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COMPOSITION OF THE VOLATILE OIL FROM AERIAL PARTS OF *LIMONIUM* GENUS

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Abstract. The chemical composition of essential oil obtained by steam distillation from the flower, leaf and stem of *Limonium caspium and Limonium leptophyllum* which are endemic to Kazakhstan, were analyzed by GC/FID and GC/MS. The oils have unpleasant smell indicating that the oil compositions are different than regular volatile oils. The components of the oil were identified by comparing their retention time and mass fragmentation patterns with those of the available references and/or with published

data as well as through GC/MS library search. This is the first report of the composition of the volatile oil of these *Limonium* genus species.

Key words: *Limonium caspium, Limonium leptophyllum*, Family Plumbaginaceae, volatile oil composition.

Introduction. *Limonium* is a genus of about 150 species of annuals, biennials, perennials, and subshrubs grown for their sprays of papery flowers in summer and autumn. They are native to coasts, salt marshes, and deserts around the world, and therefore need sandy or stony soil. Grow in a border, cutting garden, coastal garden, or rock garden, depending on species size. Members are also known as Sea Lavender, Statice, or Marsh-rosemary. *Limonium* is in Plumbaginaceae, the plumbago or leadwort family. Despite their common names, species are not related to the lavenders or to rosemary. Taxonomy: the plant belong to: Kingdom: *Plantae*; Order: *Caryophyllales*; Family: Plumbaginaceae; Subfamily: Staticoideae; Genus: *Limonium*. Literature search showed nothing had been done on the chemistry and pharmacology of *Limonium caspium* and *Limonium leptophyllum*. This encouraged us to carry out in detail phytochemical and biological studies on the aerial parts of the plants. In this manuscript, we report the chemical composition of the volatile oils isolated from the aerial parts of above mentioned plants.

Experimental part

Plant material: The aerial parts including flowers of the plants *Limonium caspium, Limonium leptophyllum* were collected during the flowering period from the Republic of Kazakhstan different regions. The plants were identified by professors of botany at Institute of Botany and Introduction MES, Almaty. The plant materials previously were air dried, then ground to a particle size in the range 2.0-3.0 mm, according to regulatory documents.

Steam distillation: The volatile oils from the aerial parts of the plants were prepared by hydrodistillation. Air-dried plant materials were subjected to steam distillation (17 hours) to yield 3.1 and 4.4 g volatile oils, respectively. The oils were dried with anhydrous Na_2SO_4, measured band transferred to glass vials and kept at temperature of -18 °C for further analysis.

Volatile Oil Solution: For GC/MS analysis the volatile oil were dissolved in dichloromethane at a concentration of 10 mg/ml. Solutions for standards (Sigma Chemical Co. and Aldrich Chemical Co. Inc.) were prepared in dichloromethane at concentrations of 1 mg/ml.

GC/MS Analysis: GC/MS analysis was carried out on a HP 6890 series GC, equipped with a split/splitless capillary injector, a HP 6890 Series injector auto sampler, and a DB-5 ms column (30 m x 0.25 mm x 0.25 μm, Agilent).The GC was interfaced to a HP 5973 quadruple mass selective detector through a transfer line set at 240^0C. The injector temperature was 250^0C, and 1 μl injections were performed in the split (1:10) mode. Column flow was set at a constant pressure of 5.66 psi, giving an initial flow of 0.7 ml/min, using helium as carrier gas. The

oven temperature was raised from 70^0C to 200^0C at rate 2^0C/minute. Then continue at 200^0C for 15 minutes. The total run was 80 minutes. The filament was operated at 70 eV. The multiplier voltage was automatically set to 2247 V. The ion source and quadruple temperatures were 230 and 150^0C, respectively. The acquisition range was m/z 30–800 at 1.95 scans per second, starting 3.5 min after injection. As well as the oil samples were analyzed by GC-FID on a Agilent 5975 C inert XL MSD with triple axis detector/7890A GC system equipped with an Agilent 7693 Autosampler, with a silica capillary column (film thickness of 0.25 μm) operated in the above mentioned conditions (injection volume, 1 μl (split on FID, split ratio 50:1); FID temperature was 330°C).

