N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2019.2518-1491.19**
Volume 2, Number 434 (2019), 55 – 60

UDC 547.99

A.I. Zhussupova, Y.S. Ikhsanov, A.A. Mamutova, G.E. Zhusupova

Al-Farabi Kazakh National University
Center for Physical and Chemical Methods of Analysis
Republic of Kazakhstan, 050012, Almaty, Karasay Batyr St., 95a
Aizhan.Zhussupova@kaznu.kz, erbol.ih@gmail.com, Alua.Mamutova@kaznu.kz, zhusupova@gmail.com

COMPARATIVE ANALYSIS OF THE NONPOLAR FRACTION OF THE AERIAL AND UNDERGROUND PARTS OF THE *LIMONIUM GMELINII* PLANTS BY THE GC-MS METHOD

Abstract. This article discusses the chemical composition of the non-polar fraction obtained from the aerial and underground parts of *Limonium gmelini*i (Willd.) harvested in the Almaty region in 2018. Extracts were obtained by the method of solvent extraction with hexane and studied by means of chromato-mass spectrometry on a gas chromatograph with a mass-selective detector.

As a result, 22 compounds were isolated from the aerial part of *Limonium gmelinii* plant, out of which dominating both quantitatively and qualitatively are hydrocarbons, such as genicosane and eicosane and tricosane; quinoline and phytol derivatives were isolated as well. High content of phytol acetate related to derivatives of acyclic diterpene alcohols has been revealed. In addition, the higher alcohol 3,7,11,15-tetramethyl-2-hexadecan-1-ol has been identified.

Analysis of the non-polar extract obtained from the roots of *Limonium gmelinii* allowed us to isolate 14 compounds, out of which the major share in the amount belongs to the esters of higher carboxylic acids and hydrocarbons. Esters are represented as ethyl esters of hexadecanoic, oleic and linoleic acids with prevalence of polyene acids in them. Among the hydrocarbons, tridecane, tetradecane, heptadecane, octadecane and tetracosane are the most abundant.

Keywords: *Limonium gmelinii*, non-polar fraction, GC-MS, chemical composition.

Introduction

Limonium is a widespread plant genus with about 300 species present on the territory of Central and Western Asia. On the territory of CIS, 35 *Limonium* species have been identified. Usually it is accommodated on coniferous soils and dry mountain ranges, mainly in the south-eastern part of Europe, Caucasus, and Central Asia. In Kazakhstan, out of 18 species the most significant and productive is *Limonium gmelinii* (Willd.). The area of its distribution includes major part of Kazakhstan, Western and Eastern Siberia, European part of Russia, Central Asia, Southeastern Europe, Western China and Mongolia. Currently, the roots and the aerial parts of *L.gmelinii* plants have been introduced into the medicine and State Pharmacopoeia of the Republic of Kazakhstan, harmonized with the European Pharmacopoeia [1-8]; with effective drugs obtained and standardized on the basis of its roots [9-12].

The purpose of this work is a comparative analysis of the chemical composition of hexane extracts obtained from the aerial and underground parts of *L.gmelinii* plants, in order to establish their effect on the biological activity of the studied extracts.

Methods

Extracts from the aerial and underground parts of *L.gmelinii* plants were obtained by the method presented below:

A weighed amount of pre-treated, dried and crushed vegetable raw materials, according to their quality indicators, corresponding to the requirements of the State Pharmacopoeia of the Republic of Kazakhstan, weighing 10 g, was extracted with hexane at a ratio of 1:5 for 48 hours. The extract obtained was filtered and concentrated to 10 ml. The resulting total non-polar extract was studied on a gas chromatograph with a mass selective detector model Agilent 7890N/ 5973N (Agilent Technologies, USA). At the same time, the volume of the gas phase to be taken equals 1.00 μl; the sample introduction temperature is 250°C without division of the flow. Separation was performed using a DB-35 MS chromatographic capillary column with a length of 30 m, an inner diameter of 0.25 mm and a film thickness of 0.25 μm at a constant carrier gas (helium) rate of 1 ml/min. The temperature of chromatography was programmed from 40°C to 200°C with a heating rate of 10°C/min.

The software Agilent MSD ChemStation, version 1701EA) was used to control the gas chromatography system, record and process the obtained results and data. Data processing included determination of retention times, peak areas, as well as processing of spectral information obtained using a mass spectrometric detector. The Wiley 7th edition and NIST'02 libraries were used to decipher the mass spectra obtained (the total number of spectra in the libraries exceeds 550,000 items).

Results and discussion

As a result of studying the hexane fraction obtained from the aerial part of plants of the *Limonium gmelinii* species, 22 compounds were identified, most of which belong to the class of hydrocarbons (Table 1 and Figure 1).

