THE PREPARATIVE CHROMATOGRAPHIC SEPARATION OF SOME COMPONENTS OF THE ESSENTIAL OIL OF THE LARCH

R. D. Kolesnikova, V. G. Latysh, N. I. Popova, R. I. Deryuzhkin, and L. V. Krasnoboyarova

UDC 543.54:668.48

The essential oils of various plants and of coniferous trees form complex mixtures of aromatic substances. In recent years, gas-liquid chromatographic methods have been widely used to investigate various natural compounds. Thus, to study alkaloids, Rudloff [1] has used preparative chromatography with temperature programming. Ono and Hatanaka [2] have isolated alcohols and aldehydes from the leaves of plants. Blight and McDonald [3] have obtained sabinene and β-pinene from the essential oil of plants by the same method. Australian workers [4] have isolated a number of terpene hydrocarbons from the essential oil of eucalyptuses. By preparative gas-liquid chromatography, E. P. Dontsova [5] has isolated and studied five monoterpene hydrocarbons from the turpentines of domestic coniferous species.

We have determined the chemical composition of the essential oil of the larch by using the methods of analytical and preparative gas-liquid chromatography.

Preliminary investigations on the separation of the essential oil of the larch were performed on a Tswett-3 analytical chromatograph with a katharometer under isothermal conditions using liquid phases of different polarities. About 40 components were detected in the larch (Fig. 1).

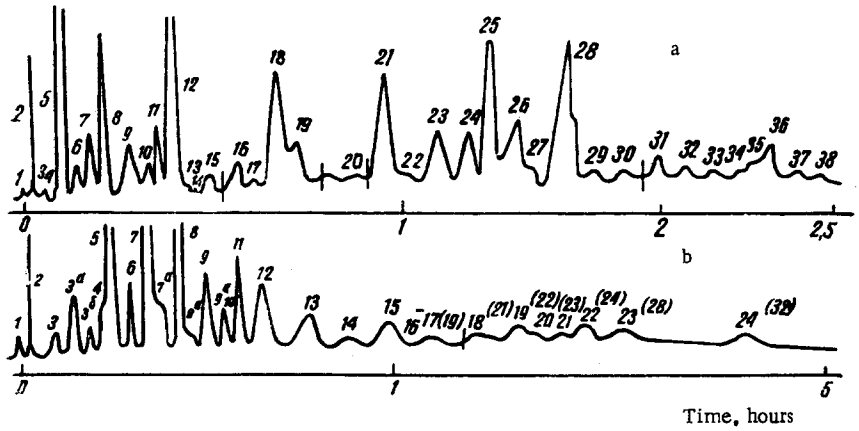

Fig. 1. Separation of larch essential oil (thermostat temperature 116° C; columns 6 m long and 3 mm in diameter; carrier gas helium): a) polar phase (PEGA, 10% on diatomite; b) nonpolar phase (8% of tricresyl phosphate on diatomite); 1) air; 2) ether; 3) unidentified; 4) tricyclene; 5) α-pinene; 6) camphene; 7) β-pinene + myrcene; 8) Δ^3-carene + phellandrene; 9) dipentene + α-terpinene; 10) β-phellandrene; 11) cineole; 12) γ-terpinene; 13) p-cymene; 14) unidentified; 15) terpinolene; 16-38) sesquiterpenes and oxygen-containing compounds.

Voronezh Institute of Wood Technology. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 612-615, September-October, 1972. Original article submitted February 28, 1972.

TABLE 1. Results of a Single Purification of the Components of Larch Essential Oil on a Preparative Chromatograph

Product purified	Impurities													
	tri-cyclene	α-pinene	camphene	β-pinene + myrcene	Δ^3-carene	α-phellandrene	α-terpinene	limonene	β-phellandrene	cineole	γ-terpinene	p-cymene	terpinolene	unidentified
α-pinene	0,6*	45,2	10,5	10,2	—	—	2,4	7,0	2,1	—	2,0	9,6	9,1	1,3
	0,2†	84,0	4,2	6,4	—	—	None	2,1	Traces	—	1,2	None	1,9	None
Δ^3-carene	—	1,6	0,2	0,90	75,1	2,2	14,0	1,1	3,0	—	—	—	—	1,8
	—	0,2	0,1	0,2	98,7	None	None	Traces	0,8	—	—	—	—	None
terpinolene	—	—	—	0,4	0,5	—	0,3	2,0	0,2	—	13,7	—	79,8	3,1
	—	—	—	0,1	0,2	—	0,2	0,7	0,1	—	2,9	—	95,8	None

*Amount of impurities (%) before purification on the chromatograph.