Results and Discussion

The oils were light yellow in colors. GC/MS analysis of the oils resulted in the identification of 21 components in the plant of *L. caspium* species only (table 1), as well as 31 components in the plant of *L. leptophyllum* species (table 2), and 10 were presented in both plants (table 3). The components of the oil were identified by comparing their retention time and mass fragmentation patterns with those of the available references and/or with published data as well as through GC/MS library search. This is the first report of the composition of the volatile oils of the plants.

Table 1 – Chemical composition of the volatile oil of the plant *L. caspium*

Retention time, min	% of each peak	Identification
6.612	0,23	Camphene
6.850	1,85	Benzaldehyde
8.874	0,13	1,2,4-trimethyl-Benzene
8.941	0,86	o-Cymene
9.110	0,40	D-Limonene
9.189	8,87	Eucalyptol
10.385	2,11	Acetophenone
11.506	0,42	Benzoic acid, methyl ester
11.732	0,49	gamma-Terpinene
13.527	20,82	(+)-2-Bornanone
13.924	0,79	5-methyl-2-(1-methylethyl)-,(2R-cis)-Cyclohexanone
14.929	1,36	2,6-Dimethyl-1,3,5,7-octatetraene E,E
15.091	1,03	Naphthalene
15.227	0,87	1-methyl-4-(1-methylethenyl)-Benzene
17.119	0,81	1-methyl-4-(1-methylethylidene)-Cyclohexene
19.766	1,74	1-methyl-Naphthalene
20.465	0,43	2-methyl-Naphthalene
28.445	0,53	Dodecane
30.664	0,46	gamma-Neoclovene
31.215	1,02	Dodecanoic acid
36.621	0,83	2,6-Diisopropylnaphthalene

Table 2 – Chemical composition of the volatile oil of the plant *L. leptophyllum*

Retention time, min	% of each peak	Identification
25,645	0,19	1,2-dihydro-2,5,8-trimethyl-Naphthalene
26.961	0.58	8-methyl-Heptadecane
29.462	0,31	4,6,8-Trimethylazulene
30.068	0,08	1,4,6-trimethyl-Naphthalene
34.508	0,50	Alloaromadendrene
34.755	0,35	1,4,5,8-Tetramethylnaphthalene
36.028	4,79	Heptadecane
36.251	1,40	2,6,10,14-tetramethyl-Pentadecane
37.008	1,03	Chamazulene
37.587	0,17	[1,1'-Biphenyl]-4-methanol
38.477	2,68	Anthracene
39.870	1,64	Hentriacontane
40.070	0,56	9,10-dihydro-1-methyl-Phenanthrene
41.673	1,96	5-cyclohexyl-Undecane
41.698	1,62	Cyclotetradecane
41.953	0,61	Methyl 7,9-tridecadienyl ether
42.406	1,31	2-methyl-Phenanthrene
42.590	1,08	1-methyl-Phenanthrene
43.200	1,72	1a,9b-dihydro-1H-Cyclopropa[l]phenanthren
43.373	1,19	2-methyl-Anthracene
44.444	1,15	tetradecyl-Oxirane
45.221	1,17	Heptadecanoic acid, heptadecyl ester
46.130	7,71	Eicosane
46.877	0,64	di-p-Tolylacetylene
47.233	0,36	1,7-dimethyl-Phenanthrene
48.967	0,38	decahydro-2-methyl-Naphthalene
49.197	4,69	Heneicosane
49.592	2,55	3,7,11,15-Tetramethyl-2-hexadecen- 1-ol
52.127	1,03	Docosane
54.968	3,35	Octacosane
60.287	0,28	Tetratetracontane

Table 3 – Chemical composition of the oils presented in both plants *L.caspium* and *L. leptophyllum*

