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## Chemical composition and properties of essential oil of *Ferula foetida* (Bunge) Regel growing on Mangyshlak peninsula

The medicinal plant, *Ferula foetida*, has been studied, which has a wide range of pharmacological properties. Since ancient times, ferules have been used in folk medicine in various countries (Central Asia, Iran, China, India) for treatment of scabies, wounds, tumors, syphilis, tuberculosis, seizures, hysteria, the gastrointestinal tract, and as an antiparasitic remedy. Chemical composition of *Ferula foetida* essential oil has been analyzed. The samples were taken from two different populations on Mangyshlak peninsula — on loamy and sandy massifs. Use of GC-MS analyses helped identifying 47 compounds comprising 91.5 % of the total components in the oil. Components of essential oil of two populations — Tuyesu sands and Tynymbay Shoky hills — differ through growing phase. 2,5-Diethylthiophene, 3,4-diethylthiophene, bulnesol, guaiol, myristicine,  $\alpha$ -pinene, caryophyllene oxide, 2,5-dipropylthiophene, elemicine, 1-heptatriacontanol,  $\beta$ -*trans*-caryophyllene,  $\beta$ -*cis*-caryophyllene,  $\alpha$ -caryophyllene,  $\beta$ -pinene, dimethyl trisulfide,  $\alpha$ -eudesmol,  $\beta$ -eudesmol;  $\beta$ -eudesmene, 2-methylthieno[3.2-b]thiophene, 5,5-dimethyl-4-[(1E)-3-methyl-1,3-butadienyl]-1-oxa-spiro[2.5]octane, S-(9-thiabicyclo[3.3.1]non-6-en-2-yl) are common for both populations. These components have acaricide, antitussive, expectorate effect, as well as anxiolytic, antidepressant, antioxidant, growth stimulating properties. Concentration of major components is higher in plants growing in harsher edaphic conditions. Comparative analysis of essential oil of *Ferula foetida* growing in Iran, Turkey and Kazakhstan shows differences in the composition. The differences are caused by the climatic conditions. The results of the studies may further be used for standardization of the raw materials.

**Keywords:** essential oil, *Ferula foetida*, herbs, Mangyshlak, GC-MS, climate, arid zone, latex.

### Introduction

Aromatic plants and essential oils were used for millennia in medicine, cosmetics and perfumery. It is believed that therapeutic properties of essential oils as treatment-and-prophylactic drugs are not fully studied. However, huge experience of using separate essential oils as inhalator and antifungal remedy, was accumulated in literature and applied medicine. Many oils are capable of reducing arterial pressure. They are effective at treatment of hypostases, rheumatism, inflammations, skin and other diseases.

Synthesis and accumulation of separate classes of biologically active agents in wild-growing herbs are mostly defined by climatic conditions in the respective growth areas [1].

Therefore, comprehensive study of separate groups of plants, including composition of essential oils, is critical for definition of main spheres for their use as treatment-and-prophylactic drugs. It may as well include a number of scientific tasks like studying of mechanism of synthesis of separate compounds in the raw materials in different phases of growth and development, metabolism of separate compounds, developing methods for their identification and allocation. Widespread use of phytogenic products is caused by their biological activity, mild effect and less side effects compared to synthetic products [2].

The greatest number of essential oil plants leads to *Apiacea* families. *Ferula* L. genus is the largest genus of *Apiacea* family and contains more than 170 species, the majority of which is herbs. One of these plants is *Ferula foetida* (Bunge) Regel, which is used in traditional medicine in Central Asia, China, Iran and India since ancient time.

*Ferula foetida* is a very polymorphic species. The plant has a specific, unpleasant smell. It grows up to 2 m high, has a massive stalk of 5–8 cm in diameter at the basis. The leaves are 30–40 cm long, ternate-pinnate. The flowers are yellow and form a spherical inflorescence [3].

The main medical component of *Ferula foetida* is rhizome latex [4]. Solidified latex of *Ferula foetida* consists of resin (40–65 %), gum (12–25 %) and essential oil (5–20 %). Generally, the essential oil contains organic sulfides, which give onion-garlic smell [5], and  $\alpha$ -pinene, umbelliferone, coumarin and other compounds [6, 7].

