2. R. A. W. Johnstone, Mass Spectrometry for Organic Chemists, Cambridge University Press, Cambridge (1972).
3. A. Ya. Revo, Practical Handbook of Organic Chemistry. Qualitative Microchemical Reactions [in Russian], Moscow (1971), p. 26.
4. Determination of Structure of Organic Compounds by Physical and Chemical Methods [in Russian],* Moscow, Vol. 1 (1967), p. 70.
5. S. Sasaki, Y. Itagaki, T. Kurokawa, F. Watanabe, and T. Aoyama, Mass Spectroscopy (Jpn.), 14, No. 2, 82 (1966).
6. Y. Itagaki, T. Kurokawa, S. Sasaki, C. Chang, and F. Chen, Bull. Chem. Soc., Jpn., 39, 538 (1966).
7. A. E. Bird and A. C. Marshall, J. Chem. Soc., (C), 2418 (1969).
8. W. A. Koenig, C. Krauss, and H. Zaehner, Helv. Chim. Acta, 60 (6), 2071 (1977).
9. A. I. Syrchina, M. G. Voronkov, and N. A. Tyukavkina, Khim. Prir. Soedin., 807 (1978).

---

*Perhaps a translation of K. W. Bentley, Elucidation of Structures by Physical and Chemical Methods, Interscience, New York (1963).

CHEMICAL COMPOSITION OF THE ESSENTIAL OILS OF MONGOLIAN WORMWOODS *Artemisia xerophytica* and *A. xantaphora*

M. I. Goryaev, F. S. Sharipova,
L. A. El'chibekova, S. Shatar,
and L. K. Tikhonova

UDC 547.913.001.2

The chemical compositions of the hydrocarbon fractions of the essential oils of endemic wormwoods of Mongolia, *Artemisia xerophytica* (xerophytic wormwood) and *Artemisia xantaphora* (yellow wormwood), have been investigated. In the essential oil of *A. xerophytica* 22 hydrocarbons out of 26 have been identified and in that of *A. xantaphora* 18 out of 27.

The plant world of Mongolia is an inexhaustible source of natural compounds and, in particular, of essential oils. Particular interest is presented by the *Artemesia* genus which in Mongolia numbers more than 58 species, some of them being endemic [1]. Many species of wormwood (*Artemisia xerophytica, A. scoparia, A. adamsis, A. sieversiana*) form the main plant coverage of the steppe, semidesert, and desert.

The present paper gives the results of an investigation of the terpene and sesquiterpene hydrocarbons of the essential oils of the wormwoods *A. xerophytica* and *A. xantaphora* (xerophytic wormwood and yellow wormwood), which are endemic plants of Mongolia and have not been studied previously.

In the essential oil of *A. xerophytica* we found 43% of terpene hydrocarbons and 25% of sesquiterpene hydrocarbons (Fig. 1), and in that of *A. xantapora* 40% of terpene hydrocarbons and 12% of sesquiterpene hydrocarbons (Fig. 2).

We attempted to investigate the biogenetic link between the terpene and sesquiterpene hydrocarbons in the essential oils considered. Some workers consider that monoterpene hydrocarbons of a definite structure presuppose the presence in an essential oil of the corresponding sesquiterpene hydrocarbons differing from the former by one isoprene group [3]. This hypothesis is confirmed in the oils that we have investigated as examples. Thus, in the essential oil of *A. xerophytica* there is the monoterpenoid camphene and the sesquiterpene hydrocarbon β-santalene, the structures of which are similar. In addition, the simultaneous presence of α-santalene, longifolene, β-santalene, and logicyclene suggest that their biogenesis from a common precursor is possible. β-Santalene probably undergoes cyclization through one of the unsaturated centers of the molecule, leading to the formation of α-santa-

---

Institute of Chemical Sciences, Academy of Sciences of the Kazakh SSR, Alma-Ata. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 501-505, July-August, 1980. Original article submitted February 25, 1980.

