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INVESTIGATION OF THE INFLUENCE OF THE POLARITY OF THE SOLVENT ON THE COMPOSITION OF THE EXTRACTIVE SUBSTANCES AND POST-EXTRACTION RESIDUES OF THE BARK OF *Abies sibirica*

V. M. Ushanova and S. M. Repyakh

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The chemical compositions of the initial bark of the Siberian fir Abies sibirica *and of the solid residues after extraction with carbon dioxide, water, and alcohol have been studied. On successive extraction, the yield of extractive substances amounted to 25.05% of the absolutely dry bark. The carbon dioxide, aqueous, and alcoholic extracts obtained have been investigated. The carbon dioxide extract was found to contain 34.97% of essential oil, while only traces of it were detected in the aqueous and alcoholic extracts.*

The bark of the Siberian fir *Abies sibirica* is a multitonnage waste of the timber-processing industry and amounts to 13% of the wood gathered [1].

Fir oil is obtained from the fir bark, and the post-extraction residues are used for the creation of "thermal" hothouse soils.

The task of the present work was to increase the yield of extractive substances by the successive extraction of fir bark. We investigated the influence of the type of extractant on the composition and yield of extractive substances from the bark. The extractants used were liquified carbon dioxide, water, and ethyl alcohol.

In the successive method of extraction that was selected, the yield of extractive substances amounted to 25.05%. Moreover, extraction at room temperature excludes the degradation of non-heat-stable components. By using liquid carbon dioxide, which has a low boiling point, as the extractant, the substances extracted are obtained in the native state.

The carbon dioxide extract from fir bark consisted of a complex mixture of biologically active substances containing essential oil, waxy substances, vitamins, provitamins, and other useful substances. Thanks to the presence of such components, it possessed high biogenostimulating and bactericidal properties.

The use of ethyl alcohol as solvent does not exclude the possibility of the extraction of water-soluble components (salts, sugars, amino acids, etc.). To eliminate these substances from the extract, provision was made for preliminary extraction with water. The physicochemical indices of the extracts obtained and their compositions are given in Table 1. As can be seen from Table 1, the physicochemical indices of the extracts depended on the solvent used for extraction.

As is known, the aroma of extracts is due to the presence in them of essential oils and odoriferous substances. On extraction with liquefied carbon dioxide almost the whole of the essential oil contained in fir bark is extracted, and only traces of it is detected in aqueous and alcoholic extracts.

The most important components of aqueous extracts of the bark are carbohydrates, tannins, ascorbic acid, and polysaccharides. The tannins are readily isolated and impart a brownish color to the aqueous extracts.

The results of the investigations showed that a considerable part of the components of the bark (16.42%) was extracted by ethyl alcohol. Aliphatic hydrocarbons, alcohols, and fatty acids formed the main group of substances soluble in nonpolar solvents. The nonpolar fraction also contained fats (esters of higher fatty acids with glycerol, with higher aliphatic alcohols, and with sterols) [2].

We have studied the composition of the post-extraction residues with the aim of using them as a fodder product.

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TABLE 1. Characteristics of Extracts Obtained from the Bark of the Siberian Fir

Index	Extract		
	carbon dioxide	aqueous	alcoholic
External form, color	Orange-yellow oily liquid	Light brown liquid	Red-brown liquid
Smell	Bark	Bark	Bark
Refractive index n_D^{20}, 20±2°C	1.5028	1.3340	1.3708
Density, g/cm³, 20±2°C	0.960	1.001	0.830
Content of extractive substances, % on a.d.w.	6.50	2.13	16.42
Ash, %	Not det.	0.0584	0.010
Acid No., mg KOH	38.20	7.00	4.62
Ester No., mg KOH	52.82	2.10	11.29
Content of:			
reducing substances, %	0.386	0.167	Not det.
vitamin C, mg %	25.75	11.42	Not det.
essential oils, %	34.97	Tr.	Tr.
chlorophylls, mg %	1.40	–	2.30
vitamin E, mg per 100 g of extract	25.60	–	Not det.
tannides, %	0.019	0.810	

TABLE 2. Characteristics of the Initial Samples and Post-Extraction Residues of Siberian Fir Bark

Index	Initial bark	Residue of the fir bark after extraction with		
		CO_2	CO_2 and H_2O	CO_2, H_2O and C_2H_5OH
Lignin substances, %	42.84	41.59	41.19	34.85
Ash, %	4.21	3.46	3.03	2.78
Vitamin C, mg %	48.40	2.80	Abs.	Abs.
Polysaccharides, %:				
readily hydrolysable	9.72	12.11	9.45	10.14
difficultly hydrolysable	16.63	18.90	17.87	11.63
Mass fraction of cellulose, % a.d w.	75.6	54.8	40.5	42.6
Digestibility, %m	32.3	41.2	40.3	31.5

The bark contained a considerable amount of lignin and other polymeric phenol compounds. This fraction had a composition and properties differing from the corresponding fraction of wood. The composition of the bark lignin was more heterogeneous than that of the wood lignin.

