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ESSENTIAL OILS OF MONGOLIAN PLANTS

A STUDY OF THE ESSENTIAL OIL OF Artemisia rutifolia

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The aim of the present work was to study the essential oil of *Artemisia rutifolia* Steph. ex Spreng. The material was collected by the Division for the Study of Resources of the Combined Soviet–Mongolian Comprehensive Biological Expedition in 1972 in the budding–flowering phase in the Ubsunur Iamak, close to lake Dzérén-Nur in sections of a pebbly-sandy desert. The essential oil of *Artemisia rutifolia* growing in the Pamir was investigated by M. I. Goryaev in 1959 [1].

According to preliminary results which we obtained by means of an analytical gas chromatograph, the composition of the essential oil of the *Artemisia rutifolia* growing in Mongolia is far more complex (Fig. 1). By preparative gas chromatography in column I (Table 1), we obtained a fraction of the readily volatile components present in the oil in trace amounts. Its composition was studied by analytical gas chromatography on column V (see Table 1), identification being made by the addition of authentic compounds. The chromatogram of the monoterpine fraction is shown in Fig. 2. Six compounds were identified: α-pinene, camphene, β-pinene, limonene, β-phellandrene, and p-cymene.

The oxygen-containing compounds were isolated by preparative gas chromatography using column I and were identified by physical and chemical methods [2, 3]; the purity of the compounds isolated was checked by analytical gas chromatography in columns II, III, and IV (see Table 1).

The complete composition of the oil is shown in Table 2. The compounds corresponding to peaks 11-16 could not be identified from their IR spectra.

The IR spectrum of substance (11) showed the absorption bands of a monosubstituted aromatic ring (700, 760, 1500 cm^{-1}) and of a carbonyl group (1715 cm^{-1}). According to its mass spectrum (M^+ 148), the substance had the formula $C_{10}H_{12}O$. In its NMR spectrum, in addition to the protons of the aromatic ring and of an acyl group, there is a multiplet (2.80 ppm, 4 H) of the protons of two neighboring methylene groups. On the basis of this spectral information, substance (11) was identified as 4-phenylbutan-2-one. The IR spectrum of 4-phenylbutan-2-one which we obtained by the hydrogenation of the product of the condensation of benzaldehyde with acetone proved to be completely identical with the IR spectrum of the natural compound (11).

Compound (13) is an aromatic alcohol. Its IR spectrum contains absorption bands of a monosubstituted aromatic ring (700, 750, 1500 cm^{-1}) and of a hydroxy group (1060, 1130, 3390 cm^{-1}). The NMR spectrum has the signals of aromatic protons and of a $CH_3-CH(OH)$ grouping (see Experimental). In addition there are two multiplet signals corresponding to two methylene groups. The mass spectrum has a strong $M^+ - 18$ peak (70%),

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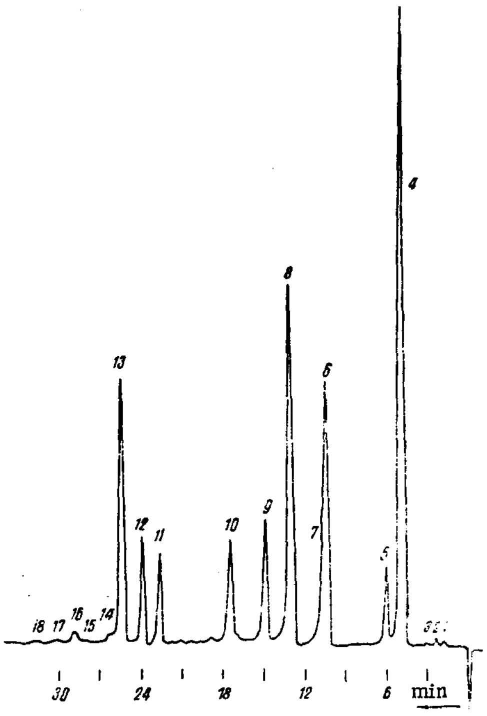

Fig. 1. Chromatogram of the essential oil of <u>Artemisia</u> <u>rutifolia</u>: 1) α-pinene; 2) camphene; 3) β-pinene; 4) 1,8-cineole + limonene + β-phellandrene; 5) p-cymene; 6) α-thujone; 7) β-thujone; 8) (+)-camphor; 9) (−)-terpinen-4-ol; 10) (−)-α-terpineol; 11) 4-phenylbutan-2-one; 12) (±)-4-phenylbut-2-yl acetate; 13) (±)-4-phenylbutan-2-ol; 14-18) unidentified. Column III (see Table 1).

