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INVESTIGATION OF THE ESSENTIAL OIL CONSTITUENTS OF *CAMPHOROSMA LESSINGII*

Annotation. Volatile oil of *Camphorosma lessingii* which grown in Almaty – Kazakhstan was extracted from the aerial parts of the plant by hydro-distillation method, the extracted oil was analyzed using gas chromatography-mass spectrometry (GC) where 70 components were identified, with high percentage of Hexanedioic acid, bis (2-ethylhexyl) ester (38.26%), 2,6-Difluoro-3-methylbenzoic acid, tridecyl ester (15.87%), *n*-Hexadecanoic acid (3.74%), and of monoterpenes identified Verbenol (1.3%) and α-pinene (1.13%) and sesquiterpene spathulenol (0.54%).

Keywords: volatile oil, gas chromatography, *Camphorosma lessingii*, *Chenopodiaceae*, hydrodistillation

Тірек создер: эфир майлары, газды хроматография, *Camphorosma lessingii*, *Chenopodiaceae*, гидродистилляция.

Ключевые слова: эфирные масла, газовая хроматография, *Camphorosma lessingii*, *Chenopodiaceae*, гидродистилляция.

Essential oils are odorous and volatile compounds found only in 10% of the plant kingdom. Essential oils and their components can be very promising biological agents, because of their relative safety, wide acceptance by consumers and exploitation for potential multi-purpose use. They are stored in plants in special brittle secretory structures, such as glands, secretory hairs, secretory ducts, secretory cavities or resin ducts.

The total essential oil content of plants is generally very low and rarely exceeds 1% by mass. Essential oils are hydrophobic and thus only slightly soluble in water. They are soluble in alcohol, non-polar or weakly polar solvents, waxes and oils. Most essential oils are colorless or pale yellow, liquid and have lower density than water. Essential oils are complex mixtures comprising many various compounds. Chemically they are derived from terpenes and their oxygenated compounds [1].

Several essential oils have been used as therapeutic agents since ancient times, and some of them have been scientifically proven to possess medicinal properties, including anti-inflammatory, antiviral, antitumor, cytotoxic, and antimicrobial activities [2].

Essential oil compounds may be classified into three main categories: terpenes (monoterpene hydrocarbons and sesquiterpene hydrocarbons), terpenoids (oxygenated monoterpenes and oxygenated sesquiterpenes) and phenylpropanoids, but into hydrocarbons and oxygenated compounds. Terpenes form structurally and functionally different classes.

Terpenes have a hydrocarbon backbone, which can be rearranged into cyclic structures by cyclases, thus forming monocyclic or bicyclic structures. The main terpenes are monoterpenes ($C_{10}H_{16}$) and sesquiterpene ($C_{15}H_{24}$), but longer chains also exist. Terpenoids are terpenes that undergo biochemical modifications via enzymes that add oxygen molecules and move or remove methyl groups. Terpenoids can be sub-divided into alcohols, esters, aldehydes, ketones, ethers, phenols and epoxides [1].

The genus *Camphorosma* (*Chenopodiaceae*) is represented by 4 species (*C. lessingii, C. Monspeliacum, C. annuum* and *C. soongoricum*) in salt marshes and rocky slopes of central and south Asia. Three species are indigenous to the flora of Kazakhstan (*C. lessingii, C. monspeliacum,* and *C. soongoricum*) [3, 4]. The genus *Camphorosma* (*Chenopodiaceae*) is known to be a source of essential oil [5] and have a value in medicine as stimulant, aphrodisiac, diuretic, diaphoretic and to treat lung diseases and used in Central Asia externally in fungal skin diseases [3, 6]. We studied previously the chemical composition of *C. monspeliacum* L., (*Chenopodiaceae*) [7, 8] and the lipophilic components of *C. lessingii* [9]. On continuation of the study of the genus *Camphorosma* we proceed now for the isolation and identification of different classes of biologically active compounds from *C. lessingii* which is not studied before.

