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The volatile compounds of some halophytes from Kazakhstan

Қазақстан өсімдіктерінің кейбір ұшқыш галофит қосылыстары

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Алғаш рет Оңтүстік және Оңтүстік Шығыс Қазақстанда жиналған, сәйкесінше, *H. belangeriana Botsch.* және *H. ammodendron Bge.* жер үсті бөлігінің ұшқыш қосылыстарының құрамы газхроматография әдісінің көмегімен анықталған. *H. belangeriana Botsch.*-тың жапырақтарының, *H. ammodendron Bge.*-нің бұтақтарының ұшқыш қосылыстары — гидродистильдеу, ал *H. ammodendron Bge.*-нің жемістерінің ұшқыш қосылыстары микродистильдеу әдістер арқылы зерттелген. Жоғарыда келтірілген өсімдік мүшелерінің ұшқыш қосылыстарының сандық және сапалық құрамдары бір-бірінен ерекшеленеді. *H. ammodendron Bge.-нің* жапырақтары үшін — 28*; H. ammodendron Bge.*-нің жемістері үшін — 31, сабақтары үшін 37 ұшқыш қосылыстар сапалы түрде табылып сәйкестірілген.

Впервые методом газовой хроматографии определен состав летучих соединений надземной части *H. belangeriana Botsch.* и *H. ammodendron Bge.,* собранных в Южном и Юго-Восточном Казахстане, соответственно. Летучие соединения листьев *H. belangeriana Botsch.,* стеблей *H. ammodendron Bge.* получены методом гидродистилляции; а фруктов *H. ammodendron Bge.* — микродистилляции. Качественный и количественный состав летучих соединений приведенных выше органов растений отличаются друг от друга. Качественно идентифицированы 28 летучих соединений для листьев *H. belangeriana Botsch.*; 31 — фруктов, 37 — для стеблей *H. ammodendron Bge.*

Two species of halophytes *Haloxylon ammodendron Bge*. (H. ammodendron Bge.) and *Halostachys belangeriana Botsch.* (H. belangeriana Botsch.) belong to the family Chenopodiaceae which comprises 100 genera and 1400 species [1]. In Kazakhstan this family is represented by 53 genera [2].

Halostachys is monotypic genus, containing the single species *H. belangeriana Botsch. Halostachys* affects toxically the plant pests. Plants are 3.5 m tall. Stems erect, much branched; older branches are usually leafless, annual ones blue-green, fleshy, jointed, densely finely papillate. Leaves opposite are scale-like, connate basally, apex is acute. Spikes are decussate, terete, 15–30 × 2–3 mm; peduncle is jointed. Perianth is obovoid, apically 3-lobed; lobes are incurved. Ovary is ovoid, subulate, papillate. Utricle is ovoid too; pericarp is membranous. Seeds are red-brown, ovoid or cylindric-ovoid, 6–7 mm in diameter. Flowers and fruits in between July-September.

Only three species of genus *Haloxylon* are found in Kazakstan: *H. aphyllum* Bge. (black saxaul), *H. persicum* Bge. (white saxaul) and *H. ammodendron* Bge. (zaisanii saxaul). *H. ammodendron Bge.'s* shrub up to 2 meters, with thick gnarled trunk of light green colour, leaves undeveloped, obtusish; puberulous fruiting calyx has large suborbicular wings

The genus Haloxylon is traditionally reported for its toxicity and applied externally on scorpion and snake stings. The ash is used for internal ulcers [3, 4].

Early phytochemical studies on *H. belangeriana Botsch.* have indicated the presence of alkaloid (halostachine) [5]. The composition of lipids from the aerial parts of *Halostachys caspica* C.A.Mey. was determined [6]. Neutral lipids (NL, 62.1 %) dominated the total lipids (TL) of this plant. More than a third of the NL was esters of aliphatic alcohols and phytosterols (FAE). Fatty acids 16:0, 18:1, and 18:2 dominated the acids of FAE; 16:0, 18:1, and 18:3, the phospholipids. The principal fatty acids of glycolipids were unsaturated acids (68.3 %) with linolenic acid dominating (44.9 %).