Table 1 – Research data by GC-MS of the aerial part of *Limonium gmelinii* plant species

No.	Retention time, min	Name of compound	Content %
1	8.05	Dodecane	0.20
2	9.52	Tridecane	0.50
3	10.91	Tetradecane	1.21
4	11.54	Dodecane, 2,6,10-trimethyl-	0.60
5	12.23	Pentadecane	2.44
6	12.91	Dichloroacetic acid tridecyl ester	0.57
7	13.49	Hexadecane	3.50
8	13.88	1,2-dihydro-2,2,4-trimethyl Quinoline	0.72
9	14.48	2,6,10,14-tetramethyl-Pentadecane	1.16
10	14.68	Heptadecane	3.14
11	15.35	1-Decanol, 2-hexyl	0.36
12	15.,69	Tetracontan	1.29
13	15.81	Octadecane	2.71
14	16.45	Phytol acetate	12.88
15	16.99	Nonadecan	2.80
16	17.07	3,7,11,15-Tetramethyl-2-hexadecan-1-ol	5.17
17	17.20	2-Pentadecanone 6,10,14-trimethyl	2.46
18	18.48	Eicosane	1.93
19	20.47	Genicosan	7.82
20	22.53	1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	0.35
21	22.87	Phytol	0.75
22	27.16	Tricosane	47.44
Total			100.00

As can be seen from the data presented in Table 1, the tricosane hydrocarbon (47.44%) dominates in the obtained hexane extract from the aerial part of the plants *Limonium gmelinii*. A high content of phytol acetate (12.88%) related to derivatives of acyclic diterpene alcohols has been established, in addition, the highest alcohol 3,7,11,15-tetramethyl-2-hexadecan-1-ol, detected in the amount of 5.17%, has been identified.

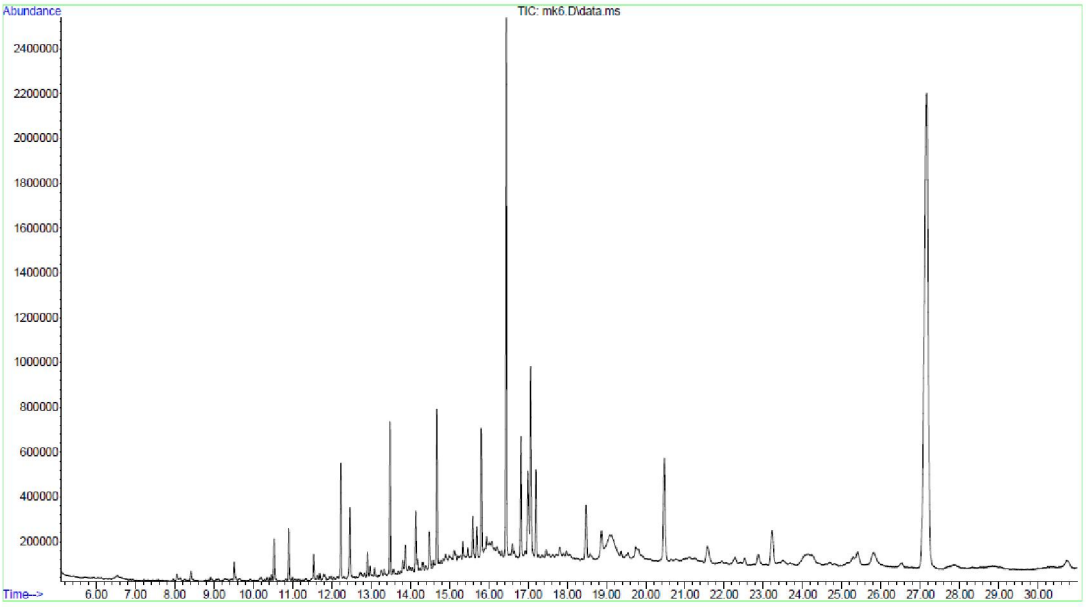

Figure 1 – GC-MS chromatogram of the aerial part of the plant species *Limonium gmelinii*

As can be seen from the data presented in Figure 1, the largest peaks are observed at 16.45 minutes and 27.16 minutes, which advises the extracts that are dominant in the extract, phytol acetate and tricosane, the other compounds are found in significant concentrations such as 3,7,11,15-tetramethyl-2-hexadecan-1-ol, genicosan, hexadecane are also clearly marked on the chart.

From the literature sources it is known that the underground parts of plants, as a rule, contain a relatively small amount of non-polar compounds, since the latter, phytol, in particular, are involved in the process of biosynthesis at the stage of photosynthesis and predominate in chloroplasts. The accumulation of other non-polar and weakly polar compounds, such as hydrocarbons, is more characteristic of the aerial parts of plants, while in the underground parts of plants, respectively, water-soluble carbohydrates and polyphenols dominate [13-23].