The bulk of the bark lignin (30-50%) was similar to the wood lignin, while the remainder, insoluble in 72% sulfuric acid, differed from the wood lignin by the fact that it contained a high level of carboxy groups and few methoxy groups [2].

The extracted bark consisted of three different groups of substances: cellulose and other unextractable polysaccharides, lignin, and suberin or a hydroxyacid complex. The carbohydrate fraction was the largest fraction in the bark; nevertheless, it was not so large as in the wood. The polysaccharides of the bark were predominantly cellulose and pentosans. About 10% of the carbohydrates was present in the aqueous solutions. The amount of hexosans and pentosans in the bark averaged about 30-45%. Of the components of the hydroxyacid complex, the most abundant was suberin, which is a constituent part of the walls of the cork cells of the outer layer of the bark. The suberin of coniferous species contains ferulic acid [2]. Bark contains 2-5% of mineral substances, which is considerably more than in wood. The high ash content is a consequence of the relatively large accumulation of calcium carbonate crystals in the bark tissues, and it also depends largely on the conditions of the growth site of the stands of timber [2].

Table 2 gives the ash contents of the initial fir bark and of the post-extraction residues. The results of the investigations show a decrease in the ash contents at each successive extraction.

As can be seen from Table 2, in the performance of succesive extractions the vitamin C content fell from 48.40 mg % in the initial bark to 2.80 mg % in the residue after carbon dioxide extraction. This is due to the fact that a considerable part (25.75 mg %) of the vitamin C was present in the CO_2 extract and 11.42 mg % in the aqueous extract. No vitamin C was detected in the residues after extraction with water and ethyl alcohol, since the residual vitamin C was partially extracted with water (11.42 mg %) and was partially decomposed under the action of the high temperature.

Polyphenols and triterpenes resembling lignin in some degree are an intrinsic part of the bark. The lignin present in the cell walls of the bark apparently does not differ appreciably from wood lignin. Lignin is regarded as an encrusting substance imparting great strength to the cell wall. We determined the lignin content by the use of 72% sulfuric acid. The results of the investigations showed an insignificant change in the level of lignin substances from 42.84% in the initial bark to 41.59% after extraction with carbon dioxide and 41.19% after extraction with water. Subsequent extraction with ethyl alcohol had a considerable effect on the level of lignin substances in the residue: it amounted to only 34.85%. This may be explained by the assumption that the polyphenols dissolved in the alcohol and the lignin proper remained behind.

The bulk of the substances in plant materials belongs to the carbohydrate part of the solid residue, represented by readily and difficulty hydrolyzable polysaccharides. The readily hydrolyzable polysaccharides form the main mass of hemicelluloses. In the performance of analysis, the hemicelluloses undergo hydrolysis with the formation of monosaccharides. The amount of monosaccharides formed is determined from their reducing capacity.

The ratio beween readily and difficultly hydrolyzable polysaccharides remains unchanged and is not affected by the extractant (see Table 2).

We determined the food values of the post-extraction residues — the mass fractions of cellulose in them and their digestibilities.

According to the technical specifications for the production of coniferous fodder-flour [3], the fodder product must have a digestibility of not less than 30% and the mass fraction of cellulose should not exceed 32%. The cellulose content shows how readily the fodder is assimilated. It can be seen from Table 2 that the mass fraction of cellulose was higher than permissible both in the initial bark (75.6%) and in the post-extraction residues (54.8, 40.5, and 42.6%), which shows the poor digestibility of these products.

To evaluate food value we used the digestibility index. The digestibility values obtained were higher than the threshold laid down by the technical specifications.

EXPERIMENTAL

The initial fir bark was moistened and ground in a laboratory mill and was then extracted with liquefied carbon dioxide for 5 h at a liquor ratio of 6, a temperature of 20°C, and a pressure of 5.7 MPa. After the production of a CO_2 extract with a high content of biologically active substances and essential oils (in the first stage), the solid residue was subjected to flow-through extraction [4] with water at 105°C for 3 h (in the second stage). The resulting aqueous extract was filtered and its composition was studied; the solid residue was then dried to the air-dry state and was extracted with ethyl alcohol at 80°C for 3 h (in the third stage). Waxy substances were separated from the cooled extract, and the alcohol was distilled off and was used in repeat treatments of the material. The regeneration coefficient was 0.70.

By using known methods, in the extracts obtained we determined physicochemical indices, acid and ester Nos. [5], and levels of essential oil, ascorbic acid [6], reducing substances, ash [7], vitamin E [8], and chlorophylls [9].

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