0009-3130/80/1604-0358$07.50

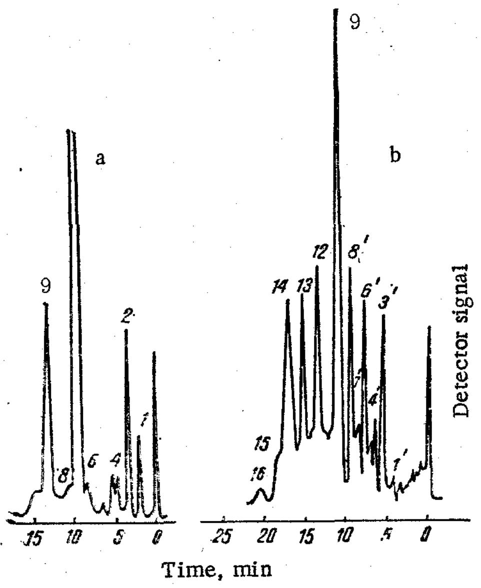

Fig. 1

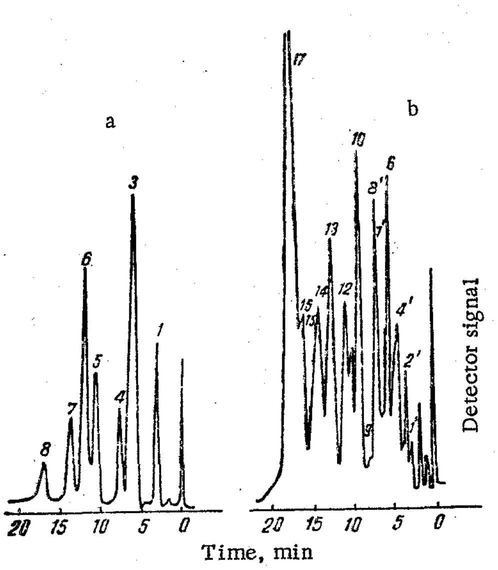

Fig. 2

Fig. 1. Chromatogram of the terpene (a) and sesquiterpene (b) hydrocarbons of the essential oil of *A. xerophytica:* 1) α-piene: 2) camphene; 3) β-pinene; 4) sabinene; 5) α-terpinene; 6) limonene; 7) cineole; 8) γ-terpinene; 9) p-cymene; 1'-4') unidentified hydrocarbons; 5') ylangene; 6') longicyclene; 7') α-santalene; 8') longifolene; 9') epi-β-santalene; 10) β-santalene; 12) α-himachalene; 13) γ-bisabolene; 14) δ-cadinene; 15) γ-cadinene; 16) calamenene.

Fig. 2. Chromatogram of the monoterpene (a) and sesquiterpene (b) hydrocarbons from the essential oil of A. *xantaphora*: 1) α-pinene; 2) camphene; 3) β-pinene; 4) Δ^3-carene; 5) limonene; 6) cineole; 7) δ-terpinene; 8) p-cymene; 1'-6') unidentified hydrocarbons; 8') ylangene; 9) α-gurjunene; 10) β-bergamotene; 11) β-gurjunene; 12) β-bergamotene; 13) caryophyllene; 14) β-humulene; 15) α-humulene; 16) β-bisabolene; 17) δ-cadinene.

lene or longifolene. In its turn, the cyclization of these two hydrocarbons may lead to the formation of the tetracyclic sesquiterpene longicyclene.

The essential oil of *A. xantophora* contains in addition to considerable amounts of α- and β-pinene and limonene, the compounds with close structures α-bergamotene, β-bergamotene, and β-bisabolene.

EXPERIMENTAL

The essential oils were obtained by the steam-distillation of the air-dry plants in the budding phase. The investigation was carried out by the methods of vacuum distillation, chromatographic separation on alumina, and gas–liquid chromatography in a Vyrukhrom mod. A-1 apparatus using a flame-ionization detector with a steel column 3 m × 0.3 cm containing as stationary phase 10% of Reoplex 400 on a solid support (Celite, 60–80 mesh) with helium as the carrier gas at the rate of 45 ml/min. In the separation of the sesquiterpene hydrocarbons, naphthalene was used as internal standard to determine relative retention times [3].

The preparative separation of the terpene hydrocarbons was carried out on a UKh-2 universal chromatograph using a column 100 × 0.6 cm filled with Celite 545 (60–80 mesh) impregnated with 20% of Reoplex 400. Quantitative compositions were determined by the internal-normalization method [4].

Artemisia xerophytica is a semishrub with a woody stem 5–8 cm high that is distributed in the Gobi desert-steppe zone. The oil has a yellow-brown color, a pleasant smell, and the following physicochemical constants: n_D^{20} 1.4630; acid No. 14.2; ester No. 45.0. Yield of oil 1.2%.

The essential oil (10 g) was treated with a 50% solution of sodium carbonate to isolate the acids and with a 30% solution of caustic soda to isolate the phenols. The methyl esters of the acids isolated (0.01% on the whole oil) were obtained with diazomethane [2], and these were analyzed in a gas–liquid chromatograph at 118°C. The following free acids were found in the essential oil: acetic, propionic, butyric, valeric, caproic, caprylic, pelargonic, and capric. No phenols were detected.