Materials and methods

Plant materials. The aerial parts of *Camphorosma lessinigii* collected in August 2013 from Almaty city (Kazakhstan). The identification of the plant materials was confirmed by Botanist, Biodiversity and Bioresource Department, faculty of Biology and Biotechnology, Al-Farabi Kazakh National University. The green leaves were air-dried for one week, stored at room temperature. The dried samples were ground using a mill to obtain coarse powder.

Extraction procedures. According to the standard methods for essential oils preparation, it is needed air-dried plant materials such as leaves, flowers, fruit, berries and branches. The oils contained within plant cells are liberated through heat and pressure from these parts of the plant matter, and the color may vary from a pale to deep yellow depending of the plant part used. The extraction of essential oils from plant material can be achieved by various methods, of which the most commonly used methods include hydro-distillation (with a collecting solvent which is then removed under vacuum), steam and steam/water distillation.

The plant material was pulverized, passed through 24-mesh sieve, and then placed in a steam distillation vessel. The sample was soaked for 4 h and subjected to hydro-distillation using Ginsberg's apparatus for 8 h. NaCl was added until saturation was reached. Cholroform was then used as the solvent to extract the oil for three times. The extraction was enriched to 2 ml. The sample was dried by anhydrous Na_2SO_4, filtered by a microporous membrane, stored in a sealed container, and refrigerated prior to analysis.

Analysis of volatile compounds on gas chromatography: Extracted volatile compounds were analyzed using gas chromatography (GC) equipped with mass spectroscopic detector 7890A/5975C (Agilent, USA) and auto sampler Combi-PAL (CTC Analytics, Switzerland).

For sample preparation, we used the solid-phase micro-extraction SPME, which allows to efficiently concentrating the volatile organic compounds contained in the sample from micro-polymer coating.

For analysis, the samples were placed in pre-conditioned 20 ml vials (Agilent, USA) and sealed with lids conditioned silicone gaskets / Teflon (PTFE). Samples were extracted with an auto-sampler at temperature 30 ?C for 30 seconds.

Extracted volatile compounds were desorbed by inserting the SPME fiber into the injector port (splitless mode, 240 °C) of a GC. The desorption time was 1 min.

The desorbed volatile compounds were separated on a capillary column, DB-5MS (60-m length, internal diameter 0.32-mm, film thickness 0.2-μm). Helium was used as the carrier gas at a flow rate of 1 ml/min.

The oven temperature was initially set at 40 °C for 10 min, increased to 240 °C at a rate of 10 °C /min, and held at 240 °C for 20 min. MSD interface temperature was 280 ° C.

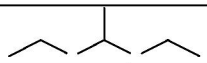
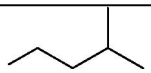
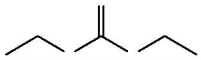
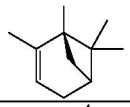
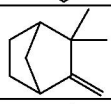
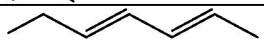
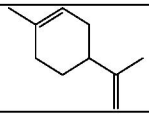
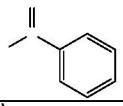
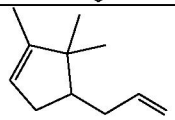
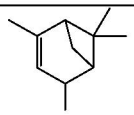
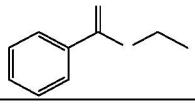
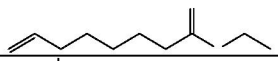
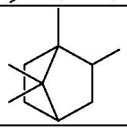
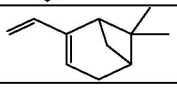
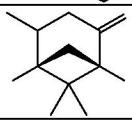
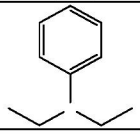
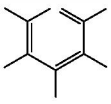
Data is collected in the selected-ion-monitoring (SIM) mode; in the range of mass numbers 35-350. Response factor of the detector is adjusted to 1.0 and delay of solvent was 5.00 minutes.

