LITERATURE CITED

1. M. G. Van Golde, A. F. A. Zwall, L. L. M. Van Deenen, Proc. Koninkl. Ned. Acad. Wetenschap., Ser. B, 68, 255 (1965).
2. A. Kuksis and L. Maral, Lipids, 2, 217 (1968).
3. K. Hasegawa and T. Suzuki, Lipids, 8, 631 (1973).
4. K. Hasegawa and T. Suzuki, Lipids, 10, 667 (1975).
5. E. V. Dyatlovitskaya, G. V. Yanchevskaya, and L. D. Bergel'son, Biokhimiya, 39, 432 (1974).
6. Yu. A. Tadzhibaev, Kh. S. Mukhamedova, and S. T. Akramov, Khim. Prirodn. Soedin., 435 (1976).
7. Yu. A. Tadzhibaev, Kh. S. Mukhamedova, and S. T. Akramov, Khim. Prirodn. Soedin., 109 (1977).
8. Yu. A. Tadzhibaev, Kh. S. Mukhamedova, and S. T. Akramov, Khim. Prirodn. Soedin., 502 (1977).
9. A. L. Markman, T. V. Chernenko, and A. U. Umerov, Prikl. Biokhim. Mikrobiol., 5, 616 (1969).
10. W. Staffal, F. Chu, and E. H. Ahrens, Anal. Chem., 31, 307 (1959).
11. A. Sh. Isamukhamedov, L. A. Shustanova, and S. T. Akramov, Khim. Prirodn. Soedin., 324 (1977).

THE MONOTERPENES OF THE ESSENTIAL OILS OF CONIFEROUS TREES OF SIBERIA

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In connection with the growing volumes of lumbering operations in the felling areas of our country there is an accumulation of tree verdure which is being used inadequately. The cells of tree verdure contain about 40% of biologically active substances (calculated on the dry matter) [1]. One of the possible products of its processing consists of essential oils which, as is well known, may be effective medicinal agents: antimicrobial, antiviral, bactericidal, and fungicidal effects of coniferous essential oils are known [2, 3].

The essential oils of Siberian coniferous trees are not obtained on the industrial scale, with the exception of fir oil, in spite of the large reserves of raw material. One of the reasons for this is the inadequacy of the study of their compositions. Isolated items of information concerning the composition and physical properties of essential oils from the verdure of some coniferous trees growing in Siberia have appeared in the literature [4-8].

The essential oils from the needles and lopping litter differ from one another [7, 9] and, in addition, the compositions of the essential oils depend on the growth site [10, 11]. It must also be noted that all the investigations mentioned were devoted to an investigation of the essential oils from needles or from lopping litter obtained under laboratory conditions.

We have investigated essential oils isolated from the technical verdure of some coniferous trees of Siberia under industrial conditions. The physicochemical characteristics of the coniferous essential oils from technical verdure were as follows:

Index	*Pinus sylvestris Ldb.*	*Pinus sibirica Mayr.*	*Abies sibirica Ldb.*	*Picea obovata Ldb.*
Density, ρ, g/cm³	0,8855	1,8782	0,8955	1,8895
Refractive index, n_D^{20}	1,4785	1,4744	1,4730	1,4789
Acid No., g KOH/g	1,19	0,86	0,99	2,62
Saponification No. g KOH/g	82,00	53,27	129,50	65,39
Ester No., g KOH/g	81,81	52,41	128,51	62,77

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The coniferous oils the physicochemical characteristics of which are given above were free from the acid fraction, since, on the one hand, in the presence of acidic agents the capacity of terpenes for various chemical transformations rises and, on the other hand, information on the amounts of acids and phenols in the essential oils is of independent interest. There is some information in the literature on the amounts of acids and phenols in coniferous essential oils [12], but we have found no information at all on their presence in the essential oil of Siberian coniferous trees.

The oils that we investigated contained acids and phenols in very small amounts (% on the essential oils):

	Pinus sylvestris	*Pinus sibirica*	*Abies sibirica*	*Picea obovata*
Acids	0,34	0,17	0,35	0,87
Phenols	0,13	0,62	0,15	0,21

The bulk of the neutral substances of the coniferous essential oils consisted of fractions distilling at a temperature of up to 60°C under a residual pressure of 665 Pa.

The amounts of this fraction in the neutral parts of the essential oils of the coniferous trees investigated were different (%):

Pinus sylvestris	69,68
Pinus sibirica	90,58
Abies sibirica	57,99
Picea obovata	74,32

The results of the investigation show that the fraction distilled over consists of terpene hydrocarbons (see below). In the case of fir oil, in addition to terpene hydrocarbons a considerable amount of bornyl acetate distils over.

All the oils contained large amounts of α-pinene. α-Pinene is the main component in pine oil and, particularly, in cedar oil. Fir and spruce oils contain a large amount of camphene, even exceeding the amount of α-pinene in them. Fir and spruce oils are similar: they contain considerable amounts of santene and tricyclene. Cedar oil differs from the oils of the other coniferous trees by a high content of β-phellandrene and a particularly low content of Δ^3-carene in the monoterpene fraction.

The main information on the composition of the monoterpenes of the essential oils of the trees that we investigated agrees with that found previously [6-8] for essential oils isolated under laboratory conditions.