†After a single purification on the chromatograph.

The components were identified by their retention times using the method of graphical correlation, and also by the addition of individual pure components to the mixture. The same phases were used for the preparative chromatographic separation.

A polar phase [poly(ethylene adipate)] can be used for the preparative separation of the monoterpenes and also a number of di-, tri-, and sesquiterpene hydrocarbons and oxygen-containing compounds. However, pairs of components (β-pinene and myrcene, Δ^3-carene and α-phellandrene, and dipentene and α-terpinene) have very similar retention times on this phase, which complicates their preparative isolation on poly(ethylene adipate).

A nonpolar phase – tricresyl phosphate – can be used for the preparative separation of a number of monoterpene hydrocarbons. On this phase, the retention times are similar for the pairs tricyclene and α-pinene, β-pinene and myrcene, Δ^3-carene and α-phellandrene, and dipentene and α-terpinene, which must be taken into account in the separation of the monoterpene hydrocarbons in a preparative chromatograph.

The components of the larch essential oil were separated preparatively on a gas-liquid chromatograph of type PGK-3 made by the Special Design Bureau of the Academy of Sciences of the Estonian SSR. The essential oil was first subjected to fractional distillation. Fractions of the essential oil containing individual groups of terpene hydrocarbons with a predominance of one of the components – α-pinene, terpinolene, and Δ^3-carene – were taken for separation on the preparative chromatograph. Thus, the amount of α-pinene in the mixture was ≈45%; the amount of other terpene hydrocarbons was about 55%; in the case of the Δ^3-carene, the main substance made up 75% of the mixture. In the terpinolene fraction, there was about 80% of terpinolene.

In the investigation, the length of the column, the temperature, and the size of the sample were selected appropriately for the groups of hydrocarbons mentioned. Larger samples considerably decrease the efficiency of the column. But since it is permissible to overload the columns in preparative chromatography, an optimum sample size of 0.8-1 ml was found. The fractions were separated on columns 5 m long and 14 mm in diameter. Particular attention was devoted to the choice of the temperature conditions. Thus, for α-pinene the temperature of chromatography did not exceed 75°C, for Δ^3-carene it was 85-90°C, and for terpinolene not more than 100-110°C in view of the fact that these hydrocarbons readily polymerize. The components of the freshly distilled oil are particularly labile.

Analyses of the terpene hydrocarbons isolated in the preparative chromatograph showed a considerable decrease in the amount of impurities (Table 1). As can be seen from the table, the purity of the α-pinene after one purification was 84%, that of the Δ^3-carene 98.7%, and that of the terpinolene 95.8%. The amounts of a number of impurities had decreased and some had been removed completely. Before purification, the α-pinene contained 10 impurities (total percentage 54.8); after purification six (16%) remained. The Δ^3-carene contained eight impurities (24.9%) before purification and four (1.3%) afterwards; the terpinolene contained seven (20.2%) before purification and six (4.2%) afterwards.

SUMMARY

The analytical separation of larch essential oil has been performed on a Tswett-3 chromatograph, and conditions have been selected which have permitted the detection of 40 components in the larch essential oil.

Conditions (temperature, sorbent, length of the column, and size of the sample) have been selected for the preparative chromatographic isolation of α-pinene, Δ^3-carene, and terpinolene on a PGK-3 preparative chromatograph.

It has been shown that the method of preparative gas-liquid chromatography enables the purity of the individual components of larch essential oil to be increased over that achievable by fractional distillation even in a single purification treatment.

LITERATURE CITED

1. E. Rudloff, Chem. Ind. (London), 1962, No. 16, 743.
2. M. Ono and A. Hatanaka, Sci. Insect. Control, 25, No. 4, 166 (1960).
3. M. M. Blight and I. R. C. McDonald, New Zealand J. Sci, 6, No. 2, 220 (1963).
4. L. H. Briggs and J. R. Bartley, Austral. J. Chem., 23, No. 7, 1499 (1970).
5. E. P. Dontsova, Author's Abstract of Candidate's Dissertation [in Russian], Minsk (1970).