Antioxidative, antimicrobial, antifungal, anti-diabetic effects have been revealed as a result of pharmacological studies of this species [8, 9]. Therapeutic effect of medications based on the herbal raw materials is defined by a combination of all compounds contained in the plants: tannins, flavonoids, saponins, terpenoids, vitamins, sesquiterpenes, coumarins and essential oil [8]. Therefore, assessment of essential oil composition of useful plants is a vital and practical task at this time.

The purpose of the research is to assess the quantitative and qualitative composition of essential oil obtained from the roots of *Ferula foetida* (Bunge) Regel growing on Mangyshlak peninsula.

#### Methodology

The raw material has been collected from natural places of growth on Mangyshlak peninsula in arid zone. The samples were collected in spring of 2014 during vegetation and full blossoming phase. Collecting and preparation (air drying) of raw materials and obtaining of essential oil (hydro distillation) were carried out by the standard techniques. The studied samples are named by their geographical places near the place of collection of the raw materials. Characteristics of the collected samples are given in Table 1. The site map of *Ferula foetida* growth area is shown on Figure 1.

Table 1

Characteristics of the collected samples

No.	Local name	Ontogenesis phase	Identified compounds number
1	Tuyesy sands	Vegetation	42–47
		Blossoming	43
2	West Tynymbay Shoky hill	Vegetation	31–45
		Blossoming	44

Roots of the plants were ground, and a portion of 100 g sharp, has been measured for each sample. Essential oil has been separated by hydro distillation method with the use of Clevenger apparatus. Duration of hydro distillation was 2 hours. The compounds were identified by GC-MS method.

Definition of composition of the essential oil was carried out on Clarus-SQ 8 (Perkin Elmer) gas chromatograph with mass and spectrometer detector.

Preparation of essential oil sample: 25 mg of *Ferula foetida* essential oil was placed in a measuring flask with the capacity of 25 ml, dissolved in 15 ml of hexane, brought to the tag, and mixed.

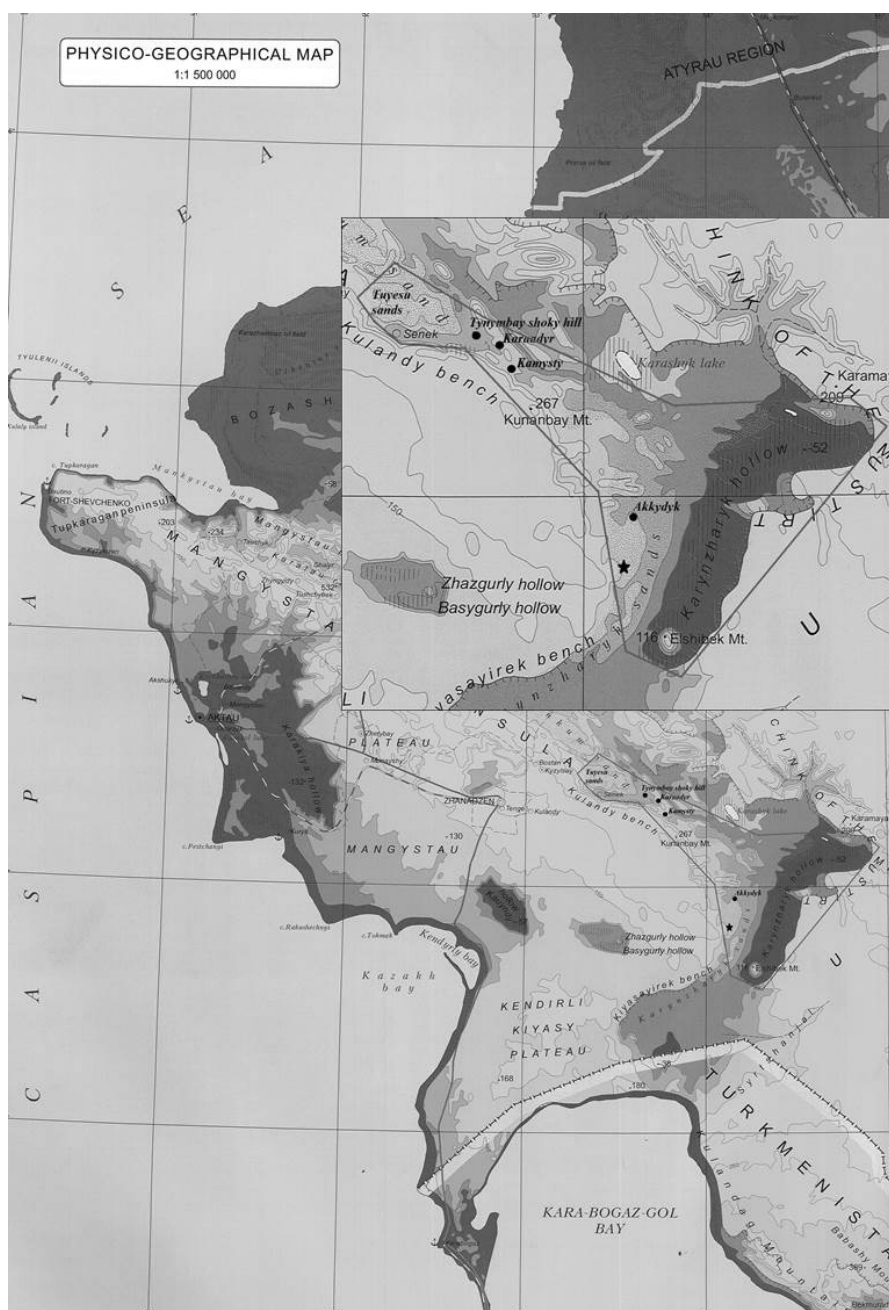
Chromatographic conditions: capillary column Restek Rxi®-1 ms of 0.25 mm × 30 m × 0.25 microns; sample volume: 1.0 µl; gas carrier He, gas carrier velocity is 1 ml/min., split ratio 1:25; column temperature: 40 °C, build-up — 2 °C/min. to 280 °C, evaporator temperature is 280 °C; the mass and spectrometer detector:  $t$  — 240 °C, EI+ = 70 eV; scanning time from 4 to 120 min; the mode of ions scanning: 39–500 m/z. Percentage of the components was calculated automatically, proceeding from the areas of peaks of the general ions chromatogram. The components were identified by the mass-spectrums and retention time, with the use of the National Institute of Standard and Technology Library.

