alcohols. Crystallization of the latter from diethyl ether gave 0.1 g of δ-cadinol with $[\alpha]_D^{20}$ + 110° (c 0.5; chloroform); literature data [12]: $[\alpha]_D^{20}$ + 118.4° (ethanol). A mixture with an authentic sample of δ-cadinol melted without depression.

Separation of the Fraction of Di- and Polyfunctional Compounds. The chromatography of 0.14 g of this fraction on 30 g of SiO_2 yielded: 0.04 g of pinusolide with mp 82-83°C (from diethyl ether), $[\alpha]_D^{20}$ + 55° (c 1.5; chloroform) giving no depression of the melting point with an authentic sample; 0.02 g of a mixture of methyl isocupressate and isoagatholal (25% of diethyl ether in the eluent); and 0.02 g of agathadiol (50% of diethyl ether in the eluent) with mp 108-109°C (from ethanol), giving no depression of the melting point with an authentic sample.

SUMMARY

A scheme has been proposed for the group separation of the components of conifer oleoresins, and the mono-, sesqui- and diterpenes of the oleoresins of the European stone pine have been investigated by means of this scheme.

2. The composition of the oleoresin of the European stone pine is very similar to those of the Siberian pine and of the Korean pine, but differs from the latter by the absence of cis-abienol and bisabolol.

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A CHROMATOGRAPHIC INVESTIGATION OF THE n-HEPTANE IN THE ESSENTIAL OIL OF REPRESENTATIVES OF THE FAMILY PINACEAE

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There is no information in the literature on the presence of n-heptane, C_7H_{16} in the essential oils of the family Pinaceae. Heptane has been found previously in an investigation of the turpentine [1] in nine species of pine.

We have analyzed the oil of the needles and 1-yr shoots of the following larches: European larch (Larix decidua Mill.), Sukaczev's larch (L. sukaczewii Djil.), Siberian larch (L. sibirica Ledeb.), Dahurian larch (L. dahurica, Turcz.), Japanese larch (L. leptolepis Gord.), eastern larch (L. americana Michx. [L. laricina]), western larch (L. occidentalis Nutt.), and the Altai variety of the Siberian larch (L. sibirica var. altaica).

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TABLE 1. Compositions of the Components of the Essential Oils of Representatives of the Family Pinaceae

Species	Raw material	Composition of the components, wt.%															
		n-heptane	unidentified	unidentified	santene	tricyclene	α-pinene	camphene	β-pinene	myrcene	Δ^3-carene	α-terpinene	dipentene (limonene)	β-phellandrene	1,8-cineol	γ-terpinene	p-cymene	terpinolene
Pseudotsuga taxifolia (Poir.) Brit.	Needles	Tr.	Tr.	Tr.	Tr.	Tr.	15,98	4,26	15,93†		8,90	6,98	8,91	5,71	9,05	7,84	1,03	15,41
Abies sibirica Ledeb.	Spurs	0,73	Tr.	Tr.	Tr.	Tr.	30,58*		50,35†		6,42	1,37	3,12	1,10	4,68	Tr.	Tr.	1,65
Picea excelsa Link.	Needles	0,03	Tr.	Tr.	1,05	Tr.	32,25	20,87	3,22	5,58	3,17	0,60	22,13	9,88	Tr.	Tr.	Tr.	1,22
Larix sibirica var. altaica, f. typica	Needles	1,64	Tr.	Tr.	Tr.	Tr.	79,66	3,34	8,36†		7,00	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.
Djil.	Shoots	0,08	Tr.	Tr.	Tr.	Tr.	42,50	9,25	28,63†		4,40	1,04	3,85	9,48	Tr.	Tr.	Tr.	0,77
Larix leptolepis	Needles	0,41	Tr.	Tr.	Tr.	Tr.	34,90	9,78	16,16‡		13,37	2,82	11,95	9,13	Tr.	Tr.	Tr.	1,48
Gord.	Shoots	0,70	Tr.	Tr.	Tr.	Tr.	22,01	7,74	23,41†		16,48	2,71	13,70	11,03	Tr.	Tr.	Tr.	2,22
Larix decidua Mill.	Needles	0,00	Tr.	Tr.	Tr.	Tr.	63,87	3,85	8,89	14,92‡		0,88	3,26	2,76	Tr.	Tr.	Tr.	1,48
	Shoots	Tr.	Tr.	Tr.	Tr.	Tr.	31,85	5,25	16,74†		18,31	6,77	9,18	7,19	Tr.	Tr.	Tr.	4,71
Larix Sukaczewii	Needles	Tr.	Tr.	Tr.	Tr.	Tr.	17,17	1,70	5,85	58,44‡		3,12	5,69	2,26	Tr.	Tr.	Tr.	5,77
Djil.	Shoots	1,80	Tr.	Tr.	Tr.	Tr.	13,0	4,30	5,70	45,03‡		Tr.	20,10	8,60	Tr.	Tr.	Tr.	1,50
Larix sibirica	Needles	0,87	Tr.	Tr.	Tr.	Tr.	25,24	2,87	9,57	56,50‡		Tr.	2,56	2,39	Tr.	Tr.	Tr.	Tr.
Ledeb.	Shoots	0,77	Tr.	Tr.	Tr.	Tr.	22,47	2,86	13,17	42,52‡		Tr.	8,37	3,72	Tr.	Tr.	Tr.	6,12
Larix dahurica	Needles	0,93	Tr.	Tr.	Tr.	Tr.	40,11	4,07	9,16	33,70‡		Tr.	4,29	4,48	Tr.	Tr.	Tr.	3,26
Turcz.	Shoots	0,22	Tr.	Tr.	Tr.	Tr.	26,16	3,88	24,20†		18,67	6,33	7,15	10,26	Tr.	Tr.	Tr.	1,73
Larix americana	Needles	0,40	Tr.	Tr.	Tr.	Tr.	42,63	13,38	9,80	26,61‡		Tr.	3,78	2,30	Tr.	Tr.	Tr.	1,10
Michx.	Shoots	0,01	Tr.	Tr.	Tr.	Tr.	29,58	8,66	23,80‡		18,64	Tr.	9,20	7,56	Tr.	Tr.	Tr.	2,46
Larix occidentalis	Needles	Tr.	Tr.	Tr.	Tr.	Tr.	35,62	8,76	24,55‡		20,27	Tr.	7,65	2,05	Tr.	Tr.	Tr.	1,10
Nutt.	Shoots	0,13	Tr.	Tr.	Tr.	Tr.	29,59	2,30	34,98†		22,77	Tr.	5,05	3,59	Tr.	Tr.	Tr.	1,59
Pinus silvestris L.	Needles	1,25	Tr.	Tr.	—	Tr.	15,07	3,24	3,93	33,17‡		0,96	21,48	18,80	Tr.	Tr.	Tr.	2,10

