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The qualitative and quantitative compositions of the essential oils of the woody verdure and bark of the Siberian fir have been studied. It has been shown that the oils investigated differ both in their amount and in the ratio of their individual components. The annual dynamics of the main substances are also different.

The traditional raw material for obtaining fir oil is considered to be the woody verdure of the Siberian fir. However, an essential oil with a similar qualitative composition can also be obtained from the bark of this plant.

We have shown previously that the chemical composition of fir oil is affected by the conditions of growth and the species variety of the stand of fir trees [1], and at the same time the composition of the oil does not remain constant during the year.

Two maxima appear in the accumulation of the oil in the woody verdure: one in the initial stage of the vegetation process (May), and the other, larger, at the end of the vegetation period (Fig. 1). It must be mentioned that the maximum amount of oil in the woody verdure corresponds to the minimum amount of it in the bark.

The results of the quantitative investigation of the essential oils being compared (Tables 1 and 2) show that the oil from the verdure contains 1.6 times more oxygen-containing compounds than the oil from the bark. At the same time, the latter is characterized by a higher amount of sesquiterpene hydrocarbons (14.8 and 5.5%, respectively). The qualitative compositions of the oils under investigation were the same, with the exception of the γ -, and α -muurolenes, which are absent from the oil from the verdure.

The predominating compounds of the oil of the woody verdure were bornyl acetate (38.2%), camphene (18.6%), Δ^3 -carene (11.2%), α -pinene (8.1%), and β -phellandrene (5.4%), and of the oil of the bark α -pinene (23.7%), bornyl acetate (20.1%), β -pinene (12.3%), β -phellandrene (8.0%), camphene (7.9%), caryophyllene (6.9%), Δ^3 -carene (6.0%), and β -humulene (5.9%).

The annual dynamics of these compounds in the oils from different parts of the tree are different. In the woody verdure of the fir the amount of limonene, camphene, and Δ^3 -carene rises during the growth of the needles at the expense of the fall in the amount of α - and β -pinenes. These results agree well with those obtained by other authors [2].

Of the oxygen-containing compounds, only for bornyl acetate is there a slight accumulation at the end of the vegetation period (42.7%). The amounts of the other components change in wave-like fashion in the course of the year.

The main representative of the sesquiterpene hydrocarbons of the essential oil of the woody verdure is carophyllene, the proportion of which ranges from 25 to 48% (of the total sesquiterpenes) according to the time of year, the maximum amount of this compound being recorded in the period of the preparation for deep dormancy and in the period of deep dormancy.

The essential oil of the bark of the fir retains its amount of the main monocyclic terpenes and of Δ^3 -carene during the vegetation process. This takes place through a continuous rise in the amount of α -pinene [3]. During this period, the camphene content remains practically constant. From January to the end of the vegetation period, the amount of β -pinene falls, while the concentration of bornyl acetate rises (from 12.7 to 27.4%), which is probably connected with the hydration of the β -pinene [2].

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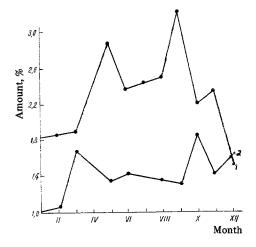


Fig. 1. Annual variability in the amounts of the essential oil of the Siberian fir: 1) woody verdure; 2) bark.

TABLE 1. Seasonal Dynamics of the Amounts of the Components of the Essential Oil of the Woody Verdure of the Siberian Fir (%)