In the mentioned work research-scientific complex is carried out on finding out, extracting and separating biologically active substances which can be found in *H. belangeriana Botsch.* [7]. It is found out, that basic groups of biologically active substances can be represented by flavonoids, amino acids, phenols, kumarin, alkoloids, vitamins C, E, macro- and microelements. Also, phytochemical value of the mentioned plant which grows in Almaty, Semipalatinsk, Qzylorda regions, and it is claimed that in plants growing in Semipalatinsk region the amount of plavonoids, amin acids organical acids are higher than in pants from other regions.

The new chemical compounds 12-(7'-oxymethylen), kumarin 17-O-α-D-glukopiranozido-12,16,16,20-tetramethyl-13-en-decalin were isolated and characterized. In individual condition such flavonoids as: chrisoeriol-7-O-β-D-glukopiranozil-(6–1)-O-α-L-ramnopiranozid, isoramnitin-3-O-β-D-glukopiranosil-(6-1)-α-L-arabopiranosid, 3-O-β-D-glukopiranosil (6–1)-arabopiranesido-7-O-α-L-ramnopiranesid-5,4-dihydroxy-3-metoxy-flavonol were extracted from ethylacetat fraction by chromatography on polyamide. Water-alcohol based phyto preparation extract of *H. belangeriana Botsc* on concentration 400 mg/mL inhibits mushroom *allescheria doydii* for 50 %, mushroom *trichophyton mentagrophytes* 49.23 %, and ethyl acetate extract inhibits *candida albicans* 51.62 %

H. ammodendron Bge. very few researches were done on it's phytochemical content. Alkaloid ammodendrine was found in it [8]. The qualitative composition and quantitative content of the biological active compounds of aerial part of *H. ammodendron Bge.*were found to be as: flavonoids (0.60 %), phenolic acids (1.49 %), carbohydrates (1.56 %), amino acids (1,18 %) and tannins (3.64 %). In the mineral composition of the ashy residue of the plant material 42 elements were found with strontium, iron, phosphorus and manganese as major constituents [9]. Extracts from the aerial part of *H. ammodendron Bge.* show high antioxidant activity [10].

Literature surveys revealed that volatile compounds of the aerial parts of *H. ammodendron Bge*. and *H. belangeriana Botsch.* has not been chemically studied previously and this article deals with the detailed quantative analysis of the volatiles prepared by hydrodistillation and microdistillation by GC/FID and GC/MS.

28 compounds of *H. belangeriana Botsch.* were characterized, representing 88 % of the total volatiles which were detected and are listed in table 1 with their percentage composition. The major volatile components such as hexadecanoic acid (24.3 %), hexahydrofarnesyl acetone (14.5 %), tricosane (7.3 %), pentacosane (7.1 %), heptacosane (5.1 %), heneicosane (2.7 %), 4-vinyl guaiacol (2.6 %), 3,4-dimethyl-5-pentylidene-2(5H)-furanone (2.2 %), docosane (2.2 %) were found.

Table 1

Chemical composition of the volatiles from leaves of *H. belangeriana Botsch.*

RRI	Compound	Leaves, %	RRI	Compound	Leaves, %
1400	Nonanal	1.0	2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	2.2
1496	2-Ethyl hexanol	0.9	2218	4-Vinyl guaiacol	2.6
1500	Pentadecane	0.6	2220	6,10,14-Trimethylpentadecan-2-ol	1.3
1562	Octanol	0.8	2220	3,4-Dimethyl-5pentyl-5H-furan-2-one	1.0
1600	Hexadecane	1.6	2224	Docosane	2.2
1700	Heptadecane	1.6	2307	Tricosane	7.3
1800	Octadecane	1.2	2400	Tetracosane	1.6
1868	(E)-Geranyl acetone	1.3	2500	Pentacosane	7.1
1900	Nonadecane	1.1	2600	Hexacosane	1.3
1958	(E)-β-Ionone	1.5	2607	1-Octadecanol	1.0
1993	*trans*-β-Ionone-5,6-epoxide	0.3	2622	Phytol	0.9
1995	(E)-5-Eicosene*	1.0	2700	Heptacosane	5.1
2100	Heneicosane	2.7	2740	Anthracene	tr
2131	Hexahydrofarnesyl acetone	14.5	2931	Hexadecanoic acid	24.3
			TOTAL		88.0