In the underground part of the studied plants, 14 compounds were identified (Table 2 and Figure 2).

Table 2 – Research data by GC-MS of the roots of plants of the *Limonium gmelinii* species

No.	Retention time, min	Name of compound	Content, %
1	6.53	Undecane	0.94
2	8.05	Dodecane	2.66
3	9.52	Tridecan	4.07
4	10.91	Tetradecane	4.15
5	10.99	7-Tetradecene, (Z)	0.89
6	12.23	9-methylheptadecane	3.22
7	13.49	Heptadecane	7.62
8	13.83	Phenol, 2,4-bis (1,1-dimethylethyl) -	1.72
9	13.88	Quinoline, 1,2-dihydro-2,2,4-trimethyl-	4.18
10	15.69	Tetracosan	3.43
11	15.81	Octadecane	5.26
12	19.78	Hexadecanoic acid ethyl ester	24.51
13	25.40	Oleic acid ethyl ester	11.16
14	25.78	Ethyl linoleic ester	26.19
Total			100.00

It was established on table 2 that the distinctive feature of the hexane extract of the roots of the studied plants is the predominance of esters of higher carboxylic acids in the amount of 61.86% and hydrocarbons – 32.24%.

The esters are represented as ethyl esters of hexadecanoic, oleic and linoleic acids, with the predominance of polyene acids (60.38%) in them, of which hexadecanoic acid ethyl ester and linoleic acid ethyl ester are the most abundant.

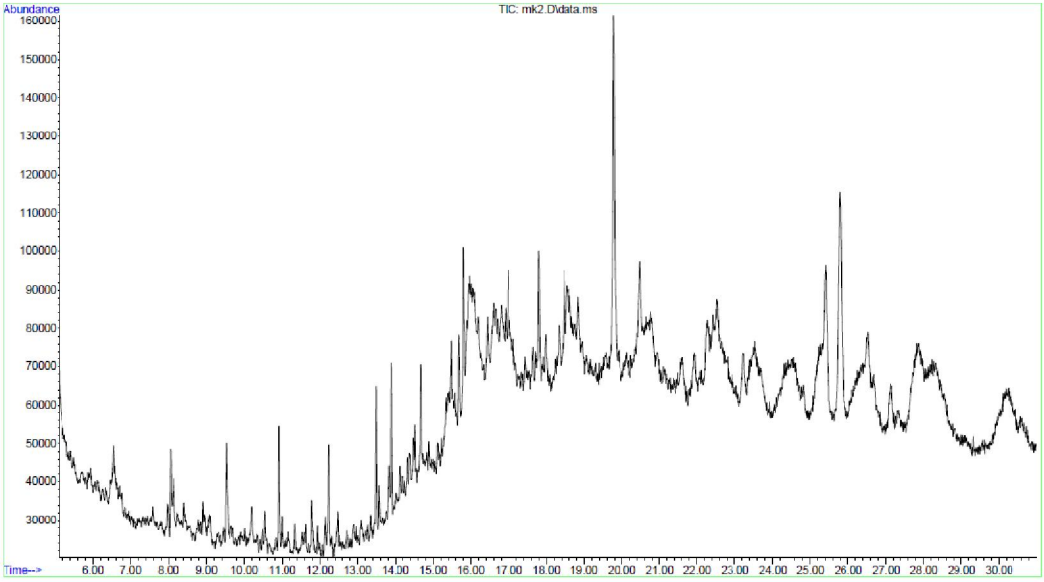

Figure 2 – GC-MS chromatogram of the roots of the plant species *Limonium gmelinii*

From the data presented in Figure 2, it can be seen that most of the dominant in the non-polar fraction of the roots of the plant *Limonium gmelinii* substances, namely Hexadecanoic acid ethyl ester, Oleic acid ethyl ester and Ethyl linoleic ester, belong to the class of organic esters is allocated at the final stages of analysis. The quinoline and phenol derivatives stand out between 1 and 5 minutes of the process. Most of the analysis recorded various compounds belonging to the class of hydrocarbons.

Conclusion

As a result, it was established that in the hexane extract obtained from the aerial part of the plant *Limonium gmelinii*, the dominant groups of substances are hydrocarbons among which the tridecane, tetradecane, heptadecane, octadecane and tetracosane dominate, 76.09%. Also in hexane extract obtained from the aerial part of the plant *Limonium gmelinii* was identified derivatives of phytol and quinoline.

The hexane extract obtained from the roots of the plant *Limonium gmelinii* is dominated by fatty acid esters whose total content is 61.86% in contrast to the aerial part of the plant. In addition, a significant amount of quinoline derivatives was found in the hexane extract from the roots of the plant *Limonium gmelinii*, while in the aerial part of the plant it is represented in trace amounts.