		Time of collecting samples										
Component	January	February	March	April	Мау	June	July	August	September	October	November	December
Santene a-Pinene Camphene β-Pinene Δ3-Carene Limonene β-Phellandrene Terpinolene	2,1 13,0 13,2 4,6 10,4 3,0 5,0 2.5	2,2 11,8 16,2 4,4 9,8 2,8 6,0 1,3	2,8 9.9 17,1 3,4 9.7 3.3 6,2 1,6	1,6 8,5 19,5 3,6 10,6 3,3 6,2 2,1	6.7 20.1 3.6 11.6 4.7 5.1 1,7	1.1 3,0 21.0 3,0 12,2 6.2 6.1 1.0	0 5 2,5 21.6 2,0 13.0 6.8 7,0 1,0	1.8 1.6 22,2 1.5 13,1 6,0 7.7 0.9	1.0 6,8 20 3 1 3 12.0 5 5 5.5 1.8	1.4 9.6 19.2 2.7 11.0 3.8 3.0 1.2	1,6 10,9 17,1 3,6 10,4 3.0 2,8 1,7	0.8 12,9 15,2 4.0 10,1 3.0 4,6 2.1
Sum of the monoterpenes Fenchone Isofenchone Fenchol \$\beta\$-Terpineol Camphor \$\gamma\$-Terpineol Isoborneol Borneol Bornyl acetate \$a\$-Terpenyl acetate Sum of the oxygen-	53,8 0,2 0,3 0,2 0,1 0,6 0,4 0,2 1,0 36,2 0,2	54,5 0.3 0.4 0.2 Tr. 0,7 0,5 0 4 0,4 35,6 0,1	54,0 0,2 0,3 Tr. 0,2 0,4 0,4 0,3 0,6 35,6 0,1	55,4 0.2 0.3 0.2 0.2 0.2 0.6 0.4 1,1 37,0 0,1	53,5 0,1 0,1 Tr. 0,2 0,1 0,2 0,2 0,4 40,3 0,1	53,6 0,1 0,2 0,1 0,2 0,3 0,2 0,6 39,8 0,2	54.4 0,1 0,1 0,1 0,3 0,2 0,2 0,5 39.7 0,1	54,8 0,1 0,2 0,1 0,4 0,2 0,3 0,5 39,3 0,1	54,2 0,2 0,1 Tr. Tr. 0,2 0,4 0,3 0,3 41,1 0,1	51,9 0,3 0,4 0,1 Tr. 0,2 0,5 0,5 1,0 38,8 0,1	51,1 0,2 0,3 0,3 0,3 0,6 0,4 0,5 1,2 37,2 0,2	52.7 0.4 0,4 0.3 Tr. 0.6 0.2 0.2 1.0 36.8 0.3
containing compounds Longifolene Caryophyllene ε-Muurolene β-Humulene β-Bisabolene Sum of the sesqui- terpenes	39.4 0.3 3,0 0,4 1,7 1.4 6,8	38 6 0,3 3,1 0,5 1,6 1.4 6,9	39 1 0,5 3.2 0,3 1,7 1,2 6.9	40,3 0,2 1,9 0,2 1,1 0,9 4,3	41.7 0.2 1.7 0.4 1.2 1.3 4,8	41.8 0.4 1.4 0,4 1.1 1.3 4,6	41.4 0.3 1.3 0.4 1.0 1.2 4.2	41.3 0.4 1.0 0.2 1.1 1.2 3.9	42,7 0,4 1,0 0.5 0.5 0.7 3,1	41.9 0 4 3.0 0.2 0.8 1.8 6,2	41,2 0,4 3,2 0,5 1,7 1,9 7,7	40,2 0,4 3,2 0,3 1,7 1,5 7,1

Thus, the results obtained indicate that the oils investigated differ both in the amounts of the individual components that they contain and also in their annual dynamics.

EXPERIMENTAL

Isolation of the Essential Oils. The woody verdure of the Siberian fir was collected every month over a year from 25-30 trees growing in the Kansk-region (Poima timber industry enterprise), Krasnoyarsk krai. Samples of the bark were taken from 20 trees of the same timber industry enterprise. The woody verdure and the bark were ground and mixed, and average

TABLE 2. Seasonal Dynamics of the Amounts of the Components of the Essential Oil of the Bark of the Siberian Fir (%)

