Information on the composition of the resinous substances of the needles of species growing in Siberia is practically nonexistent.

The aim of the present work was to study the group composition of the resinous substances of the needles of the pine *Pinus silvestris* obtained by extraction of the initial raw material successively with organic solvents (Table 1).

As can be seen from Table 1, with the selected method of extraction a considerable yield of resinous substances was achieved — about 19%. Furthermore, extraction at room temperature excluded the destruction of components unstable to heat. The use of isopropanol as solvent did not exclude the possibility of the extraction of water-soluble components (salts, sugars, and amino acids, etc.). To eliminate these substances from the extract, provision was made for its preliminary washing with water. After this, the group composition of the extract isolated was determined. The following groups of substances were then isolated: neutral substances, glycolipids, and phospholipids. The residue on the silica gel, the oxidized substances, was eluted with a mixture of ethanol and benzene. The results of the determination of the group compositions of the resinous substances isolated are given at the top of the next page, immediately following Table 1.

Thus, the extractive substances isolated consisted to the extent of 65% of the group of so-called neutral substances.

TABLE 1. Extraction of Pine Needles with Organic Solvents

Extraction	Yield of resinous sub., % on	
	abs. dry weight	extractive substances
Solvent—benzene		
1	7.03	36.27
2	1.75	9.05
3	0.41	2.18
4	0.36	1.81
5	0.26	1.34
6	0.20	1.03
7	0.19	0.98
8	0.10	0.51
Total	10.30	53.15
Solvent — isopropanol		
1	2.96	15.29
2	1.75	9.03
3	0.91	4.69
4	0.30	1.43
Total	5.92	30.44
Extraction with chloroform — isopropanol (1:1)		
1	1.09	5.62
2	0.99	5.18
3	0.61	3.15
4	0.40	2.05
5	0.09	0.41
Total	3.18	16.41
Grand total	19.40	100.00

Eluent Group of substances Yield of the fractions, % by weight on

		Extractive substances	Absolutely dry needles
Chloroform	Neutral	65.85	12.76
Acetone	Glycolipids	17.20	3.34
Methanol	Phospholipids	9.35	1.81
Ethanol—benzene	Oxidized + losses	7.60	1.47
Total		100.00	19.33

In view of this, the next step in the work was to determine the group composition of these substances:

Eluent	Group of substances	Amount, % on the neutral substances
Hexane	Hydrocarbons	15.90
Hexane—ether	Sterol esters	3.70
99:1	Triglycerides	1.05
95:5	Fatty acids	2.10
92:8	Diglycerides	10.70
85:15	Monoglycerides	7.40
Ether	Wax	27.69
Isopropanol		
Ethanol—benzene	Substances extractable by the mixture + losses	31.46
Total		100.00

Thus, the bulk of the neutral substances is represented by hydrocarbons, diglycerides, and waxy substances. Fatty acids make up only 2.1% of the neutral substances.

EXPERIMENTAL

The initial needles were dried in vacuum over calcium chloride and were extracted by the steeping method at room temperature with organic solvents for 12-20 h, until decoloration was complete. The choice of solvent was governed by its capacity for breaking the bonds of the resinous substances with the other components of the needles and for eluting the extractive substances [5]. On this basis, we used the following solvents: benzene, isopropanol, and chloroform + isopropanol (1:1).

The following scheme is proposed for studying the composition of the resinous substances:

1. Initial needles; drying in vacuum; successive extraction with organic solvent; evaporation of the extracts in vacuum followed by dissolution in chloroform; treatment of the extract obtained with water; drying the extract.

2. Extract of the resinous substances in chloroform: column chromatography; group composition: column chromatography of the neutral substances isolated.

According to the proposed scheme of investigation, the isolated resinous substances were separated with the aid of column chromatography on type KSK silica gel (100-300 mesh) as adsorbent. Chloroform → acetone → methanol were used as eluents, eluting, respectively, substances of neutral character, glycolipids, and phospholipids. The neutral substances were also separated by eluent column chromatography [5].

SUMMARY

1. Resinous substances amounting to 19.40% on the absolutely dry weight have been isolated from pine needles by successive extraction with a series of organic solvents.

2. The resinous substances consist of neutral compounds (65.8%), glycolipids (17.2%), and phospholipids (9.3%).

3. The neutral substances are represented mainly by hydrocarbons (about 16%), diglycerides (about 11%), and waxy substances (about 28%).

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