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Sesquiterpene lactones in the aerial part of *Artemisia maritima* L.

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Abstract: Three substances are separated from the above-ground part of *Artemisia maritima* L. by column chromatography method in an individual state: $C_{15}H_{18}O_3$ with a m.p. of 171-172°C (substance 1), $C_{15}H_{18}O_3$ with a melting temperature of 130-131°C (substance 2), $C_{15}H_{18}O_4$ with a melting point of 201- 202°C (substance 3), which are identified as α-santonin, glabellin and artemisin on the basis of ^{1}H NMR spectra and direct comparison of IR spectra.

Key Words: *spectroscopy, eudesmanolides, ^{1}H NMR, chemical shift, spin-spin interaction constant, tetramethylsilane*

INTRODUCTION

The usefulness of plants is estimated by the presence of biologically active substances in its composition. Most plants of the genus *Artemisia* L., *Helenium* L., *Ferula* L. are rich in such substances. In particular, sesquiterpene lactones found in these plants have a wide therapeutic spectrum of action against fungi (knitcin, arctiopicrin), anthelmintic (α-santonin, gafrinin, alantactactone, isoalantholactone) [Rybalko, 1978], malignant tumors (arglabin, gailarin, artenolide, costunolide, vernolide) [Rybalko, 1978; Kagarlitsky et al., 1987, Lucas et al., 1964], painkillers (amaralin), in the treatment of trophic ulcers (badhyzin), as antioxidants (alkhanin, alkhanol, alkhanen, erivanin), antineoplastic (arglabin, gayllardin, parthenin, vernolide, etc.) [Rybalko, 1978; Kagarlitsky et al., 1987], analgesic (amaralin) [Lucas et al., 1964], anti-inflammatory, antiburn, anti-trophic-ulcer properties (badhyzin) [Serkerov, 2005].

Given the above useful properties, we decided to study the sesquiterpene lactones in the aerial part of *Artemisia maritima* L., distributed in the territory of the Republic of Azerbaijan.

MATERIAL AND METHODS

Plant material. The material for the study was the aerial part of *Artemisia maritima* L., collected in the beginning of budding in the vicinity of the village of Buzovna, Absheron in June 18, 2016.

Extraction. Finely ground air-dry material of 191, 0 g was extracted with acetone three times, each time for 3 days. Before the use the acetone was filtered and distilled off in a hot water bath. The obtained dark green resin was 30.0 g and yield was 15.70%.

Extractive substances with an amount of 30.0 g was dissolved in 50 ml of chloroform and chromatographed on a column of Al_2O_3 neutral III-IV degree of activity (h=80, d=2.5 cm) was eluted with hexane: a mixture of hexane/benzene in the ratio 1: 1, 1: 2, 1: 3; benzene, a mixture of benzene and chloroform 3: 1, 3: 2, 1: 1; chlorophyll with alcohol in a ratio of 95: 5.

The volume of each fraction (total 26 fractions) was 100 ml. Three substances were individually identified.

For obtaining biologically active substances in an individual form (sesquiterpene lactones), the finely modified dry aerial part was extracted with acetone (three times, three days each time), the resulting amount of extractive substances was chromatographed on a column filled with neutral, III-IV degree of Al_2O_3 activity. The IR spectra of the individual substances obtained were recorded on a Varian 640 spectrometer. IR spectra of ^{1}H NMR were taken on a Bruker 300 spectrometer with a resonant frequency of 300 MHz. Solvent was DMSO-d6. Chemical shifts are given on the δ-scale (ppm). Internal standard was TMS. The individuality of the isolated compounds was determined on Silufol UV-254 plates, the melting point on the Boetiusa table.

From fractions 4-6, eluted mixture of hexane and benzene in a ratio of 1: 3 was isolated crystalline substance $C_{15}H_{18}O_3$ with melting point 171-172° C (from aqueous ethanol) (substance 1). From fractions 16–19, which were used with benzene, isolated substance $C_{15}H_{18}O_3$ with a melting point of 130-131 ° C (substance 2). From fractions 22-26, eluting with chlorofor, crystallized substance $C_{15}H_{18}O_4$ with melting point 201-202° C (substance 3) was obtained from aqueous ethanol.

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RESULTS AND DISCUSSION

Using the column chromatography method, three substances were isolated from the sum of the extractive substances of the aerial part of *Artemisia maritima* in an individual state.

Substance 1 has the composition $C_{15}H_{18}O_3$ with melting temperature of 171-172°C. In the IR spectrum has bands of γ-lactone carbonyl (1785 cm^{-1}) of the ketone group (1660 cm^{-1}) and conjugated double bonds (1630, 1620 cm^{-1}). In the 1H NMR spectrum of the compound appear signals of the secondary methyl group 1.25 ppm. (3H, d, J = 7.00 Hz, CH3-CH -), 1, 31 (CH3-C -), 2.10 (3H, s, CH3-C =), 5.80 (1H, d, J = 9.90 Hz, CH =), 6.88 ppm (1H, d, J = 9.90 Hz, CH =). Based on the 1H NMR spectrum, as well as by direct comparison of the IR spectra, the substance was identified with α-santonin [Serkerov, Aleskerova, 2006, Tolstykh, 1974].

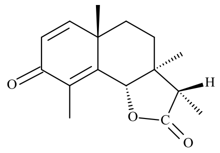
Substance 2. $C_{15}H_{18}O_3$ and m.p. 130-131°C. The IR spectrum has bands of the CO-influenza γ-lactone cycle (1755 cm^{-1}), cyclopentanone (1700 cm^{-1}) and a double bond (1655 cm^{-1}).