#### Results and discussion

Results of the studies on composition of essential oil of *Ferula foetida* growing in two different ecological populations of Mangyshlak peninsula are reported in this article.

Natural populations of *Ferula foetida* are widespread as a part of the East Mangyshlak geobotanical district, in the southern part of the peninsula. They grow on the fixed and semi-fixed sands of the loamy plains of Middle and South deserts. Also, *Ferula* is spread in wormwood, saxaul, saltwort communities, often as a co-dominant of spring communities.

Tuyesu sands are located in the south of Mangyshlak peninsula, close to Senek village, where *Ferula* is involved in saxaul–ferula–sagebrush–psammophyte–shrubs associations. The relief has slides, hilly ridges, and wavy fixed sandy massifs. The soils are sandy and sabulous, mostly non-saline or sub-saline. Tuyesu sands have shallow fresh waters and potable top waters. Groundwater depth varies from 3–5 m to 41 m. The thickness of watered eolian sand massif is around 5 m to 33.3 m.

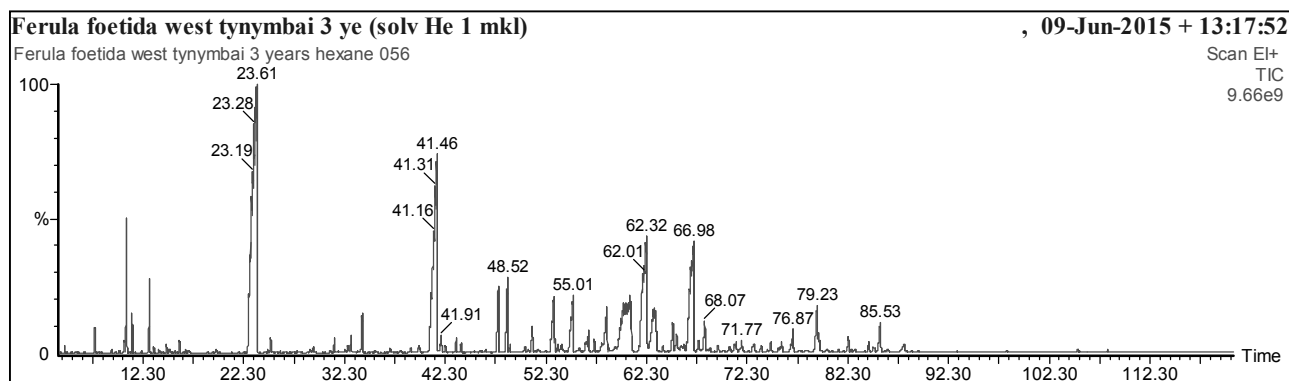


- Survey boundary;  
●— Mass growth places

Figure 1. Site map of *Ferula foetida* growth area (Mangyshlak peninsula)