EXPERIMENTAL

Isolation of the Essential Oils. The raw material for obtaining the essential oils was technical verdure (coniferous spurs not more than 35 cm long and not more than 8 mm thick) of *Pinus sylvestris*, *Pinus sibirica*, *Abies sibirica*, and *Picea obovata* growing in Krasnoyarsk territory. The essential oils were obtained in the Poima timber enterprise on an industrial apparatus of the Western Siberian type. The indices of the technological process were kept the same as envisaged for the production of fir oil [13]. The time of distillation of the oils was 16 h. The oils obtained were dried over anhydrous sodium sulfate and filtered. The compositions of the monoterpene fractions of the coniferous essential oils were as follows (% on the fractions):

Component	*Pinus* sylvestris	*Pinus sibirica*	*Abies sibirica*	*Picea obovata*
Santene	Tr.	Tr.	4,43	1,56
Tricyclene	0,82	Tr.	3,39	2,54
α-Pinene	52,72	64,26	18,70	21,05
Camphene	6,04	2,12	37,44	25,82
β-Pinene	7,60	5,60	2,44	7,25
Myrcene	5,71	1,51	0,39	3,55
Δ^3-Carene	13,93	1,11	12,80	16,28
Dipentene	6,64	12,39	8,31	12,97
β-Phellandrene	4,69	11,94	3,97	2,14
Terpinolene	0,65	0,44	0,24	1,47
γ-Terpinene	Tr.	Tr.	—	—
Bornyl acetate	0,89	0,52	8,61	4,78

The physicochemical characteristics of the essential oils were determined by known methods [14].

The acids and phenols were extracted from the essential oils successively with 5% solutions of sodium carbonate and sodium hydroxide by the generally adopted method [14].

To determine the individual compositions of the monoterpenes from the neutral fraction of the essential oils, the terpene hydrocarbon fraction was distilled off at a temperature of up to 60°C and a residual pressure of 665 Pa, which corresponds approximately to their boiling points. The qualitative and quantitative compositions of the fraction isolated were determined by the GLC method on an LKhM-72 chromatograph with a flame-ionization detector in two columns:

column 1, 6000 × 4 mm; stationary liquid phase 16% of TCEP (1,2,3-tris(cyanoethoxy)propane); solid support Chromaton N-AW-HMDS, grain size 0.20-0.25 mm; and column 2, 3000 × 4 mm, stationary liquid phase 5% of Silicone SE-30 + 2% of PEG-2000 (polyethylene glycol) on Chromaton N-AW-DMCS with a grain size of 0.20-0.25 mm.

The columns were heated with programming of the temperature from 60 to 110°C at the rate of 0.5 deg/min. The temperature of the detector was 200°C and that of the evaporator 250°C. Helium was used as the carrier gas and a rate of flow of 70 ml/min.

SUMMARY

1. The essential oils of some coniferous Siberian trees isolated under industrial conditions have been investigated.

2. The physicochemical characteristics and group compositions of the essential oils have been determined.

3. The substance compositions of the monoterpene hydrocarbons have been determined by the GLC method.

LITERATURE CITED

1. L. V. Vasil'eva and S. I. Ladinskaya, Izv. Vyssh. Uchebn. Zaved., Lesnoi Zh., No. 4, 115 (1975).
2. P. Toleva and I. Tolev, in: Fourth International Congress on Essential Oils, Tbilisi, September, 1968 [in Russian], Vol. 1, Tbilisi (1971), p. 355.
3. F. T. Solodkii, in: The Use of the Living Elements of Wood, Proceedings of the Leningrad Academy of Wood Technology [in Russian], No. 119, Leningrad (1969), p. 7.
4. G. V. Pigulevskii, The Formation and Transformation of Essential Oils in Conifers [in Russian], Moscow—Leningrad (1939).
5. A. P. Pentegov and M. A. Chirkova, in: Collection of Papers on the Results of Investigations in the Field of Forestry and the Timber Industry in the Taiga Zone of the USSR [in Russian], Moscow—Leningrad (1957), p. 283.
6. A. N. Vol'skii, Zh. V. Dubovenko, N. A. Gershtein, and V. A. Pentegova, Khim. Prirodn. Soedin., 382 (1965).
7. G. A. Rudakov and Yu. P. Poltavchenko, in: Fourth International Congress on Essential Oils, Tbilisi, September, 1968 [in Russian], Vol. I, Tbilisi (1971), p. 289.
8. Yu. A. Poltavchenko and G. A. Rudakov, in: Synthetic Products from Rosin and Turpentine [in Russian], Gor'kii (1970), p. 82.
9. M. von Schantz and S. Juvonen, Acta Botanica Fennica, 73, 1 (1966).
10. S. Juvonen, Acta Botanica Fennica, 71, 1 (1966).
11. R. I. Tomchuk and G. N. Tomchuk, Tree Verdure and Its Utilization in the National Economy [in Russian], Moscow (1973).
12. K. Hannus and M. Pensar, Papper Och Trä, 7, 509 (1973).
13. A. M. Kalinin and G. V. Nikiton, The Production of Fir Oil [in Russian], Moscow (1969).
14. M. I. Goryaev and I. Pliva, Methods of Investigating Essential Oils [in Russian], Alma-Ata (1962).