dinary polarimeter (c 0.65-0.1), and melting points in an instrument containing concentrated sulfuric acid. The elementary analyses of all the compounds corresponded to the calculated figures.

SUMMARY

The amounts of flavan substances and their qualitative compositions in various organs of *Hibiscus cannabinus* according to vegetation periods have been established.

In all vegetation periods, flavan compounds are formed in the phloem and roots of kenaf; their amount reaches a maximum in the flowering period and becomes almost constant by the moment of harvesting. Among the monomeric flavans, (−)-epicatechin predominates.

(−)-Epicatechin gallate, (+)-catechin, (−)-epigallocatechin gallate, and (−)-epicatechin have been identified in the products of hydrolysis of the tannin.

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ESSENTIAL OIL OF *Artemisia scoparia*

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The chemical composition of the essential oil of oriental wormwood growing in Kazathstan has been investigated. Of the components of the oil, 28 have been identified, and the structure of an acetylenic hydrocarbon has been refined.

Oriental wormwood (*Artemisia scoparia* W. et K.) is widely distributed in the lower European part of the USSR, Kazakhstan, Central Asia, Asia Minor, Western and Eastern Siberia, in the Maritime Territory, Manchuria, and Mongolia. It grows on the steppes and in deserts, in river valleys, and also in the low mountain zone.

The essential oil is present in the roots and epigeal part of the plant. The epigeal part contains about 1% of essential oil which, depending on the regions of growth of the wormwood, is subject to considerable quantitative and qualitative changes [1]. This species of wormwood has been used in folk medicine from ancient times [2, 3]. The broad action of the essential oil of the oriental wormwood has attracted attention and it has been studied repeatedly [4-7]. In the publications cited, the phases of development of the plant and the various methods of extracting the essential oils and investigating them are not stated. This possibly explains the diversity of the compositions of the essential oils.

We have investigated the essential oil of oriental wormwood obtained from plants collected in the Samarskoe district, East Kazakhstan province, in the budding phase. The oil contained a considerable amount of scoparone, some of which deposited on prolonged standing (mp 143-144°C). The phenol fraction, consisting of thymol, cis- and trans-eugenols, also contained 2-acetoxy-4,5-dimethoxycinnamic acid (mp 198-199°C), which is formed from scoparone

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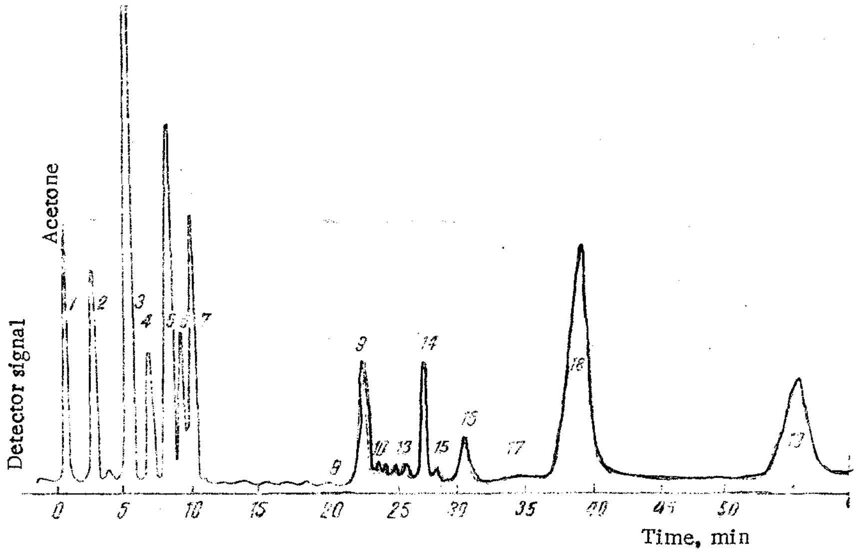

Fig. 1. Chromatogram of the hydrocarbon fraction of the oil of oriental wormwood: 1) α-pinene; 2) camphene; 3) β-pinene; 4) sabinene; 5) α-phellandrene; 6) limonene; 7) β-phellandrene; 8) p-cymene; 9) longicyclene; 10) longifolene; 11) β-santalene; 12) himachalene; 13) bisabolene; 14) δ-cadinene; 16) curcumene; 18) 1-phenylhex-2-en-4-yne; 19) 1-phenylhexa-2,5-diyne; 15, 17) unidentified compounds.

when the essential oil is treated with aqueous caustic soda solution. When the essential oil was subjected to chromatographic separation on alumina, the residual scoparone was eluted with petroleum ether together with the hydrocarbon fraction. The total scoparone content of the oil was about 12%.