Tynymbay Shoky hill is located near Kunabay Mountain. *Ferula foetida* is observed in saxaul-ferula-santolina-mugwort, sedge-artemisia terrae-albae-ferula associations. The region is significantly different from the others both on mechanical makeup, and salinity of the soil. The sandy loam soil occurs at a depth of 30 cm, low loamy — from 30 to 50 cm and mid loamy — from 50 to 100 cm. Salinity level is low from the surface down to 50 cm, middle level — from 50 to 80 cm and high level — from 80 to 100 cm. Watering of the region is extremely low. The plants take up liquid from atmospheric precipitation and shallow ground waters with various salinity levels.

From 31 to 47 components were detected and identified in the examined samples, using the gas-chromato-mass-spectrometry (GC-MS), which constitute 88.2–92.5 % of the whole essential oil. Ether oil of *Ferula foetida* represents liquid of yellow color with specific garlic-onion-like odor which is caused by the presence of sulphide compounds. Chromatogram of essential oil of *Ferula foetida* roots is given in Figure 2.

Figure 2. Chromatogramm of essential oil of *Ferula foetida* roots

The main compounds of essential oil of Mangyshlak's *Ferula foetida* plants are: 2,5-diethylthiophene, 3,4-diethylthiophene, bulnesol, guaiol, caryophyllene oxide, myristicine,  $\beta$ -*trans*-caryophyllene,  $\alpha$ -pinene,  $\beta$ -pinene, dimethyl trisulfide,  $\beta$ -*cis*-caryophyllene;  $\beta$ -*cis*-caryophyllene,  $\alpha$ -caryophyllene,  $\alpha$ -eudesmol,  $\beta$ -eudesmol, 1-heptatriacontanol,  $\beta$ -eudesmene, 2-methylthieno[3.2-b]thiophene, 5,5-dimethyl-4-[(1E)-3-methyl-1,3-butadienyl]-1-oxaspiro[2.5]octane, S-(9-thiabicyclo[3.3.1]non-6-en-2-yl), elemicine and 2,5-di-propylthiophene.

The composition of essential oil varies from sample to sample, except for the main components. The structure of the main components is almost constant throughout all the samples. The quantitative content of the main components is higher in West Tynymbai Shoky hill populations, i.e. in plants growing in harsher edaphic conditions. Presence of certain substances only in individual samples is caused by the fact that population, and even individual plants, occur with significantly different composition for this species or population [10].

Thus, the obtained data show that composition of essential oil from two populations of Mangyshlak peninsula differs by the content of the main components. Composition of essential oils can vary depending on the age, growth phase and habitat.

Comparison of essential oil components with species growing in various regions of Iran shows a significant difference in the qualitative and quantitative content of components both between species, growing in Iran, and between species growing in different countries. Comparison results of gum resin, aerial organs and essential oils composition in different populations are shown in the Tables 2–4.

Table 2

**The main components of Iran and Pakistan *Ferula foetida* essential oil obtained from oleo-gum resin, %**

Components	Location					
	Larestan, Iran	Yazd province, Iran	Kerman, Iran	Isfahan, Iran	Darab mountain, Iran	Pakistan
(E)-1-propenyl sec-butyl disulfide	20.3–23.9 [11]	40.1–44.4 [12]	58.9 [13]	22.1 [14]		
10- <i>epi</i> - $\gamma$ -eudesmol	15.1 [11]					
(Z)-1-Propenyl sec-butyl disulfide	27.7 [11]	23.9–28 [12]		35.1 [14]		
Guaiol		3.1–5.5 [12]				
Carotol		1.6–5.1 [12]				
$\beta$ -Pinene					1 [15]	
$\alpha$ -Pinene				12.2 [14]	21.4 [15]	
(Z)- $\beta$ -Ocimene			11.9 [13]			
(E)- $\beta$ -Ocimene			9 [13]			
Phelandrene						6.49 [16]
Propenyl sec-butyl disulfide						51.9 [16]
Undecylsulfonyl acetic acid						18.8 [16]

Table 3

The main components of Iran and Pakistan *Ferula foetida* essential oil obtained from root, %