The essential oil (9 g) from acid and phenols was vacuum-distilled into the following fractions: 1) 1.24 g, 14%, bp 40°C (5 mm); 2) 2.87 g, 32%, bp 60-80°C (5 mm); and residue 4.8 g, 53%.

The first and second fractions consisted of terpene hydrocarbons, and they were analyzed in a gas–liquid chromatograph at 90°C. The following hydrocarbons were identified (Fig. 1a) (in % on the total oil): α-pinene, 2.0; camphene, 4.5; β-pinene, 1.1; sabinene, 1.1; α-terpinene, 0.3; limonene, 1.0; cineole, 25; γ-terpinene, 1.0; and p-cymene, 7.0. Such hydrocarbons as α-terpinene and γ-terpinene were identified from their retention times and from the increase in the size of the corresponding peaks when the pure substances were added to a sample of the oil. The remaining hydrocarbons were isolated preparatively and their IR spectra were recorded and their physicochemical constants were determined, these agreeing with literature characteristics [5].

The residue consisted of a mixture of oxygen-containing compounds, sesquiterpene hydrocarbons, and resins. To separate the hydrocarbons from the oxygen-containing compounds, fraction 3 was passed through a column filled with alumine (Brockmann activity grade II, in a ratio of 1:100), and was eluted successively with petroleum ether and ethanol. The fraction eluted by petroleum ether (2.6 g) consisted of sequiterpene hydrocarbons. It was analyzed in a chromatograph at a temperature of 150°C. By comparing the relative retention times with literature figures [3], the following hydrocarbons were identified (Fig. 1b) (in % on the whole oil): ylangene, 0.59; longicyclene, 1.68; α-santalene, 0.7; longifolene, 1.9; epi-β-santalene, 5.9; β-santalene, 0.2; α-himachalene, 3.0; γ-bisabolene, 2.5; δ-cadinene, 3.4; γ-cadinene, 0.6; calamenene, 0.3.

The essential oil of *A. xantaphora* had a yellow-brown color, a pleasant smell, and the following physicochemical constants: n_D^{20} 1.5090; acid No. 1.8; ester No. 36.7. Yield of oil 1.4%.

The essential oil (12 g) was freed from phenols and acids and was distilled into the following fractions: 1) 3.09 g, 25%, bp 52-56°C (10 mm); 2) 1.5 g, 12.5%, bp 58-60°C (10 mm); and residue 7.3 g, 60.8%.

The first and second fractions were analyzed in a gas–liquid chromatograph at a temperature of 92°C, and the following components were identified (Fig. 2a) (in % on the whole oil); α-pinene, 6.1; camphene, traces; β-pinene, 11.6; Δ^3-carene, 3.6; limonene, 5.0; cineole, 8.1; γ-terpinene, 3.0; p-cymene, 2.0. The third fraction was chromatographed on alumina. It was eluted successively with petroleum ether benzene, and ethanol.

The solvent was distilled off from the petroleum fraction, which left the sesquiterpene hydrocarbons, and these were analyzed at 150°C. The following hydrocarbons were identified (Fig. 2b) (in % on the whole oil); ylangene, 0.5; α-gurjunene, 0.3; α-bergamotene, 1.75; β-gurjunene, 0.7; β-bergamotene, 1.0; caryophyllene, 1.5; β-humulene, 1.1; α-humulene, 0.8; β-bisabolene, 0.9; and δ-cadinene, 3.0.

SUMMARY

1. The chemical compositions of the hydrocarbon fractions of the essential oils of *Artemisia xerophytica* and *A. xantaphora* growing in Mongolia have been investigated.

2. In the essential oils of *A. xerophytica* 26 hydrocarbons have been detected of which 22 have been identified, and in that of *A. xantaphora* 27 hydrocarbons of which 18 have been identified.

LITERATURE CITED

1. V. I. Grubov, A Summary of the Flora of the Mongolian People's Republic [in Russian], Moscow–Leningrad (1955).
2. F. Arndt, Org. Synth., Coll. II (1943), p. 165.
3. I. C. Nigam and L. Levi, J. Chromatogr., 23, 217 (1966).
4. K. A. Gol'bert and M. S. Vil'dergauz, A Course of Gas Chromatography [in Russian], Moscow (1967), p. 245.
5. M. I. Goryaev and I. Pliva, Methods of Investigating Essential Oils [in Russian], Alma-Ata (1962), p. 231.