RRI — Relative retention indices calculated against n-alkanes; % calculated from FID data; tr — Trase (<0.1 %).

Qualitive and quantitive composition of volatile compounds of fruits and stems of *H. ammodendron Bge.* differ from each other. 31 compounds in fruits, 37 in stems of *H. ammodendron Bge.* were identificated.

The fruits of *H. ammodendron Bge.* were found to be rich in 2,4-dimethylether phloroacetophenone (16,5 %), heptacosane (13.9 %), hexadecanoic acid (13.0 %), hexahydrofarnesyl acetone (10.1 %) nonacosane (8.8 %), pentacosane (4.2 %); whereas stem in — hexadecanoic acid (37.6 %), phytol (9.9 %) (table 2).

Thus, for the first time researches on overground parts of *H. ammodendron Bge.* и *H. belangeriana Botsch.* were carried out by gas chromatography method.

Table 2

Chemical composition of the volatiles from the aerial parts of *H. ammodendron Bge.*

RRI	Compound	Fruit, %	Stem, %	RRI	Compound	Fruit, %	Stem, %
1198	Dehydro-1,8-cineole		0.3	2131	Hexahydrofarnesyl acetone	10.1	3.4
1203	Limonene		0.2	2179	3,4-Dimethyl-5-pentylidene-2(5)-furanone		0.6
1244	Amyl furan (2-pentyl furan)		0.3	2179	Tetradecanol		0.8
1360	Hexanol		0.3	2181	Isothymol (2-Isopropyl-4-methyl phenol)	1.1	0.1
1400	Nonanal	2.2	0.4	2218	4-Vinyl guaiacol	1.9	0.2
1400	Tetradecane	0.5		2220	3,4-Dimethyl-5-pentyl-5H-furan-2-one	0.3	tr
1500	Pentadecane	0.3	0.3	2221	Isocarvacrol (4-Isopropyl-2-methyl phenol)	0.4	
1506	Decanal	0.4	0.1	2226	Methyl hexadecanoate (methyl palmitate)	0.4	
1525	Theaspirane A		0.3	2239	Carvacrol		0.5
1541	Benzaldehyde	1.3		2298	Decanoic acid	0.8	
1569	Theaspirane B		0.2	2301	Dibenzofurane		0.3
1600	Hexadecane	0.3		2307	Tricosane	0.3	0.5
1673	Safranal		0.9	2380	Dihydroactinidiolide	2.5	
1700	Heptadecane	0.4		2382	9-H-Fluorene		2.1
1706	б-Terpineol	0.4	0.4	2395	Hexylcinnamic aldehyde		0.3
1763	Naphthalene		0.3	2397	Farnesyl acetone		0.5
1827	(E, E)-2,4-Decadienal		tr	2500	Pentacosane	4.2	1.4
1830	Tridecanal	1.1		2503	Dodecanoic acid	2.3	3.3
1838	(E)-β-Damascenone		0.4	2600	Hexacosane		0.2
1868	(E)-Geranyl acetone	0.8	1.4	2607	1-Octadecanol	0.6	
1910	1-Izobutyl 4-isopropyl 3-isopropyl 2,2-dimethyl succinate		0.3	2615	2,4-Dimethylether phloroacetophenone (Adams, 97 %, WileyNIST)*	16.5	
1933	Tetradecanal	0.4		2622	Phytol	0.5	9.9
1958	(E)-β-Ionone		1.2	2670	Tetradecanoic acid	1.7	
1973	Dodecanol	1.9	tr	2700	Heptacosane	13.9	
1985	Trans-β-Ionone-5,6-epoxide		tr	2900	Nonacosane	8.8	5.4
2041	Pentadecanal	0.3		2931	Hexadecanoic acid	13.0	37.6
				TOTAL		89.6	74.4