Components	Location		
	Gonabad, Iran	Tabas, Iran	Mangyshlak peninsula, Kazakhstan
(E)-1-Propenyl sec-butyl disulfide	30.7 [17]	18.8 [17]	
10- <i>epi</i> - $\gamma$ -Eudesmol	12.7 [17]	18.7 [17]	
(Z)-1-Propenyl sec-butyl disulfide	12.4 [17]	9.2 [17]	
$\beta$ -Pinene			0.1–1.0
$\alpha$ -Pinene			0.3–3.1
2,5-Diethylthiophene			11.0–26.2
3,4-Diethylthiophene			8.5–35.3
Bulnesol			5.6–20.7
Guaiol			5.8–19.3
Caryophyllene oxide			0.9–4.7
Myristicine			0.6–7.6
1-Heptatriacontanol			0.3–3.2
2,5-Dipropylthiophene			0.5–5.6
Elemicine			0.5–6.1

Table 4

The main components of *Ferula foetida* aerial organs growing in Iran and Turkey, %

Components	Aerial organs				Fruits	Leaves	
	Location				Mount Telesm, Kerman-shah, Iran	Kashana region, Isfahan, Iran	No information
	Kerman, Iran	Turkey	Sari forest, Iran	Neishabour mountains, Iran			
1	2	3	4	5	6	7	8
1-Methylpropyl (1E)-prop-1-en-1-yl disulfide	32.8 [18]						
$\alpha$ -Pinene	11.3 [18]	59.9 [19]		3.4 [21]	1.7 [22]	12.8 [23]	1.5 [24]
Germacrene B	5.5 [18]						
$\beta$ -Pinene		13.5 [19]				6.2 [23]	
Limonene		3.2 [19]					
Bornyl acetate		2.1 [19]					
2-Methyl-5-(1-methylethyl)			18.2 [20]				
$\alpha$ -Bisabobol			10.4 [20]				
Arsinetriethyl			8.7 [20]				
Cyclopropa[a]naphthalene octahydrotetramethyl			6.6 [20]				
<i>trans</i> -2-Undecen-1-ol						17.3 [23]	
Thymol						10.9 [23]	
Dodecanal						9.7 [23]	
Spathulenol						8.5 [23]	
$\beta$ -Eudesmol					1.9 [22]	6.8 [23]	
$\gamma$ -Elemene						32.2 [23]	
Eremophilene							31.3 [24]
$\delta$ -Cadinene							22.0 [24]
Longiborneol							12.1 [24]
Dehydroaromadendrene							39.7 [24]
Isoledene							36.4 [24]
$\tau$ -Gurjunene							3.9 [24]
$j$ -Guaiene							3.5 [24]
Ledenoxid							1 [24]

1	2	3	4	5	6	7	8
<i>trans</i> -Caryophyllene							1 [24]
$\alpha$ -Gurjumene							1 [24]
2-j-Pinene							0.2 [24]
( <i>E</i> )-1-Propenyl sec-butyl disulfide				53.8 [21]	1.1 [22]		
( <i>Z</i> )-1-propenyl sec-butyl disulfide				35.6 [21]	5.9 [22]		

Chemical composition of essential oils obtained from *Ferula foetida* oleo-gum resin of two different sites in the central part of Iran, Yazd and Tabas, were identified in 2008. 39 substances were identified in the essential oil, which included 77.7 % (Tabas) and 72.4 % (Yazd) of sulphur-containing compounds; monoterpene hydrocarbons (2.8 and 3.4 %), sesquiterpene hydrocarbons (4.6 and 7.3 %); oxylene hydrocarbons sesquiterpenes (6.3 % and 12.4 %)[12].

Sefidkon et al. assert that the main component of Iran *Ferula foetida* essential oil is (*E*)-1-propenyl sec-butyl disulfide (58.9 %) which might be responsible for the positive properties of the essential oil, such as insecticidal, repellent (scaring insects) effect [15, 5]. Meanwhile, this component was not detected in the samples of the populations growing in Mangyshlak peninsula. However, other components, which were not previously identified, have been revealed: 2,5-diethylthiophene (11.0–26.2 %) and 3,4-diethylthiophene (8.5–35.3 %), which feature acaricidal activity and are used for treatment of animal scab [25].

The following basic components were also identified in essential oil of *Ferula foetida* growing in Mangyshlak: bulnesol (5.6–20.7 %), guaialol (10.6–19.3 %). Concentration of the other components detected in all the samples was below 2 %.