The separation of the hydrocarbon fraction was performed by rechromatography in a column of alumina and by preparative chromatography in a chromatograph.

Among the monoterpene hydrocarbons the following were identified (their amounts being given as %'s of the whole oil): α-pinene, 2.2; camphene, 0.2; β-pinene, 10.2; sabinene, 1.4; α-phellandrene, 5.6; limonene, 2.1; β-phellandrene, 3.6; p-cymene, 0.1. The sesquiterpene hydrocarbons included: longicyclene, 2.2; longifolene, 0.2; santalene, 0.2; α-himachalene, 0.2; δ-bisabolene, 0.4; δ-cadinene, 2.1; curcumene, 0.8. In addition, a considerable amount of acetylenic hydrocarbons was detected in this fraction.

Acetylenic hydrocarbons were first isolated from the essential oil of oriental wormwood by Golmov and Afanas'ev [4]. These authors recorded that they consisted of a mixture of "agropyrene" ($C_{12}H_{12}$) and of 1-phenylhexa-2,4-diyne ($C_{12}H_{10}$).

We isolated the acetylenic hydrocarbons (peaks 18 and 19 in Fig. 1) by rechromatography of the hydrocarbon fraction on alumina. This fraction consisted of yellow oils with R_f 0.87 and 0.59 (TLC, Al_2O_3, activity grade I, eluent hexane).

Substance 1 (peak 19, R_f 0.59) had constants corresponding to Triebs' "agropyrene", which he isolated from the essential oil of the roots of *Agropyrum repens* [8]. The IR spectrum of the hydrocarbon contained absorption bands corresponding to deformation (700, 735 cm^{-1}) and skeletal (1500, 1605 cm^{-1}) C—H vibrations and to the (=C—H) stretching vibrations of an aromatic ring (3040, 3070, 3100 cm^{-1}); the intensity of the stretching vibration of an ethylenic bond ($-C=C<$) (1650 cm^{-1}) was increased because of its conjugation with a disubstituted ethynyl bond appearing in the form of a band in the 2235 cm^{-1} region. The PMR spectrum was characterized by the signals of the following protons: those of an aromatic nucleus (singlet at 7.1 ppm), of a methylene group (singlet at 3.5 ppm), of a cis-olefin (quartet at 5.5 ppm, J = 7 Hz), and of a methyl group (1.5 ppm). According to the spectra, the substance isolated was 1-phenylhex-2-en-4-yne.

Substance 2 (peak 18, R_f 0.87) represented an acetylenic hydrocarbon, $C_{12}H_{10}$. Its IR spectrum contained, together with the absorption bands of an aromatic ring and of a dialkyl-substituted acetylenic bond, the absorption bands characteristic for a monosubstituted acetylenic bond — deformation vibrations (665 cm^{-1}), stretching vibration (2160 cm^{-1}), and a strong narrow band at 3300 cm^{-1} in the region of stretching vibrations.

The PMR spectrum was disinguished by its simplicity: a singlet at 7.1 ppm of five aromatic protons, two singlets at 3.4 and 3.5 ppm belonging to methylene groups adjacent to an acetylenic bond and to an aromatic ring, respectively, and the singlet of the proton of a terminal acetylenic bond at 2.2 ppm. According to the spectrum, the substance isolated is not 1-phenylhexa-2,4-diyne, as Nesmelova and Sidyakin [5] considered, but 1-phenylhexa-2,5-diyne.

The oxygen-containing fraction was eluted with benzene and diethyl ether. It consisted of monoterpene alcohols and ketones. The ketones were isolated from the mixture in the form of the 2,4-dinitrophenylhydrazones, which, after separation on a column containing alumina, had the melting points: 115°C (mixture of α- and β-thujones — 1.9%); 189°C (d-carvone — 0.4%); and 173°C (camphor — 1.8%).

The terpene alcohols were isolated preparatively by GLC. The following were identified by a comparison of their IR spectra and the corresponding constants [9]: linalool — 4.5%; thujyl alcohol — 0.66%; geranyl acetate — 0.7%; borneol — 0.38%; 4-terpineol — 3.6%; and α-terpineol — 0.9%.