TABLE 1. Chromatographic Columns and Conditions of Analysis of the Essential Oil of Artemisia rutifolia

Number of the column	Stationary phase*	Dimensions of the column	Analytical conditions	
			$T_{thermostat}$, °C	V_{gas}, ml/
I	15% of Carbowax 20 M	4,6m×9,1 mm	130	60
II	10% of Apiezon L	1,0m×4,0 mm	80—200 4 deg/min	30
III	10% of PEGA	1,5m×4,0 mm	80—180,4 deg/min	30
IV	15% of Carbowax 20 M	1,5m×4,0 mm	80—190,4 deg/min	30
V	12% of di (β-cyanoethyl) ether (β, β'-ODPN)	1,5m×4,0 mm	80	30

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*The stationary phase was deposited on Chromaton N (0.20-0.35 mm) for column I and on Chromaton N AW-DMCS (0.16-0.20 mm) for the others.

†Argon.

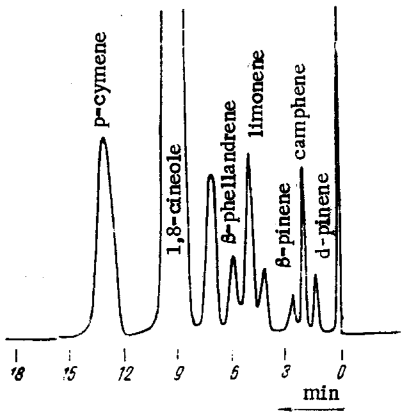
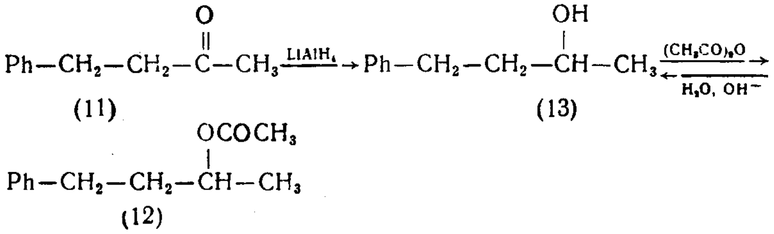


Fig. 2. Chromatogram of the low-boiling fraction of the essential oil of Artemisia rutifolia. Column V (see Table 2).

which is characteristic for alcohols. On the basis of the spectral information obtained, alcohol (13) was identified as 4-phenylbutan-2-ol. To confirm the identification, 4-phenylbutan-2-one was reduced to the corresponding alcohol. The IR spectrum of the 4-phenylbutan-2-ol obtained in this way coincided completely with the spectrum of the natural compound.

The IR spectrum of compound (12) shows absorption bands of a monosubstituted aromatic ring (700, 750, 1500 cm^{-1}) and of an ester group (1250, 1740 cm^{-1}). The alkaline hydrolysis of (12) gave 4-phenylbutan-2-ol (13). When the 4-phenylbutan-2-ol isolated from the oil was acetylated, phenylbut-2-yl acetate was obtained, which had an IR spectrum identical with that of the natural compound (12). The compounds (12) and (13) isolated from the oil were optically inactive.

Thus, on the basis of spectral characteristics and the reactions



$$\underset{(11)}{Ph{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3} \xrightarrow{LiAlH_4} \underset{(13)}{Ph{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}CH_3} \underset{H_2O,\ OH^-}{\overset{(CH_3CO)_2O}{\rightleftarrows}}$$

$$\underset{(12)}{Ph{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle OCOCH_3}{|}}{CH}{-}CH_3}$$

compounds (11), (12), and (13) have been identified as 4-phenylbutan-2-one, (±)-4-phenylbut-2-yl acetate, and (±)-4-phenylbutan-2-ol, respectively.

Compounds (15) and (16) (see Fig. 1), which were isolated in very small amounts, could not be identified. The investigation of the minor components of the oil will be continued.