Properties of the identified components are diverse; thus, bulnesol and guaialol feature anti-tussive activity, while bulnesol and  $\alpha$ -cadinol (detected only in blooming samples of the plants growing westwards Tynymbay Shoky hill) feature expectorative activity.

$\beta$ -Caryophyllene is effective in treatment of anxiety and depression since it possesses anxiolytic and antidepressant properties. This terpenoid is also contained in cannabis and is linked to one of the two cannabinoid receptors — CB<sub>2</sub> — the ones that are impacted by marijuana, and thus does not lead to euphoria [26]. Myristicine is responsible for psychoactive effects. During metabolism, the components are aminating, which turns them into the centralized active amphetamine derivatives. In the course of amination, Myristicine gives MMDA — a well-known entactogenic compound acting similar to ecstasy. Pinenes are used in perfumery, and more seldom — as lacquer and paint solvents. Pinenes are well sensed by insects and act as important regulator of their chemical communication. Eudesmol features antioxidant activity.

Dimethyl-trisulphide confers a specific garlic-onion-like odor upon the plant and is used as a flavoring agent and food supplements. Eudesmol features antioxidant activity. Triacontanol features high biological activity and influences plant growth by increasing assimilation of carbon dioxide and improving the photosynthesis. It allows a plant to acquire more nutritive agents from the environment, which leads to enhanced growth of the plant and increases the yield. Minimal concentrations manifest the maximum effect [27].

Moreover, in the studied samples we have identified such materials depicted in samples of the plants growing in other countries as:  $\alpha$ -pinene,  $\beta$ -pinene, *epi*- $\gamma$ -eudesmol,  $\beta$ -eudesmol, germacrene B,  $\alpha$ -bisabolol,  $\delta$ -cadinene,  $\beta$ -*trans*-caryophyllene, guaiane. Concentration of these materials in the root resin of *Ferula foetida* growing in Mangyshlak was lower by more than 10 % compared to plants growing in Iran.

Composition analysis of ether oil exuded from oleo-gum resin, roots and leaves of *Ferula foetida* from different areas of Iran and Turkey reveals differences both, in qualitative and quantitative indicators.

Thus, composition of *Ferula foetida* essential oil differs both, by number of determined components, and by their quantity within one population as well as between the populations. This can be caused by natural and climatic conditions and by other genetic factors [3, 24].

### Conclusions

Two different populations of *Ferula foetida* collected from loamy and sandy massifs on Mangyshlak have been analyzed. 47 compounds out of 48, comprising 91.5 % of the total components, were identified in the oil by GC-MS. Essential oil components of two populations — Tuyesu sands and Tynymbay Shoky hill — differ through growing phase. 2,5-Diethylthiophene, 3,4-diethylthiophene, bulnesol, guaialol,

myristicine,  $\alpha$ -pinene, caryophyllene oxide, 2,5-dipropylthiophene, elemicin, 1-heptatriacontanol,  $\beta$ -*trans*-caryophyllene,  $\beta$ -*cis*-caryophyllene,  $\alpha$ -caryophyllene,  $\beta$ -pinene, dimethyl trisulfide,  $\alpha$ -eudesmol;  $\beta$ -eudesmol,  $\beta$ -eudesmene, 2-methylthieno[3.2-b] thiophene, 5,5-dimethyl-4-[(1E)-3-methyl-1,3-butadienyl]-1-oxaspiro[2.5]octane, S-(9-thiabicyclo[3.3.1]non-6-en-2-yl) are constant components for both Mangyshlak populations. These components have acaricide, antitussive, expectorate effect, as well as anxiolytic, antidepressant, antioxidant, growth stimulating properties.

Concentration of major components is higher in plants growing in harsher edaphic conditions. Comparative analysis of essential oil of *Ferula foetida* growing in Iran, Turkey and Kazakhstan shows differences in the composition. The differences are caused by the climatic conditions.