		Time of collecting the sample										
Component	January	February	March	April	May	June	July	August	Septem-	October	November	December
Santene a-Pinene Camphene b-Pinene A-Carene Limonene b-Phellandrene Terpinolene Sum of the monoterpenes Fenchone Isofenchone Fenchol b-Terpineol Camphor Terpineol Isoborneol Borneol Borneol Bornyl acetate Terpenylacetate Sum of the oxygen-	0,2 30,3 6,4 13,7 6,2 1,3 9,0 1,1 68,2 0,1 Tr. 0,1 0,4 0,2 0,6 12,7	0 2 30.5 7,0 13,4 6.8 1,8 8,4 0.6 68,7 Tr. Tr. 0,1 0,2 0,2 0,3 1,0 13.8 1.7	26.8 7.6 12.5 6.3 2.0 8.0 0.6 63.8 0.1 0,1 0,2 0,3 0,2 1.0 16.5 1,6	0.2 17,0 9,4 13,8 -7,1 4,4 9.7 0,6 62.2 0.1 Tr. 0.2 0.3 0,3 0,1 0.6 18,3	0.1 18,3 8,0 13.0 7.2 4.2 8,1 0,5 59.4 Tr. 0.2 0.3 0.3 0.3 0.2 0,8 20.9 2.0	0.1 19.1 8.1 11,9 6,0 3,6 8,4 0,6 57,7 Tr. 0.1 0,2 0,2 0,2 0,2 0,8 23,5 1,8	0 2 20.0 8 5 10,7 5.6 3.0 0,6 55,6 0,1 Tr. 0,1 0,2 0,3 0,3 0.1 0,6 26,8 1,9	0,2 21,4 8,3 10,0 4,7 2,6 6,4 0,7 54,3 Tr. Tr. 0,1 0,2 0,4 0,1 0,7 27,4 1,6	0,1 22,9 8,2 9,4 4,9 2,1 6,0 0,7 54,3 0,1 0,2 0,3 0,3 0,1 1,0 26,3 1,7	0,4 24,9 8,1 12,4 6,1 2,2 7,0 0,7 61,8 Tr. 0,2 0,2 0,2 0,2 0,3 0,3 0,5 20,1 1,6	0,2 25,0 7,3 13,6 6,0 1,9 8,2 1.0 63,2 0,1 0,3 0,1 0,4 0,3 1,0 18,8 1,6	0 3 27.7 7.4 13.4 4 5.2 1.8 9.5 1.0 66.3 Tr. 0.1 0.3 0.2 0.3 0.2 0.3 0.9 15.8 2.0
containing compounds Longifolene Caryophyllene e-Muurolene β-Humulene γ-Muurolene β-Bisabolene α- Muurolene Sum of the sesquiterpenes	16.2 0,3 0,5 0,4 0,4 0,4 15.6	7,5 0,3 6,1 Tr. 5,4 0,1 1,7 0,2	20.3 0.4 6.6 0.2 6.3 2.0 0,4	21, 9 0, 5 6, 4 0, 1 6, 3 1, 9 0, 5	25.1 0 2 6,6 Tr. 6.7 0.4 1.3 0,3	27.2 0.3 6.7 0.1 6,4 0.3 1.1 0.2	30,4 0,3 7,0 0,2 6.5 Tr. Tr.	30,6 0,2 7,6 0,2 6,7 0,2 - 0,2 15,1	30,3 0,3 7,8 Tr. 6,4 Tr. 0,2	23 6 0 2 7 4 0,1 5,3 0,2 0,7 0,7	23.1 0,2 7,1 Tr. 5,0 0 1 1.0 0.3	20,1 0,2 6,4 Tr. 5,0 0 2 1,3 0,5 13.6

samples were prepared by the quartering method. The essential oil was extracted by steam distillation. In working with the bark, a specially constructed large-scale apparatus [4] was used.

The essential oils were analyzed on a Chrom-3 chromatograph with a flame-ionization detector. Conditions of separation: column 6800×6 mm; stationary phase Chromaton with 5% dinonly phthalate and 0.2% of polyethyleneglycol-600; carrier gas helium at a rate of flow of 50 ml/min, thermal regime from 90 to 135°C at the rate of 3 deg/min.

SUMMARY

- 1. The chemical compositions of the essential oils isolated from the woody verdure and bark of the Siberian fir have been studied.
- 2. It has been shown that the quantitative and qualitative compositions of the oils change in the course of the year.

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