SEASONAL CHANGE IN THE ESSENTIAL OIL OF *Larix sibirica*

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Information is given on the qualitative and quantitative changes in the essential oil from the woody verdure of the Siberian larch. It has been established that during the vegetation period not only does the amount of essential oil in the woody verdure of the Siberian larch change but so also does the ratio of its individual components.

The Siberian larch (*Larix sibirica* Ldb.) occupies more than half the forest area of Siberia and the Far East. The comprehensive processing of the woody verdure of the larch, one of the products of which is an essential oil, is therefore extremely promising. Questions of the seasonal change in the amount of essential oil of the litter of the larch and its component composition, are therefore acquiring great importance.

We have studied the qualitative and quantitative changes in the essential oil from Siberian larch litter over the vegetation period. It was established (Fig. 1) that the accumulation of essential oil takes place up to the end of the vegetation period. Mathematical treatment of the experimental results showed that the difference in the amounts of essential oil in larch litter in September and October is insignificant.

Over the whole of the period investigated, a large part of the essential oil consisted of hydrocarbons (Table 1). In October, they made up more than 97% of the oils. The essential oil from Siberian larch litter was richest in oxygen-containing compounds in September (13.22%). The hydrocarbons were mainly represented by monoterpenes. The amount of sesquiterpenes ranged between 3.37 and 8.63%.

As can be seen from Fig. 1, seasonal changes in the amounts of invidual components in the essential oil took place jumpwise. This is apparently connected with the fact that the litter contains various structural elements (old and young growing twigs, needles) the ratio of which constantly changes during the vegetation period. On the other hand, the essential oils of the needles of old and young shoots differ substantially in their composition [1, 2]. Furthermore, the genesis of terpenes in different organs of coniferous trees, although it proceeds in the same direction, does so at different rates [1, 2].

Nevertheless, certain regularities can be clearly traced in the seasonal variation of the composition of the essential oil from Siberian larch litter. At the beginning of the vegetation season, the proportion of old (the previous year's) twigs is still large, and the initial stages of the genesis of terpenes are proceeding more intensively in the needles. In

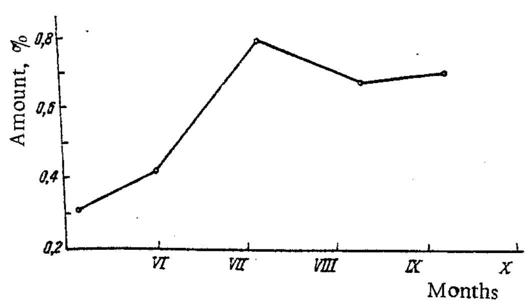

Fig. 1. Seasonal changes in the amount of essential oil in the Siberian larch.

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TABLE 1. Seasonal Dynamics of the Amounts of the Main Components of the Essential Oil of the Litter of the Siberian Larch

Component	Date of collecting the samples				
	June	July	August	September	October
Tricyclene	—	0,80	Сл.	—	—
α-Pinene	26,55	30,08	16,53	9,98	19,76
Camphene	2,03	2,51	1,80	0,68	1,98
β-Pinene	17,26	12,80	15,26	7,94	9,51
Myrcene	1,80	2,01	1,15	1,65	1,42
Δ^3-Carene	29,87	22,40	43,12	51,07	49,95
Limonene	4,68	6,02	3,10	2,75	2,81
β-Phellandrene	8,44	7,31	5,92	2,57	4,66
γ-Terpinene	0,50	0,80	0,72	Сл.	0,48
Terpinolene	1,68	0,94	2,31	2,27	1,74
Total, combined monoterpenes	87,56	85,67	89,91	78,91	92,31
Camphor	0,91	2,15	0,84	1,12	0,26
Borneol + isoborneol	0,74	0,86	1,15	3,97	0,44
Bornyl acetate	1,92	3,87	3,22	5,78	1,92
Other oxygen-containing compounds	0,24	0,70	1,51	2,35	0,21
Total oxygen-containing compounds	3,81	7,58	6,72	13,22	2,83
Caryophyllene	1,93	1,28	0,68	1,83	2,01
γ-Murolene	0,89	1,17	0,54	1,24	0,26
α-Murolene	2,96	2,48	1,11	2,83	1,65
Other sesquiterpenes	2,85	1,82	1,04	1,97	0,94
Total sesquiterpenes	8,63	6,75	3,37	7,87	4,86

this period, the essential oil is characterized by high contents of α- and β-pinenes and of β-phellandrenes and a low content of Δ^3-carene.