The 1H NMR spectrum of the test substance detects the signals of the secondary methyl group (0.96, 3H, d, J = 6.0 Hz) of the double bond in the methyl group (3H, s, 1.59, CH3-C =) of the olefin proton 5.51 (1H, t, J = 2.0 Hz, CH =), the lactone proton 3.61 (1H, d, J1 = J2 = 12.0 Hz) and the methylene double bond 5.62 (1H, d, J = 2.00 Hz and 6, 18 ppm) (1H, d, J = 2.0 Hz, CH2 = C =).

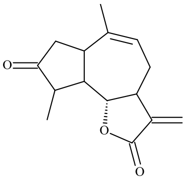
By comparing the infrared spectrum of a substance and glabellin sesquiterpene lactone, as well as based on the interpretation of the 1H NMR spectrum of the substance under investigation, the latter was identified with glabelline.

Substance 3. $C_{15}H_{18}O_4$ with m.p. 201-202° C. The IR spectrum found bands of a hydroxyl group (3500 cm^{-1}), a-lactone cycle (1770 cm^{-1}), 1670 (CO-ketone group) of a six-membered cycle (1670 cm^{-1}) and conjugated double bonds (1640, 1620 cm^{-1}).

The IR spectra of substance 3 in detail coincides with that of artemisin, which indicates the identity of substance 3 with artemisinin mixed sample of comparable samples of depression so p.m. does not give.



(1)



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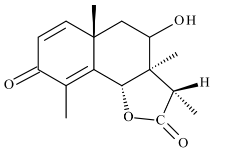

(3)

According to the literary data, sesquiterpene lactones α-santonin, artemisinin isolated from *Artemisia maritima*, growing in Azerbaijan are also isolated from *A. santonica* L. (*A. maritima* L. var. *salina* and others) [Kagarlitsky et al., 1987; Tolstykh et al., 1974].

Thus, sesquiterpene lactones α-santonin, glabellin and artemisin were identified and isolated from the aerial part of *A. maritima* L., which can be used as chemical markers in chemos-systematic studies of genus *Artemisia* L.T. The flora of Azerbaijan is rich in various biologically active substances. Sesquiterpene lactones, coumarin derivatives, steroids were obtained from representatives of the Astaraceae and Apiaceae and other families, which are widely used in medical practice. Representatives of these compounds have different pharmacological activity, are used as an anesthetic, anticoagulant, capillary strengthening, anticarcinogenic, anti-inflammatory and choleretic agent, and so on [Arzamastsev, 2004; Okamoto et al., 2005; Kang et al., 2009; Feng et al., 2010; Anand et al., 2012; Venugopala et al., 2013; Kermani et al., 2016; Zohu et al., 2017; Znati et al., 2018].

As a result of the conducted research, 64 biologically active substances and 17 new ones (gairanbatolid, artapshin, artapshinin, iskenderolide, iskenderin, artabine, merizolid, alkhanin, alkhanol, alkhanen, erivanin, artesovin, shonachalin A, shonachalin B, shonachalin C, shonachalin D) sesquiterpene lactones identified in representatives of the genus *Artemisia*. After a detailed study from a pharmacological point of view, they were proposed for use in medical practice. Ongoing research on the study of sesquiterpene lactones of species of the genus *Artemisia* L. expands our knowledge on the detection of the substance of the species within the genus [Serkerov et al., 1985; Serkerov, Aleskerova, 1987, 2011].

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Artemisia maritima L. növünün yerüstü hissələrinin seskviterpen laktonlari

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Abşeronun Buzovna kəndi ətrafından gönçələmə fazasında toplanmış *Artemisia maritima* L. (Asteraceae) növünün yerüstü hissələrindən sütunlu xromatoqrafiya metodu ilə 3 fərdi kristallik maddə: 1. $C_{15}H_{18}O_3$ ə.t. 171-172°C, 2. $C_{15}H_{18}O_3$, ə.t. 130-131° C, 3. $C_{15}H_{18}O_4$, ə.t. 201-202° C alınmışdır. Onların ^{1}H NMR-spektirlərinin aydınlaşdırılmasından alınan nəticələr əsasında və həmçinin İQ-spektrlərinin bilavasitə müqayisəsi əsasında 1,2,3 maddələri uyğun olaraq α– santonin, qlabellin və artemizinlə identifikasiya edilmişdir.

Açar sözlər: *spektroskopiya, evdesmonolidlər, ^{1}H NMRS, kimyəvi sürüşmə, spin-spin qarşılıqlı təsir konstantı, tetrometilsilan*

Сесквитерпеновые лактоны в надземной части *Artemisia maritima* L.

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Из надземной части *Artemisia maritima* L. методом колоночной хроматографии в индивидуальном состоянии выделены 3 вещества $C_{15}H_{18}O_3$ с температурой плавления 171-172° C (вещество 1), $C_{15}H_{18}O_3$ с температурой плавления 130-131° C (вещество 2), $C_{15}H_{18}O_4$ с температурой плавления 201-202°C (вещество 3), которые на основании данных ^{1}H ЯМР спектров и непосредственным сравнением ИК-спектров идентифицированы как α-сантонин, глабеллин и артемизин.

Ключевые слова: *спектроскопия, эвдесманоиды, ^{1}H ЯМР, химический сдвиг, спин-спиновые взаимодействия, тетрометилсилан*