It is interesting to note the presence of compounds of the aromatic series in the oil. This is the first time that 4-phenylbutan-2-ol and its acetate have been found in plant material (4-phenylbutan-2-one has been found previously in the essential oil of Aquillaria agallocha Roxb. (Thymelaceae) [4]).

EXPERIMENTAL

The essential oil was obtained from the epigeal part of the plant by steam distillation in a Ginzberg apparatus. The yield of oil was 1.5% of the weight of the air-dried raw material. The oil was light green with a pleasant minty-camphoraceous smell and had the following indices: n_D^{20} 1.4873, d_4^{20} 0.9701, $[\alpha]_D^{20}$ +9.0°.

Analytical gas chromatography was performed on a gas Pye-104 instrument with a flame-ionization detector, and preparative chromatography on a Pye-105 instrument. In all cases glass columns were used. The stationary phases and the chromatographic conditions are given in Table 1. The IR spectra of the components isolated were recorded on a UR-10 instrument in a thin layer or in CCl_4 solution using specially made microcells.

The NMR spectra were taken on a Varian HA-100 instrument in CCl_4 with HMDS as external standard.

Synthesis of 4-Phenylbutan-2-one. Benzylideneacetone, obtained by condensing benzaldehyde with acetone [5], was hydrogenated with Adams' catalyst in glacial acetic acid at room temperature. After the end of hydrogenation, the reaction mixture was diluted with water, the product was extracted with ether, and the ether-

TABLE 2. Composition of the Essential Oil of Artemisia rutifolia and Chromatographic Parameters of Its Components

Compound	Identification	Relative retention time in columns			Content, % of the weight of the oil ‡
		II*	III*	V†	
α-Pinene	GLC			0,24	2
Camphene	GLC			0,41	
β-Pinene	GLC			0,52	
Unidentified				0,86	
Limonene	GLC			1,00	
β-Phellandrene	GLC			1,19	
Unidentified				1,48	
p-Cymene	GLC			2,67	
1,8-Cineole	IRS	0,75	0,36		35
α-Thujone	IRS	0,83	0,77		11
β-Thujone	IRS	0,86	0,83		
(+)-Camphor	IRS	1,00	1,00		18
(−)-Terpinen-4-ol	IRS	1,18	1,12		7
(−)-α-Terpineol	IRS	1,21	1,31		5
4-Phenylbutan-2-one	IRS, NMR, Mass spectrum	1,25	1,71		5
(±)-4-Phenylbutan-2-ol	NMR, Mass spectrum	1,30	1,92		10
(±)-4-Phenylbut-2-yl acetate		1,59	1,77		6
Unidentified					1

*Residence times given relative to camphor.

†Residence times given relative to limonene.

‡The amounts of the components were calculated from the areas of the peaks by the method of internal normalization without taking sensitivity coefficients into account.

eal layer was washed with 10% sodium hydroxide solution, dried, evaporated to a volume of 1 ml, and transferred to the preparative gas chromatograph.

Reduction of 4-Phenylbutan-2-one. At room temperature 3 ml of a 0.1 N solution of $LiAlH_4$ in abs. ether was slowly added to 50 mg of 4-phenylbutan-2-one in 1 ml of abs. diethyl ether. After the end of the reaction, the excess of $LiAlH_4$ was decomposed with water, the product was extracted with ether, and, after drying, the ethereal layer was evaporated to a volume of 0.5 ml and transferred to the evaporator of the preparative gas chromatograph.

SUMMARY

1. The following compounds have been isolated by gas–liquid chromatography from the essential oil of Artemisia rutifolia Steph. ex Spreng. growing in the Mongolian People's Republic and have been identified by their IR spectra: 1,8-cineole (35%), α-thujone and β-thujone (11%), (+)-camphor (18%), (−)-α-terpineol (5%), and (−)-terpinen-4-ol (7%). By analytical gas chromatography α-pinene, β-pinene, camphene, limonene, β-phellandrene, and p-cymene have been identified in the hydrocarbon fraction.

It has been shown that apart from compounds of a terpene nature the oil contains 4-phenylbutan-2-one, (±)-4-phenyl-butan-2-ol, and (±)-4-phenylbut-2-yl acetate. This is the first time that (±)-4-phenylbutan-2-ol and its acetate has been found in plant material.

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