In the needles, the genesis of terpenes takes place very rapidly [2]. A high content of Δ^3-carene is characteristic for developed tissues of the larch. At the beginning of August, when the needles are already completely formed, the amount of Δ^3-carene in the oil is 43.12%, and in September it reaches its maximum level (51.07%). The formation of a large amount of Δ^3-carene leads to a relative fall in the proportion of bicyclic terpenes — α- and β-pinenes. The seasonal dynamics of α-pinene and of Δ^3-carene bear a mainly contrary nature. Only the change in the amount of Δ^3-carene in the essential oil of the Siberian larch in September and and October is within the limits of the experimental error.

By the end of the year, the terpene-forming processes have probably become less intensive, and processes of hydration and esterification predominate. As a result of this, the proportion of oxygen-containing compounds in the oil increases. As the tissues develop, the amount of β-phellandrene decreases.

In October, when the needles are already falling, and the tree is preparing for the period of dormancy, the amount of oxygen-containing compounds falls somewhat and the amount of pinene increases.

Thus, during the vegetation period not only the amount of essential oils in the litter of the Siberian larch but also the ratio of its individual components change.

EXPERIMENTAL

Isolation of the Essential Oil. The needle litter of the Siberian larch was collected every month in the course of the vegetation period in the region of the Biryusa leshkhoz [forestry farm], Krasnoyarsk krai, from 20-30 growing trees. The litter was ground, the samples were mixed, and the necessary amount of raw materials was taken by the quartering method. The essential oil was isolated by steam distillation under laboratory conditions.

The gas-liquid chromatography of the essential oil was performed on a LKhM-72 chromatograph with a katharometer. Separation was performed in a steel column (3 m × 4 mm) filled with Apiezon L, deposited in an amount of 15% on Chromosorb W. The column temperature was raised according to a linear program from 70 to 220°C at the rate of 4 deg/min. The temperature of the detector was 250°C and that of the evaporator 285°C. The rate of flow of helium was 120 ml/min.

CONCLUSION

1. It has been established that the accumulation of essential oil in the litter of the Siberian larch takes place up to the end of the vegetation season.

2. It has been shown that during the vegetation period not only the amount but also the composition of the essential oil from the litter of the Siberian larch changes.

LITERATURE CITED

1. S. Juvonen, Acta Botanica Fennica, 77, 4 (1966).
2. Yu. A. Poltavchenko and G. A. Rudakov, in: Synthetic Products from Rosin and Turpentine [in Russian], Gor'kii (1970), p. 82.

TERPENOIDS OF THE OLEORESIN OF *Pinus kochiana*

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The chemical composition of the oleoresin of Koch's pine growing in the Caucasus has been studied. It has been shown that, with respect to the composition of the monoterpenes and the resin acids, the oleoresin of this species does not differ from oleoresins of the subgenus *Diploxylon* studied previously. Predominating among the sesquiterpenes is germacrene D, which has not previously been found in the resins of the conifers of the USSR. The diterpenoids are represented by tricyclic compounds (pimarinol, isopimarinol, and methyl 15-hydroxydehydroabietate and the hydrocarbons corresponding to them).

The pines (genus *Pinus*) growing in the USSR are subdivided into two subgenera *Haploxylon* and *Diploxylon*. At the present time, the chemical compositions of the oleoresins of pines of the subgenus *Haploresin* have been studied, and for these a considerable content of labdane and cembrane diterpenoids is characteristic [1-4]. Of the pines of the subgenus *Diploxylon*, the oleoresin of only one species has been studied — the Scots pine. It has been established that tricyclic compounds of the pimarane and dehydroabietane types predominate in it [5].

In the present paper we give the results of a study of the terpenoids of the oleoresin of *Pinus kochiana* Koch. (Koch's pine). The name of this species is a disputed question: in the literature eight species names and seventeen in units of lower rank have been given [6, 7]. In the book "Flora Gruzii" ["The Flora of Georgia"], the pine growing in the Borzhomi gorge is named *Pinus sosnovskii* Nakai (syn. *Pinus hamata* Stev.) [6, 8]. On the basis of recent literature information [7], we shall use for this species the name *Pinus kochiana* Koch.

The compositions of the turpentine and of the resin acids of this species have been studied [9-11], but no information is available on the sesqui- and diterpenoids.

We have isolated the neutral and acid components from the oleoresin of the pine by a method described previously [4]. The neutral substances were separated by adsorption chromatogtaphy into hydrocarbons and oxygen-containing compounds, and these were fractionated by vacuum distillation into narrow groups.

The composition of the monoterpene hydrocarbons was determined by gas-liquid chromatography (GLC). α- and β-pinenes (46.7% and 46.3%, respectively) were identified as the main

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