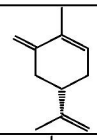
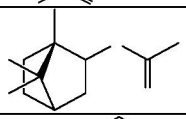
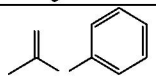
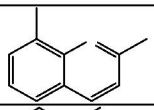
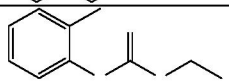
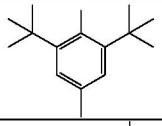
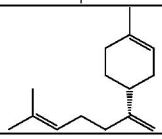
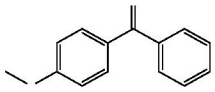
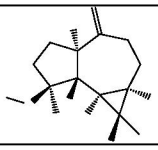
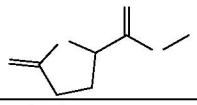
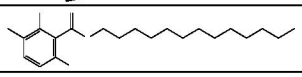
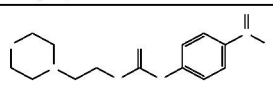
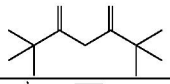
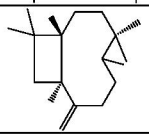
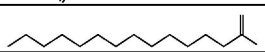
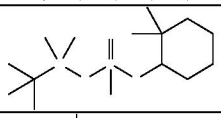
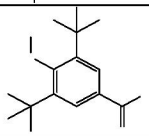
Identification of volatile compounds: Volatile compounds were identified using gas chromatography-mass spectrometry [Agilent MSD ChemStation (Ver. E.02.02 SP1)]; Separated compounds were tentatively identified by comparing the mass spectral data with the reference spectra in a mass spectral library (Natl. Inst. for Standard Technology, Manchester, U.K.) Wiley 8th edition, containing 782 thousand spectra as well as the retention indices with the reported values [10].

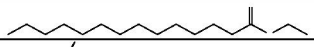
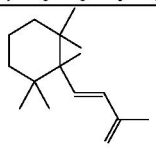
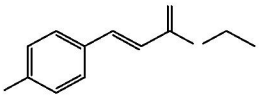
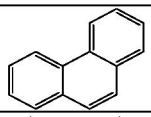
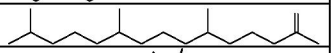
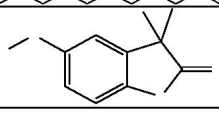
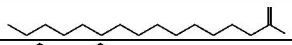
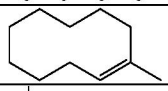
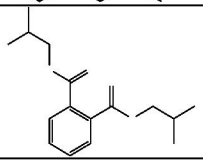
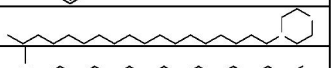
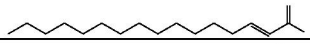
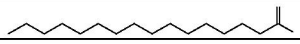
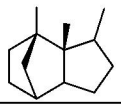
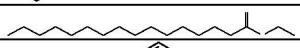
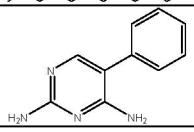
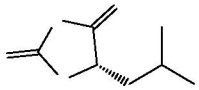
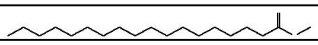
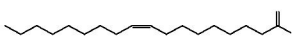
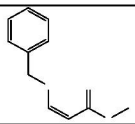
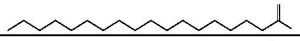
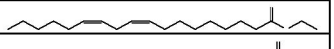
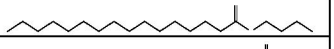
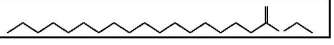
Result and discussion: Many of the aromatic components are widely used as flavors in food and cosmetics [11]. The chemical composition of the volatile oil of *Camphorosma lessingii* is presented in Table I. A total of seventy compounds were identified, which constitute about 87.79% of the volatile oil. Table 1 showed the main component of volatile oil from the aerial parts of *Camphorosma lessingii* were terpenoids (mono, sesqui and diterpenes), hydrocarbons, hydroxy compounds, esters, acids, nitrogenous and other miscellaneous compounds.

