COMPOSITION OF THE RESINOUS SUBSTANCES OF CONIFER NEEDLES.

III. WAXY SUBSTANCES FROM THE WOODY VERDURE OF *Pinus sylvestris*

O. I. Lebedeva, G. V. Tikhomirova, and S. M. Repyakh

UDC 634.0.866.1.674.0.32.4.75.4

The individual compositions of the wax isolated from an isopropyl extract of the woody verdure and of an industrial sample of needle wax have been investigated with the aid of GLC. The acids isolated from the wax have been identified, and the alcoholic fraction has been separated without identification. It has been shown that the wax obtained from the isopropyl alcohol extracts is suitable for industrial use.

On processing woody verdure, together with other products, a wax is obtained the yield of which amounts to about 0.5% (on the absolutely dry raw material). This product finds use in the perfumery and cosmetics industry, but there is practically no information on the chemical composition of the wax, and in factories it is characterized by such indices as the acid number, the ester number, the content of volatile matter, and the melting point [1].

The posing of the question of the complex processing of woody verdure requires a knowledge not only of the properties of the products obtained but also of their group and chemical compositions, which permits the area of their use to be determined. In the technological process for the complex processing of woody verdure the use of isopropyl alcohol as solvent is envisaged. We have investigated the waxy substances isolated in this way (below, wax 1). In parallel, we investigated a wax obtained under industrial conditions from gasoline solutions (below, wax 2).

The usual physicochemical characteristics of the waxes investigated were determined in accordance with the requirements of the technical conditions for conifer wax.

Both samples of wax, after saponification with caustic soda, were separated into acidic and alcoholic fractions followed by their further separation into individual components with the aid of GLC.

The samples differed little from one another with respect to their physicochemical characteristics:

Index	TU-13012-70	Wax-1	Wax-2
Acid No., not less than, mg KOH/g	30-65	58.9	51.8
Ester No., not less than, mg KOH/g	150-200	319.5	270.2
Iodine No., g/100 g	15-25	14.7	12.3
Volatile matter content, not more than, %	1-0	0.94	0.98
mp, °C	55-70	82.0	86.0
External form	Light green powder with coniferous smell	Corresponds	

Some increase in the ester no. as compared with the technical conditions does not contradict them, since indices of not less than 150-200 are specified. The increase in the melting point is due to a more accurate method of determination [1].

The results of gas–liquid chromatography showed that the acid fraction of wax 1 was represented by thirteen individual acids, while in wax 2 there were only ten. Acids with larger numbers of carbon atoms (for example behenic) were found in wax 1.

Siberian Technological Institute, Krasnoyarsk. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 264-266, March-April, 1985. Original article submitted January 13,1983.

 0009-3130/85/2102-0248$09.50

The bulk of the acids both of wax 1 and of wax 2 consisted of stearic and linolenic, and also of the unidentified acids X_2 and Y_1:

Acid	Proportion of the sum of the acids, %	Acid	Proportion of the sum of the acids, %
Wax 1		Wax 2	
X_1	1.5	Lauric	0.1
Lauric	12.3	Myristic	1.9
Tridecanoic	tr.	Y_1	34.7
Myristic	5.9	Y_2	2.2
X_2	26.0	Palmitic	2.1
Palmitic	3.0	Linolenic	14.6
Linolenic	14.0	Oleic	1.4
Linoleic	1.7	Stearic	40.0
Oleic	1.8	Y_3	1.5
Stearic	26.8	Y_4	1.6
X_3	0.3		
X_4	5.4		
Behenic	1.4		

A preliminary study of the compositions of the alcohol fraction of the samples of wax also showed that wax 1 was represented by eight individual components and wax 2 by only five. Thus, wax 1 differs from wax 2 by having a more complex component composition.

EXPERIMENTAL

A sample of wax 1 was isolated under laboratory conditions in the process of working up the coniferous paste in the extraction of the woody verdure of the pine with 85% isopropanol. The sequence of treatment was as follows: The woody verdure of the pine was subjected to extraction with isopropyl alcohol with simultaneous grinding. The extract was separated off from the solid residue and the solvent was distilled off. The last traces of organic solvents were eliminated by steam distillation. The remaining mixture of fat- and water-soluble components separated on cooling into three layers(an upper layer of resinous substances; a middle layer of aqueous extract; and, on the bottom, a mixture of waxy and resinous substances. To eliminate deposited resinous substances from the surface of the waxy substances, the wax was reprecipitated from isopropanol in the cold followed by washing with water (to eliminate traces of solvent) and was dried in the air. The prepared samples of wax were ground to a powder.

For the performance of GLC, the wax was first subjected to saponification with 3 N potassium hydroxide solution in a flask with a reflux condenser for 3 h (after which time a clear solution has been obtained). After saponification, the solution was transferred quantitatively into a separatory funnel, to which ether was added in 25-ml portions. The ethereal extracts were combined, washed with water (to neutrality), and dehydrated with sodium sulfate. Then the ether was distilled off and the residue was brought to constant weight in vacuum. The aqueous layer and the wash-waters were combined and acidified with sulfuric acid solution. After the end of the reaction the acids liberated were extracted with diethyl ether. The extracts were dehydrated and, after the extractant had been driven off, they were brought to constant weight. The samples obtained in this way were subjected to further separation with the aid of GLC.

Chromatography was carried out on an LKhM-72 chromatograph with a thermal conductivity detector. Stainless steel column, 4 mm × 3000 mm filled with chromaton N-AW upon which Apiezon L has been deposited in an amount of 15% of the weight of the solid support. The carrier gas was helium, at a rate of flow of 60 ml/min. The temperature of the detector was 300°C and that of the evaporator 215°C. The column was heated from 100 to 300°C at the rate of 3°C/min.

The sample was introduced in the form of the methyl esters of the acids, obtained by methylation with diazomethane. The qualitative composition of the acids isolated was determined by the method of adding the pure substances, and the quantitative composition by the method of internal normalization.

The alcohols isolated from the wax were separated in an identical column with heating from 50 to 300°C at the rate of 2.5°C/min.

The physicochemical characteristics of the samples of waxes investigated were determined in accordance with the technical conditions [1].

SUMMARY

A wax has been isolated from propyl alcohol extracts of the woody verdure of the pine and its physicochemical characteristics have been determined.

The individual composition of the acid fraction isolated has been determined, and the presence of 13 acids has been shown, of which nine have been identified.

An investigation of the alcohol fraction of the wax showed that the wax isolated from the woody verdure by extraction with isopropyl alcohol is not inferior in its chemical indices to industrial samples and can be recommended for industrial use.

LITERATURE CITED

1. Technical Conditions. Coniferous Wax. TU LatvSSR 012-70 [in Russian], (1976).
2. S. M. Repyakh, The Study of the Chemical Composition of the Woody Verdure of the Main Timber-Forming Trees of Siberia and the Development of Methods for Obtaining Biologically Active Substances. The Study of the Chemical Composition of the Essential Oils, Lipids, and Woody Verdure [in Russian], Krasnoyarsk (1981), P. 49.