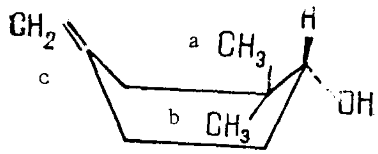
TABLE 1. (Continued)



8	1	—	—	—
	2	4,4	4,4	7,2
	3	—	—	—

EXPERIMENTAL

NMR spectra were taken on HX-90 Bruker spectrometer (in $CDCl_3$, 0 — TMS). $Eu(dpm)_3$ in CCl_4 solution was used as the lanthanoid shift reagent. The radius vectors r from the center of complex-formation to the observed protons of the cyclohexane part of the latilobinol molecule were calculated on a HP-2100S computer using a Dreiding model.

SUMMARY

The absolute configuration of a natural terpenoid coumarin — latilobinol — has been determined on the basis of its NMR spectra using lanthanoid shift reagents.

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COMPOSITION OF THE ESSENTIAL OIL OF *Tanacetum vulgare*

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UDC 547.913.001.2

The essential oil of the common tansy obtained from a population growing in the Dzhungarain Ala-Tau has been investigated. More than 50 substances have been detected, of which 39, including the main ones, have been identified.

The plant *Tanacetum vulgare* L. (common tansy) is found in almost all the regions of Kazakhstan, apart from the southern deserts. It grows in the forest and steppe zones in forest glades, on the banks and in the flood-plains of rivers, in the foothills, and in the valleys between mountains, and, as a weed, on roads and on the edges of fields and pastures.

This plant is widely used in folk medicine. A decoction of tansy flowers and fruit is an effective agent for expelling roundworms, pinworms, and tapeworms and is also used in jaundice, as a sedative in cases of rheumatism, headache, and epilepsy. In scientific

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Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 716-720, November-December, 1984. Original article submitted December 7, 1983.

medicine, tansy is used only as a vermifuge and, mixed with other plants, in disturbances of the functional activity of the gastrointestinal tract. The plant is considered poisonous and is used in strict dosage [1, 2]. Extracts of common tansy are being used successfully for the fight against aphids in orchards [3].

Common tansy is an essential-oil plant. According to the literature the yield and properties of its essential oil depend greatly on the growth site. Thus, plants gathered in the Nikitskii Botanical Garden in the period of full flowering gave 0.10% of a yellow-green essential oil with d_{20}^{20} 0.9047; n_D^{20} 1.4769; $[\alpha]_D^{20}$ +2.66°, acid No. 11.4; ester No. 80.4 [4]. From tansy growing in Yakutia a solid, light-colored essential oil with a powerful smell was obtained in a yield of 0.005%. The yield of essential oil from dry raw material collected in Voronezh province amounted to 0.089% [6], and from Uzbekistan to 0.0223% [7].

Tansy oil from Poland had a yield of 0.08%; d_{20}^{20} 0.9306; n_D^{20} 1.4747; $[\alpha]_D^{20}$ + 9.1°; acid No. 3.9; ester No. 43.7 [8]. According to other Polish authors, the yield amounts to 1.21%; d_{20}^{20} 0.9299; n_D^{20} 1.4640; $[\alpha]_D^{20}$ 30.4° [9].

Such a large difference in the amount and properties of the oils is probably connected with different species-affiliations of the samples of tansy mentioned and is due to their chemical compositions.

Information on the chemical composition of the essential oil of the common tansy is extremely contradictory. According to [10], it contains β-thujone (about 47.0%), 1-camphor, borneol, and pinene. Of 13 samples of the essential oil of the tansy growing in Central Europe, five types of essential oils were found, among which an oil was reported which consisted of umbellulone (70.0%) and thymol (20.0%), and also an oil containing mainly artemisia ketone [11-13]. The presence of the last-mentioned compound was confirmed by Hungarian scientists [14].

On the other hand, other authors [15], in a study of five samples of the essential oil of the common tansy of different geographical origins found neither artemisia ketone nor umbellulone in any of the samples but reported that the main components were isothujone, camphor, borneol, camphene, limonene, and α-pinene. Moreover, it was found that these components were the main ones for other species of tansy: *T. crispum*, *T. densuto*, and *T. pseudoachillae* [16].