Retention time, min		% of each peak		Identification
LC	*LL*	*LC*	*LL*	
22.339	22.361	0,62	0,20	1,2-dihydro-1,1,6-trimethyl-Naphthalene
24.961	24.933	0,57	0,18	2,7-dimethyl-Naphthalene
25.098	25.124	0,24	0,18	2,6-dimethyl-Naphthalene
29.213	29.232	3,58	2,18	4-methoxy-6-(2-propenyl)-1,3-Benzodioxole
32.359	32.365	5,25	3,31	2,3,4,7,8,8a-hexahydro-3,6,8,8-tetramethyl-[3R-(3.alpha.,3a.beta.,7.beta.,8a.alpha.)]-1H-3a,7-Methanoazulene
39.531	39.556	0,72	8,53	Octadecane
41.062	41.087	5,46	10,18	6,10,14-trimethyl-2-Pentadecanone
42.901	42.921	0,86	9,92	Nonadecane
43.715	43.754	1,12	2,74	Hexadecanoic acid, methyl ester
45.019	45.281	0,24	1,59	n-Hexadecanoic acid

The major constituents in the oil of the plant *L. caspium* species are (+)-2-Bornanone (camphor) 20.82% and Eucalyptol 8.87%, both of them commonly presented in the regular volatile oils. The major constituents of the oil in the plant of the *L. leptophyllum* species mostly presented with higher saturated hydrocarbons: Heptadecane 4,79 %, Eicosane 7,71%, Heneicosane 4,69%, Docosane 1,03%, Octacosane 3,35%. As shown in the table 3 hydrocarbons Octadecane 8,53% and Nonadecane 9,92% presented mainly in the plant *L. leptophyllum* species, then the plant *L. caspium* species Octadecane 0,72% and Nonadecane 0,86%. Compound 6,10,14-trimethyl-2-Pentadecanone presented in a good amount in both plants *L. caspium* and *L. leptophyllum* species as 5,46% and 10,18%, respectively.

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Резюме

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LIMONIUM ӨСІМДІК ТҮРІНІҢ ЖЕРҮСТІ БӨЛІГІНЕН АЛЫНҒАН ЭФИР МАЙЛАРЫНЫҢ ҚҰРАМЫ

Қазақстанда өсетін эндемиктер болып табылатын *Limonium caspium* мен *Limonium leptophyllum* өсімдіктерінің сабақшасы, жапырақтары, гүлдерінен су буының дистилляциясы арқылы алынған эфир майлары ГХ/ПИД мен ГХ/МС көмегімен сарапталды. Алынған май тәрізді сұйықтық эфир майлары ретінде идентифицирленді, олардың өзіне тән эфир майларының қалыпты құрамынан ерекшеленетін иісі бар. ГХ/МС кітапхана ізденісімен, қолжетімді әдебиет көздерінің мәліметтерімен сәйкес заттардың масс-фрагментация шаблондары мен ұстау уақытымен салыстыру арқылы май компонеттері идентифицирленді *Limonium* өсімдік түрінен алғаш реет эфир майлары құрамы бөлініп, анықталды .

Тірек сөздер: *Limonium caspium, Limonium leptophyllum, Plumbaginaceae* түрі, эфир майларының құрамы.

Резюме

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СОСТАВ ЭФИРНЫХ МАСЕЛ
ИЗ НАДЗЕМНОЙ ЧАСТИ РАСТЕНИЙ РОДА *LIMONIUM*

Эфирные масла, полученные дистилляцией водяным паром из цветков, листьев и стебельков растений *Limonium caspium* и *Limonium leptophyllum*, являющихся эндемиками, произрастающими в Казахстане, были проанализированы с помощью ГХ/ПИД и ГХ/МС. Полученные маслообразные жидкости отнесены к эфирным маслам, которые имели неприятный запах, отличающийся от регулярного состава эфирных масел. Компоненты масел были идентифицированы с помощью сравнения времени удерживания и шаблонов масс-фрагментации веществ с соответствующими данными из доступных литературных источников, а также через поиск библиотеки ГХ/МС. Впервые выделен и определен состав эфирных масел из данных видов растения рода *Limonium.*

Ключевые слова: *Limonium caspium*, *Limonium leptophyllum*, семейство Plumbaginaceae, состав эфирных масел.