EXPERIMENTAL

The essential oil was obtained by the distillation of the partly dried plant material with water. Gas — liquid chromatography was carried out on a Vyru-Khrom chromatograph using a flame-ionization detector.

IR spectra were recorded on a UR-20 instrument, and PMR spectra on a B487C NMR spectrometer.

The components were determined quantitatively by the method of an internal standard and internal normalization. Naphthalene was used as the internal standard for hydrocarbons, and fenchone for the oxygen-containing components.

The phenols were isolated by the usual procedure [9]. After elimination of the solvent, crystals of 2-acetoxy-4,5-dimethoxycinnamic acid with mp 198-199°C (from methanol) were deposited from the phenolic fraction [1].

The fraction was analyzed by GLC (column 2.5 × 0.3 m, PEG 1540, 7% by weight of Celite 545, 80-100 mesh). Thymol and cis- and trans-eugenols were identified by their retention times [10].

The fraction remaining after the extraction of the phenols (9.2) was chromatographed on alumina (activity grade II, 450 g). Petroleum ether eluted hydrocarbons and some scoparone, crystals of which appeared after the solvent had been eliminated. A mixture of benzene and diethyl ether eluted the oxygen-containing components.

Identification of the Hydrocarbons. The hydrocarbon fraction (6.4 g; 64% of the total oil) was chromatographed with programming of the temperature from 70 to 170°C at 2 deg/min (the same column).

Terpene and sequiterpene hydrocarbons were identified by comparing their retention times with literature figures [10, 11]. The hydrocarbon fraction was then subjected to vacuum distillation (60°C/3 mm) in order to eliminate monoterpene hydrocarbons.

The remaining hydrocarbons (3.8 g) were chromatographed on alumina (activity grade II, 380 g) with petroleum ether as the eluent. Fractions with a volume of 50 ml each were collected and their compositions were monitored by TLC. Fractions 15-25 were combined and rechromatographed on alumina (1 : 200). In this way, two hydrocarbons were isolated.

Substance I (Fig. 1, peak 19) formed a faintly yellow liquid with the composition $C_{12}H_{12}$; n_D^{20} 1.5690, d_{20}^{20} 0.9740, R_f 0.59. IR spectrum (cm^{-1}): 700, 735, 1500, 1605, 3040, 3070, 3100 — monosubstituted aromatic nucleus; 1650 — disubstituted ethylenic bond; 2235 — disubstituted ethynyl bond.

PMR spectrum (ppm): 7.1 — singlet corresponding to five protons of an aromatic nucleus; 3.5 — methylene group; 4.5 (quartet) — protons at an ethylenic bond; 1.5 — methyl group.

Substance 2 (Fig. 1, peak 18) formed a yellow liquid with the composition $C_{12}H_{10}$, n_D^{20} 1.5675, D_{20}^{20} 0.9710, R_f 0.87 (Al_2O_3, hexane).

IR spectrum (cm^{-1}): 700, 735, 1500, 1605, 3040, 3070, 3100 — monosubstituted aromatic nucleus; 665, 2160, 3300 — monosubstituted acetylenic bond; 2235 — disubstituted acetylenic bond.

PMR spectrum (ppm): 7.1 — singlet of five protons of an aromatic nucleus; singlets at 3.4 and 3.5 ppm — methylene groups; 2.2 — singlet of a single proton of an acetylenic bond.

Identification of the Carbonyl Compounds. 2,4-Dinitrophenylhydrazones were obtained by a known method [9]. They were separated on alumina (activity grade II) with benzene as eluent. Three fractions were isolated, and from these after distillation of the solvent and recrystallization from ethanol, crystals were obtained with mp 115°C (mixture of α- and β-thujones), 175°C (*l*-camphor), and 189°C (d-carvone).

The terpenols were isolated preparatively on a UKh-2 chromatograph with a 150 × 6 cm column containing 20% of PEG-2000 on Celite 545, 60-80 mesh. A comparison of the constants and IR spectra with those of known samples permitted the identification of: linalool, 4-terpineol, α-terpineol, thujyl alcohol, geranyl acetate, and borneol.

SUMMARY

1. The essential oil of the oriental wormwood growing in Kazakhstan has been studied.

2. Sesquiterpene hydrocarbons have been detected in the oil of this plant for the first time.

3. On the basis of an analysis of spectral characteristics the structure of the $C_{12}H_{10}$ acetylenic hydrocarbon has been corrected (1-phenylhexa-2,5-diyne).

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