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### Маңғышлақ түбегінде өсетін *Ferula foetida* (Bunge) Regel эфир майының химиялық құрамы мен қасиеттері

Алуан түрлі фармакологиялық қасиеттері бар сасық курай (*Ferula foetida*) дәрілік өсімдігі зерттелген. Ежелгі дәуірден бастап ферула халық медицинасында әртүрлі елдерде (Орталық Азия, Иран, Қытай, Үндістан) қышыма, жара, ісік, мерез, туберкулез, құрысулар, есірік, асқазан-ішек жолдарын емдеу үшін, сондай-ақ паразитке қарсы құрал ретінде қолданылды. Маңғышлақ түбегінің екі түрлі сазды және құмды популяцияларында таралған сасық курайдың эфир майының құрамы анықталған. Газды-хромато-масс-спектрометрия әдісімен тұтас май қосындысының 91,5% құрайтын 47 компонент табылып, анықталған. Түйесу құмдары мен Тынымбай шоқы төбешігінің батыс бөлігіндегі популяциялардың эфир майы келесі компоненттердің құрамымен ерекшеленеді: Түйесу популяциясының барлық үлгілердің құрамында диметилтрисульфид,  $\alpha$ -кариофиллен,  $\beta$ -эвдесмен, 2-метилтиено[3.2-b]-тиофен, 5,5-диметил-4-[(1E)-3-метил-1,3-бутадиенил]-1-оксапиро[2.5]октан, ал Тынымбай шоқының батыс бөлігіндегі барлық үлгілердің құрамында 2,5-дипропилтиофен и S-(9-тиабицикло[3.3.1]нон-6-ен-2-ил)этантоат болуы. Бірақ екі популяциялардың барлық үлгілерінің құрамында 2,5-диэтилтиофен, 3,4-диэтилтиофен, бульнезол, гвайол, кариофиллен оксид, миристицин,  $\beta$ -*trans*-кариофиллен бар. Олар кене жойғыш, жөтелге қарсы және қақырық түсіретін белсенділіктерімен, депрессияға және мазасыздыққа қарсы қолданылатын қасиеттерімен ерекшеленеді. Негізгі компоненттердің концентрациясы ызғарлы эдафикалық жағдайларда өсетін өсімдіктерден жоғары. Иран, Түркия және Қазақстанда өсетін сасық курайдың эфир майларының салыстырмалы талдауы климаттық жағдайларға байланысты эфир майларының құрамындағы айырмашылықтарды көрсетеді. Болашақта зерттеу нәтижелерін шикізатты стандарттау үшін қолдануға болады.

*Кілт сөздер:* эфир майы, сасық курай, дәрілік өсімдіктер, Маңғышлақ, ГХ-МС, ауа райы, құрғақ аймақ, шайыр.

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### Химический состав и свойства эфирного масла *Ferula foetida* (Bunge) Regel, произрастающей на полуострове Мангышлак

Изучено лекарственное растение ферула вонючая, которая обладает широким спектром фармакологических свойств. С древнейших времен ферула применялась в народной медицине различных государств (Иране, Китае, Индии) и Средней Азии для лечения чесотки, заживления ран, опухолей, сифилиса, туберкулеза, судорог, истерии, желудочно-кишечного тракта, а также как противопаразитарное средство. Исследован состав эфирного масла ферулы, произрастающей в двух различных популяциях полуострова Мангышлак — на суглинистых и песчаных массивах. Методом газо-хромато-масс-спектрометрии идентифицировано 47 веществ, составляющих 91,5% от суммы цельного масла. Эфирное масло популяций песков Туйесу и западное возвышенности Тынымбай шоки отличаются по содержанию: диметилтрисульфид,  $\alpha$ -кариофиллен,  $\beta$ -эвдесмен, 2-метилтиено[3.2-b]тиофен, 5,5-диметил-4-[(1E)-3-метил-1,3-бутадиенил]-1-оксапиро[2.5]октан во всех образцах популяции Туйесу и наличие 2,5-дипропилтиофена и S-(9-тиабицикло[3.3.1]нон-6-ен-2-ил)этантоата во всех образцах популяции западное возвышенности Тынымбай шоки. Однако для



них присуще наличие 2,5-диэтилтиофена, 3,4-диэтилтиофена, бульнезола, гвайола, кариофилленоксида, миристицина,  $\beta$ -*trans*-кариофиллена, обладающих акарицидной, противокашлевой и отхаркивающей активностью, а также анксиолитическими и антидепрессантными свойствами. Концентрация основных компонентов выше у растений, растущих в более суровых эдафических условиях. Сравнительный анализ эфирных масел ферулы вонючей, произрастающей в Иране, Турции и Казахстане, показывает различия в составе эфирных масел, которые вызваны климатическими условиями. Результаты исследований в дальнейшем могут быть использованы для стандартизации сырья.

*Ключевые слова:* эфирное масло, ферула вонючая, лекарственные растения, Мангышлак, ГХ-МС, климат, аридная зона, смола.

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