RRI — Relative retention indices calculated against n-alkanes; % calculated from FID data; tr — Trase (<0.1 %); * — Tentative identified.

Experimental

Plant Material and Isolation Procedure

Aerial parts of *H. belangeriana Botsch. and H. ammodendron Bge.* were collected in May 2009 from Kzylorda region in the South Kazakhstan and in September 2008, during the fruiting stage, in Almaty province of the South-Eastern Kazakhstan correspondingly.

H. belangeriana Botsch.'s leaves, *H. ammodendron Bge.'s* stem were dried at room temperature, crushed plant were hydro-distilled using a Clevenger-type apparatus for 3 h. The *H. ammodendron Bge.'s* fruit prepared by the same way passed the microdistillation *(*Eppendorf MicroDistiller).

Analysis

The volatiles were analyzed by capillary Gas Chromatography-Flame Ionization detection (GC/FID) and Gas Chromatography–Mass spectrometry (GC/MS) using an Agilent 5975 GC-MSD system. The same column and analysis conditions were used for both GC/MS and GC/FID. HP-Innowax FSC column was used with helium as a carrier gas. GC oven temperature was kept at 60 °C for 10 min and programmed to 220 °C for 10 min and then programmed to 240 °C at a rate of 1 °C/min. The split ratio was adjusted at 40:1. Flame ionization detection and injector temperature were perfomed at 250 °C. Mass spectrums were taken at 70 eV. Mass range was from *m*/*z* 35 to 450. The GC-FID analysis was carried out using an Agilent 6890N GC system. In order to obtain same elution order with GC/MS, simultaneous injection was done by using the same column and appropriate operational conditions. Identification of the volatile constituents was achieved by parallel comparison of their retention indices and mass spectra with data stored in the Wiley GC/MS Library, MassFinder software 3.0, Adams Library, NIST Library and Baser Library of Essential Oil Constituents. Relative percentage amounts of the separated compounds were calculated from FID chromatograms.

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Принцип моделирования физико-химических свойств процесса твердения бетонных изделий

The principle of modeling physical & chemical characteristics of concrete products setting process

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Мақалада бетон қоспаларының алғашқы қатаю мерзіміндегі физика-химиялық процестердің көрсеткіштері баяндалған. Бұл көрсеткіштер бетон материалдарының соңғы физикалық және механикалық қасиеттерін анықтауда қолданылады. Қатаю процестердің көрсеткіштерін анықтау үшін бетон қоспасының ылғалдығының азаю электрмоделі берілген. Ұсынылған электр модель арқылы алғашқы қатаю мерзім көрсеткіштерін дер кезінде анықтап, бетон материалдарының соңғы көрсеткіштерін басқару мүмкіндіктері туады.

Initial physical and chemical parameters of concrete mixes setting were described in the article. Initial indices of concrete setting define final physical and mechanical properties of products. Electrical models of decreasing humidity were given for determination of setting indices.With the help of electrical model proposed one can determine setting time and to control the indices of final setting of concrete.

По результатам теоретических и экспериментальных исследований установлено, что процесс набора прочности бетонных изделий связан с изменением влажности, которая определяется количественным соотношением химически связанной (ХСВ) и свободной воды [1].

Несмотря на разнообразие представлений о химизме образования структур, содержание ХСВ и может быть выражено уравнением [1, 2]:

$$\frac{dw}{dt} = \gamma f\left(w_{\infty} - w\right), \quad (1)$$