*α-Pinene + camphene.

†β-Pinene + myrcene.

‡Myrcene + Δ^3-carene.

n-Heptane was found in the essential oil of the needles and of the shoots of these species of larch.

In addition to the species mentioned, we investigated the presence of n-heptane in the essential oils of other representatives of the family Pinaceae: Douglas fir (Pseudotsuga taxifolia (Poir.) Britt.), Siberian fir (Abies sibirica Ledeb.), Norway spruce (Picea excelsa Link. [Picea abies]), and Scotch pine (Pinus sylvestris L.

It was found that the essential oils of all the representatives of the family Pinaceae include n-heptane. This was identified by adding the chromatographically pure substance.

Below we give the relative retention volumes V'_R of ether, n-heptane, and toluene on various stationary phases:

Stationary Phase	Ether	n-Heptane	Toluene
Tricresyl phosphate	0.80	1.00	3.86
Poly(ethylene adipate)	0.85	1.00	2.25
Poly(ethylene sebacate)	0.89	1.00	3.14
Carbowax 1500	0.90	1.00	2.76
Apiezon L	0.84	1.00	3.27

The smallest retention time for n-heptane was observed on tricresyl phosphate and the longest on Apiezo L. All the phases mentioned can be used for the separation of heptane and monoterpene hydrocarbons of the essential oils of coniferous species. It must be mentioned that according to the facts given above the values of V'_R of ether and n-heptane are so close that in the work concerned the syringe used for the analyses of the essential oils was washed with toluene.

Table 1 gives information on the composition of the components of the essential oils from the family Pinaceae (the percentages of the components were calculated by the simple normalization method). The greatest amount of n-heptane was found in the essential oils of L. sibirica var. altaica and of L. sukaczewii Djil.

The presence of n-heptane in all the representatives of the family Pinaceae emphasizes the uniform nature of the synthesis of their essential oils.

EXPERIMENTAL

Sampling. Pseudotsuga taxifolia (Poir.) Britt. was obtained in the plantations of the Yalta mountain-for reserve (age of trees 100-120 yr), Picea excelsa Link. in the Bystritsa plantations of the Nadvornaya timber combine of the Ivano-Frankovsk oblast (age of the trees 18-20 yr). The samples of Pinus sylvestris L. were gathered in 18- to 20-yr plantations of natural origin on the territory of the Krasnyanskii leskhoz [forestry farm], Smolensk oblast, and Abies sibirica Ledeb. was obtained from the Altai (age of the trees 80-100 yr). The specimens of the larches Larix sibirica var. altaica, L. leptolepis Gord., L. decidua Mill., L. sukaczewi Djil., L. sibirica Ledeb., L. dahurica Turcz., L. americana Michz., L. occidentalis Nut., and Pinus silvestri L. were collected in geographical plantations near Voronezh, in plantations of the central forest-steppe region, and in natural plantations of the Arkhangel, L'vov, and Irkutsk oblasts, the Yakut ASSR, and Altai territory.

The essential oil was distilled in Klevendzher apparatuses at 96°C.

The essential oils were analyzed on a "Tsvet-3" chromatograph with a 6 × 3 mm column containing as stationary phase poly(ethylene adipate), 12 wt.%, on diatomite brick, 0.25-0.5 mm; the temperature of the column was 125°C and that of the evaporator 150°C; carrier gas helium, 35 ml/min; FID, sensitivity in the analysis of n-heptane $0.25 \cdot 10^{-8}$ A and of monoterpenes $10 \cdot 10^{-8}$ A. The rate of flow of air was 300 ml/min and hydrogen 30 ml/min. The speed of the recording paper was 360 mm/h.

SUMMARY

n-Heptane has been detected for the first time and studied in the essential oils of the needles and 1-y shoots of representatives of all the genera of the family Pinaceae.

Conditions of gas–liquid chromatography for the analysis of n-heptane present in the essential oils o coniferous species have been developed.

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