We have investigated tbe essential oil from a population of common tansy growing in Eastern Kazakhstan (Dzhungarian Ala-Tau), a chromatogram of which is shown in Fig. 1. To facilitate the isolation of the substances, the oil was first separated into fractions. Gas-liquid analysis of these fractions showed that the essential oil contained not less than 50 components.

The terpene hydrocarbon fraction included α-pinene (1.0%), achillene (1.5%) [17], camphene (1.5%), β-pinen, sabinene, β-myrcene, limonene, β-phellandrene, 1.8-cineole (3.0%), γ-terpinene, p-cymene, and terpinolene.

Contrary to expectations [9, 10], the oxygen-containing fraction of the essential oil contained in largest amount (39.5%) a substance (n_D^{20} 1.4678; d_{20}^{20} 0.8762; $\alpha = 0$), the IR spectrum of which was identical with that of artemisia ketone [18]. After this was eluted achillenol (2.5%, peak 13) [19, 20], which has proved to be a synonym of santolina alcohol [21, 22]. A substance issued from the chromatogram almost together with this which had n_D^{20} 1.4507; d_{20}^{20} 0.8973; $[\alpha]_D^{20}$ −28° and was, according to its PMR and IR spectra, the acetate of a terpene alcohol. When it was saponified, an alcohol present in the essential oil in the free state (Fig. 16), was obtained with the constants n_D^{20} 1.4659; d_{20}^{20} 0.8754; $[\alpha]_D^{20}$ +69°. According to its IR and mass spectra this was an aliphatic alcohol with two multiple bonds one of which was of the vinyl type (918, 1002, 1640, 3079 cm^{-1}) and the other trisubstituted, belonging to a $-CH{=}C(CH_3)_2$ group, since a six-protein doublet with J ~ 1.5 Hz was observed in the 1.6 ppm region of the PMR spectrum.

Hydrogenation of the alcohol in ethanol over Adams platinum oxide was accompanied by the adsorption of one mole of hydrogen. This led to the disappearance of the band of the vinyl group in the IR spectrum, and in the PMR spectrum of the compound obtained a one-proton doublet was observed at 5.1 ppm (J ~ 5 Hz). A doublet also resonated in a stronger field (1 H, 3.87 ppm, J ~ 5 Hz), which obviously belonged to a hydrogen atom geminal to a hydroxyl group (3.45 ppm, −OH). The equal spin−spin coupling constants permitted us to consider that the molecule contained only two protons adjacent to one another. Finally, a weakly resolved doublet (0.95 ppm, 6 H) belonged to a $>C(CH_3)_2$ group.

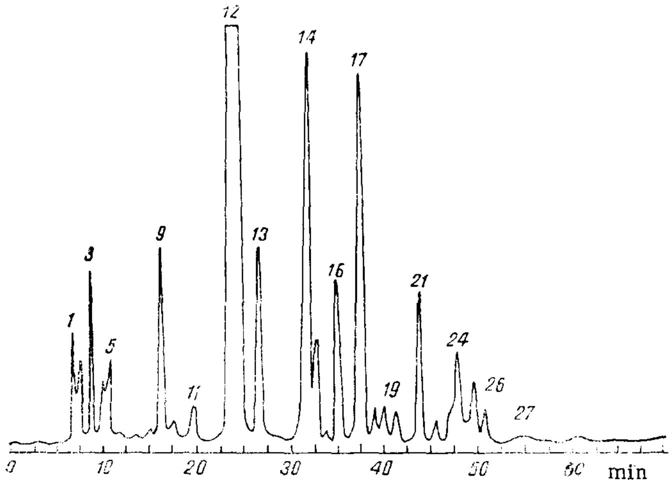

Fig. 1. Chromatogram of common tansy essential oil: 1) achillene; 2) α-pinene; 3) camphene; 4) β-pinene; 5) sabinene; 6) β-myrcene; 8) β-phellandrene; 9) 1,8-cineole; 10) γ-terpinene; 11) p-cymene; 12) artemisia ketone; 13) achillenol (santolina alcohol); 14) α-thujone; 15) β-thujone; 16) artemsyl alcohol; 17) camphor; 19) bornyl acetate; 20) terpinen-4-ol; 21) borneol; 22) α-terpineol; 24) filipendulol (epichrysanthenol); 25) carvone; 26) nerol; 27) geraniol.

