EXTRACTIVE SUBSTANCES OF THE BARK

OF Picea obovata

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A fraction of petroleum-ether-soluble substances (2.27%) of the weight of the dry bark) has been isolated previously from an acetone extract of the bark of <u>Picea</u> <u>obovata</u> Ledb. (Siberian spruce) [1] and has been separated by the usual method [2] into hydrocarbons (4.5%), neutral oxygen-containing substances (22.8%), and acids (59%).

The acids were identified by the GLC method [3] in the form of their methyl esters. It was found that the mixture of acids consisted of 25 components of the aliphatic series, both saturated and unsaturated, with numbers of carbon atoms from 8 to 24 (mainly greater than 16). The resin acids consisted of isopimaric, palustric (levopimaric), and dehydroabietic (the main component).

The hydrocarbons were separated by vacuum distillation into two fractions: a sesquiterpene fraction with bp up to 130° C/5 mm (yield 12.9%) and a residue (after additional purification on alumina, yield 38.1%). The sesquiterpene fraction (containing about 6% of monoterpenes as impurities) was studied by the GLC method. The following were identified under the conditions corresponding to the separation of sesquiterpenes [5]: longifolene (the main component), ylangene (copaene), longicyclene, α -murolene, caryophyllene, sibirene, and isolongifolene. Under the conditions described by Vol'skii et al. [6] the monoterpenes β -phellandrene, β -pinene, α -thujene, α -pinene, santene, α -phellandrene, limonene, and Δ^3 -carene, and also p-cymene, were identified.

By adsorption chromatography on a column of silica gel impregnated with silver nitrate, a mixture of paraffinic hydrocarbons (68.5%) and a macrocyclic diterpene identified by direct comparison as cembrene (10.8%) was isolated [7].

By chromatography on a column of silica gel of the neutral oxygen-containing compounds the following individual components were obtained and identified: epimanoyl oxide [8, 9], β -sitosterol and three of its esters (the acids in the saponification products were myristic, palmitic, and a C-20-neo acid, identified by the GLC method), β -sitosterol and its acetate, and also abienol [10].

In addition, a saturated monohydric alcohol $C_{24}H_{50}O$ with mp 72-73°C (from ether) was isolated and its acetate with mp 51-52°C and mol. wt. 396 (mass spectrum) was prepared.

Thin-layer chromatography on a fixed layer of silica gel and, in some cases, GLC were used to monitor the course of column chromatography and to determine the individuality and identity of the compounds.

LITERATURE CITED

- 1. G. A. Nair and E. von Rudloff, Can. J. Chem., <u>37</u>, 1608 (1959); 38, 177 (1960).
- 2. A. I. Lisina, V. K. Finogenova, L. N. Vol'skii, and V. A. Pentegova, Izv. Sibirskogo Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, Series No. 2, No. 4, 122 (1967).
- 3. H. Burchfield and E. Storrs, Biochemical Applications of Gas Chromatography, Academic Press (1962).

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- 4. E. N. Shmidt, N. K. Kashtanova, L. N. Vol'skii, M. A. Chirkova, and V. A. Pentegova, Izv. Sibirskogo Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, Series No. 5, No. 12 (1970) p. 118.
- 5. V. A. Pentegova, Zh. V. Dubovenko, L. N. Vol'skii, S. M. Vasilyuk, M. A. Chirkova, and E. N. Shmidt, Izv. Sibirskogo Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, Series No. 2, No. 4 (1968) p. 114.
- 6. L. N. Vol'skii, Zh. V. Dubovenko, N. A. Gershtein, and V. A. Pentegova, Khim. Prirodn. Soedin., <u>1</u>, 382 (1965).
- 7. W. G. Dauben, W. E. Thiessen, and P. R. Resnick, J. Amer. Chem. Soc., <u>84</u>, 2015 (1962).
- 8. E. N. Shmidt, V. Beneshova, M. A. Chirkova, and V. A. Pentegova, Izv. Sibirskogo Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, Series No. 5, No. 12 (1969) p. 116.
- 9. E. P. Swan, Can. J. Chem., <u>45</u>, No. 13, 1588 (1967).
- 10. P. S. Gray and J. S. Millis, J. Chem. Soc., 5822 (1964).