AN INVESTIGATION BY GAS LIQUID CHROMATOGRAPHY INTO THE COMPOSITION OF THE ESSENTIAL OILS OF SOME SIBERIAN CONIFERS

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Khimiya Prirodnykh Soedinenii, Vol. 1, No. 6, pp. 382-384, 1965.

Gas-liquid chromatography is widely used in working with essential oils [1]. We have used it to study the essential oils of the leaves of Pinus sibirica Rupr. Mayr. (cedar), Larix sibirica Ledeb. (larch), and Picea obovata Ledeb. (fir).

The chemical compositions of the essential oils of these species have not been investigated previously; the literature contains only fragmentary information on their composition and physical properties [2].

In this communication we give the results of an investigation into the composition of the monoterpene hydrocarbons on two stationary phases: 1, 2, 3-tris-(2-cyanoethoxy)-propane (TCEP) and polyethyleneglycol adipate (PEGA), and also preliminary information on the high-boiling fraction of these oils. Some of the components of the oils have been identified by adding authentic samples (see table), and the others by the method of graphical correlation [3] of the relative retention time values found and those previously known [4-7].

The study of the essential oils of the plants listed above has shown that santene, α-pinene, camphene, unidentified compound No. 8 (see table), β-pinene, Δ^3-carene, limonene, β-phellandrene, p-cymene, terpinolene, bornyl acetate, and borneol are common to all three species.

The compositions of the essential oils of these species are not identical: cedar oil contains mainly α-pinene, while α-pinene and Δ^3-carene predominate in larch oil, and α-pinene, Δ^3-carene, limonene, and terpinolene in fir oil. Moreover, cedar oil is characterized by the presence of β-fenchene and larch oil by α-phellandrene.

The graphical correlation used to identify the components of the oils studied confirmed the relationship found previously [3]. The results obtained on TCEP and β, β'-oxydipropionitrile [5] also correlate well with one another. Thus, the linear relationship of the logarithms of the relative retention times of the monoterpene hydrocarbons is retained for related stationary phases.

Four components were detected in the high-boling fraction of the ethereal oil from cedar, seven in the oil from larch, and six in the oil from fir. Of these we have identified only bornyl acetate, borneol, and camphor (the latter being found in the larch and the fir).

Composition and Relative Retention Times of the Monoterpene Hydrocarbons in Essential Oils

No.	Compound	Relative retention time*,		Composition, %		
		TCEP, at 80°C	PEGA, at 100°C	Pinus sibirica (Rupr.) Mayr.	Larix sibirica Ledeb.	Picea obovata Ledeb.
1	Unidentified	—	0.45	—	Traces**	—
2	Unidentified	—	0.52	—	—	Traces
3	Santene	0.81	0.73	Traces	0.2	0.2
4	(Tricyclene)***	0.96	0.85	—	Traces	Traces
5	α-Pinene	1.00	1.00	83.2	20.0	17.6
6	(β-Fenchene)	1.37	—	2.8	—	—
7	Camphene	1.57	1.35	0.4	0.2	8.4
8	Unidentified	1.75	—	Traces	5.6	4.2
9	β-Pinene	1.97	1.64	3.4	8.6	5.4
10	Δ^3-carene	2.36	2.03	0.4	42.0	11.6
11	(α Phellandrene)	2.96	2.23	—	3.6	—
12	(Myrcene)	3.04	—	0.8	—	6.4
13	Limonene	3.43	2.68	4.6	8.4	16.6
14	β-Phellandrene	3.99	2.88	4.0	5.4	6.6
15	(γ-Terpinene)	4.58	3.27	—	0.2	Traces
16	Terpinolene	5.54	4.21	0.4	Traces	19.4
17	Unidentified	6.42	—	—	—	—
18	p-Cymene	7.39	4.05	Traces	5.8	3.6

*Calculated relative to the retention time of α-pinene (4.7 min).

**Traces — less than 0.1%.

***The compounds in brackets were identified by the graphical correlation method.

Experimental

Isolation of the essential oils. The raw material was collected at the beginning of July, 1964, in the Chadansk region of the Tuva Autonomous Socialist Soviet Republic and was processed 5-10 days after collection.

The essential oils were distilled off in steam and extracted with diethyl ether, and the solution was dried over anhydrous sodium sulfate. After elimination of the solvent, the essential oils were obtained with the following yields: from cedar needles – 0.63%, from larch needles – 0.16%. from fir needles – 0.19% (on the air-dry material).

Gas-liquid chromatography. The analysis of the essential oils was carried out with chrom-1 chromatograph (Czechoslovakian SSR) with a flame-ionization detector. Nitrogen was used as the carrier gas. Its rate of flow was 24 ml/min. The hydrogen used was electrolytic hydrogen and the sensitivity of the scale of the recorder was 1 mV. The liquid phases,, 1, 2, 3-tris-(2-cyanoethoxy) propane and polyethyleneglycol adipate, which have been used previously for the separation of terpenes [10, 11], were synthesized by the methods of Bruson [8] and James [9]. The phases (20 : 100) were supported on INZ-600 brick (280-400 μ) [12].

The monoterpene hydrocarbons were separated on TCEP and PEGA at temperatures of 80 and 100°C, and the high-boiling components of the oils on TCEP at 150°C. The samples amounted to 20 μl of a 10% solution in diethyl ether.

The best separation of the components of the essential oils was obtained on TCEP; to identify the compounds, the results obtained on both stationary phases were used.

The quantitative determinations of the monoterpene hydrocarbons were carried out by the method of internal normalization with respect to the height of the peaks separated on TCEP. The accuracy of the analyses, determined on a synthetic mixture of santene and camphene, was 5.0% rel.

Summary

Eighteen monoterpene hydrocarbons have been isolated from the essential oils of Siberian species of cedar, larch, and fir. Fourteen components have been identified by gas-liquid chromatography.

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8 July 1965

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