Thus, the spectral characteristics and constants of the alcohol permitted the conclusion that the compound isolated was artemisia alcohol [23].

The essential oil contained a considerable amount (19%) of α-thugone (n_D^{20} 1.4534; d_{20}^{20} 0.9161; $[\alpha]_D^{20}$ −19.6°). According to a standard text [24], natural thujone is a mixture of two forms present in dynamic equilibrium (α-thujone ⇄ β-thujone) in a ratio of 1:2. As can be seen from Fig. 1, the ratio of the thujones in our case formed an exception.

One of the main components of the tansy oil was *l*-camphor (12%), while d-terpinenol-4, *l*-borneol, bornyl acetate, neryl acetate, geraniol, and thymol were present in small amounts.

Sesquiterpene hydrocarbons were present in an amount of 1.1%. Among them were ylangene, longicyclene, γ-elemene, P-gurgunene, β-elemene, β-caryophyllene, β-selinene, δ-cadinene, γ-cadinene, *ar*-curcumene, β-cadinene, calamenene, and calacorene.

Thus, the essential oil of the common tansy contains more than 50 components, of which 39, including the main ones, have been identified.

A comparison of the results obtained with the literature showed that the composition of the essential oil of the population of common tansy that we studied was close to that of some populations from Central Europe [13, 14], in spite of the geographical remoteness of their growth sites. In addition, we detected many other compounds, including santolin alcohol, achillene, and artemisia alcohol and its acetate.

EXPERIMENTAL

The essential oil of the common tansy was obtained from the epigeal leafy part of freshly cut plants of a population growing in the Dzhungarian Ala-Tsu between the villages of Dzerzhinskoe and Glinovka, Taldy-Kurgan province. The raw material was collected in the phase of complete flowering and was distilled with steam at a pressure of 3-5 atm.

The essential oil had a dark yellow color and a pleasant wormwood smell. Its constants were: n_D^{20} 1.4729; d_{20}^{20} 0.9331; $[\alpha]_D^{20}$ −6.9°; acid No. 1.9; ester No. 28.6. Yield 0.12%.

First, 320 g of the essential oil was separated by fractional distillation and adsorption chromatography on alumina into the following fractions:

I — a terpene hydrocarbon fraction boiling at 50-85°C/40 mm Hg (35.2 g);

II — a fraction of oxygen-containing compounds, boiling at 65-70°C/20 mm Hg and containing mainly artemisia ketone (112 g);

III — a fraction of oxygen-containing compounds boiling at 70-80°C/10 mm Hg (115 g);

IV — a fraction of oxygen-containing compounds obtained on elution of the still residue by diethyl ether and methanol (48 g); and

V — a fraction of sesquiterpene hydrocarbons obtained when the still residue was eluted with petroleum ether (3.5 g).

The substances were isolated in the individual state from the corresponding fractions with the aid of preparative GLC. UKh-2 and PAKhV-05 chromatographs were used with 190 × 0.7, 270 × 0.9, and 560 × 10 cm columns filled with specially treated INZ-600 support having a grain size of 0.20-0.25 mm and with 25% of Carbowax or 25% of PEGA.

The substances were identified by a comparison of their constants and spectral characteristics with those given in the literature, and also by performing appropriate chemical transformations. IR spectra were recorded on a UR-20 spectrophotometer, PMR spectra on a BS487C—80 MHz instrument, and mass spectra on a MI-1201 spectrometer.

Satisfactory separation of the components of the essential oil (Fig. 1) was achieved with programming of the temperature in the interval of 80-190°C, 2°C/min (Vyru-Khrom chromatograph, 300 × 0.3 cm; 15% of PEGA on Celite-535, 60-80 mesh; argon, 25 ml/min).

SUMMARY

The composition of the essential oil of *Tanacetum vulgare* has been investigated. The presence of more than 50 components has been established, of which 39 have been identified. The composition of the essential oil of the common tansy from Eastern Kazakhstan is in close agreement with the composition of the essential oils of some populations from Central Europe.

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