The obtained data can be used to improve the processing of the roots and the aerial parts of the plant *Limonium gmelinii* with the aim of obtaining drugs on its basis.

Funding

This work was carried out within the framework of the grant financing program of the SC MES RK AR05134034 "Development and creation of high-performance gels based on pharmacopoeial wild plants of Kazakhstan and their integrated research."

УДК 547.99

А.И. Жусупова, Е.С. Ихсанов, А.А. Мамутова, Г.Е. Жусупова

Әл-Фараби атындағы Қазақ ұлттық университеті
Физико-химиялық әдістер анализі орталығы
Қазақстан Республикасы, 050012, Алматы қ., Карасай батыра к., 95а,

LIMONIUM GMELINII ӨСІМДІГІНІҢ ЖЕРҮСТІ ЖӘНЕ ЖЕРАСТЫ БӨЛІКТЕРІНІҢ ПОЛЯРСЫЗ ФРАКЦИЯЛАРЫНЫҢ GC-MS ӘДІСІМЕН САЛЫСТЫРМАЛЫ АНАЛИЗІ

Аннотация. Бұл мақалада 2018 ж. Алматы облысында өңделген *Limonium gmelinii* (*Willd.)* (кермек Гмелина) өсімдігінің жерасты және жерүсті бөліктерінен алынған полярсыз фракциялардың химиялық құрамы қарастырылады. Экстракттар гексанмен сұйық экстракциялау әдісімен алынып, масс-селективті детекторлы газ хроматографта хромато-масс спектрометрия арқылы зерттелді.

Нәтижесінде *Limonium gmelinii* өсімдігінің жерүсті бөлігінен 22 қосылыс, оның ішінде сапалық және сандық тұрғыдан көмірсутектер геникозан, эйкозан және трикозан басым, сонымен қатар хинолин мен фитол туындылары бөлінді. Ациклді дитерпен спирттер туындыларының құрамы жоғары екендігі анықталды, одан бөлек 3,7,11,15-тетраметил-2-гексадекан1-ол жоғарғы спирті идентификацияланды.

Limonium gmelinii тамырынан алынған полярсыз экстракттар анализі 14 қосылыс бөліп алуға мүмкіндік берді, олардың негізгі сандық бөлігін жоғарғы карбон қышқылдарының эфилері мен көмірсутектер құрайды. Күрделі эфирлер полиен қышқылының басымдығымен линоль, олеин гексадекан қышқылдарының этил эфирлері күйінде ұсынылған. Көмірсутектер ішінде көп кездесетіні тридекан, тетрадекан, гептадекан, октадекан мен тетракозан.

Түйін сөздер: Limonium gmelinii, полярсыз фракция, хромато-масс спектрометирия, химиялық құрам.

УДК 547.99

А.И. Жусупова, Е.С. Ихсанов, А.А. Мамутова, Г.Е. Жусупова

Казахский национальный университет имени аль-Фараби
Центр физико-химических методов анализа
Республика Казахстан, 050012, г.Алматы, ул.Карасай батыра, 95а,

СРАВНИТЕЛЬНЫЙ АНАЛИЗ НЕПОЛЯРНОЙ ФРАКЦИИ НАДЗЕМНОЙ И ПОДЗЕМНОЙ ЧАСТЕЙ РАСТЕНИЙ *LIMONIUM GMELINII* МЕТОДОМ GC-MS

Аннотация. В данной статье рассматривается химический состав неполярной фракции, полученной из надземной и подземной частей растения *Limonium gmelinii* (*Willd.*) (кермек Гмелина), заготовленного в Алматинской области в 2018 году. Экстракты были получены методом жидкостной экстракции гексаном и изучены посредством хромато-масс спектрометрии на газовом хроматографе с масс-селективным детектором.

В результате исследования из надземной части растения *Limonium gmelinii* было выделено 22 соединения, доминирующими из которых, как в количественном, так и в качественном плане, являются углеводороды, такие как геникозан и эйкозан и трикозан; также были выделены производные хинолина и фитола. Установлено высокое содержание производных ациклических дитерпеновых спиртов, помимо этого идентифицирован высший спирт 3,7,11,15-тетраметил-2-гексадекан1-ол.

Анализ неполярного экстракта, полученного из корней *Limonium gmelinii* позволил выделить 14 соединений; из них основную долю в количестве составляют эфиры высших карбоновых кислот и углеводороды. Сложные эфиры представлены в форме этиловых эфиров гексадекановой, олеиновой и линолевой кислот с преобладанием в них эфиров полиеновых кислот. Среди углеводородов в наибольшем количестве присутствуют тридекан, тетрадекан, гептадекан, октадекан и тетракозан.

Ключевые слова: Limonium gmelinii, неполярная фракция, хромато-масс спектрометрия, химический состав.

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