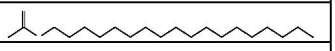
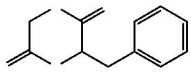
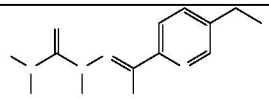
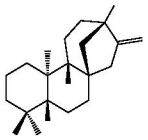
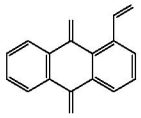
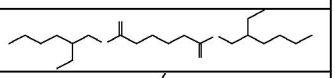
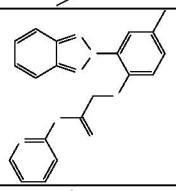
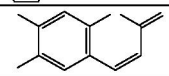
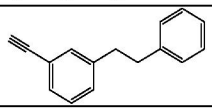
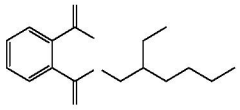
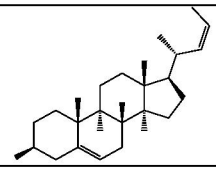
From which the main components found Hexanedioic acid, bis (2-ethylhexyl) ester (38.26%), 2,6-Difluoro-3-methylbenzoic acid, tridecyl ester (15.87%), *n*-Hexadecanoic acid (3.74%), Octadecanoic acid (3.61%), Benzenamine, N,N-diethyl (1.85%) while the main components of monoterpenes were Verbenol (1.3%) and α-pinene (1.13%) and of sesquiterpene spathulenol (0.54%) and for diterpenes found Kaur-16-ene, (8β,13β) (0.32%)

Percent composition of *Camphorosma lessingii* essential oils

Name	R_t	%	Molecular formula	Structure
1,1-diethoxy ethane	10.592	0.45	$C_6H_{14}O_2$	
1-Butanol, 3-methyl-	11.013	0.19	$C_5H_{12}O$	
Carbonic acid, diethyl ester	13.372	0.27	$C_5H_{10}O_3$	
α-Pinene	18.386	1.13	$C_{10}H_{16}$	
Camphene	18.847	0.08	$C_{10}H_{16}$	
2,4-Hexadien-1-ol	19.818	0.25	$C_6H_{10}O$	
D-Limonene	20.627	0.33	$C_{10}H_{16}$	
Nitro-benzene	21.834	0.14	$C_6H_5NO_2$	
Campholenic aldehyde	22.536	0.11	$C_{10}H_{16}O$	
2-Pinen-4-ol (Verbenol)	22.879	1.30	$C_{10}H_{16}O$	
Benzoic acid, ethyl ester	23.232	0.14	$C_9H_{10}O_2$	
7-Octenoic acid, ethyl ester	23.333	0.37	$C_{10}H_{18}O_2$	
Borneol	23.395	0.17	$C_{10}H_{18}O$	
Myrtenal	23.783	0.13	$C_{10}H_{14}O$	
2-Pinen-4-one (1S,5S)	23.968	0.52	$C_{10}H_{14}O$	
Benzenamine, N,N-diethyl	24.052	1.85	$C_{10}H_{15}N$	
Pyridine-D5-	24.266	0.14	C_5D_5N	

Name	R_t	%	Molecular formula	Structure
d-Carvone (+)	24.485	0.16	$C_{10}H_{14}O$	
Bornyl acetate	25.080	0.20	$C_{12}H_{20}O_2$	
Acetamide, N-phenyl-	26.265	1.19	C_8H_9NO	
2,8-Dimethylquinoline	26.506	0.32	$C_{11}H_{11}N$	
Ethyl N-(2-methylphenyl) carbamate	27.590	0.16	$C_{10}H_{13}NO_2$	
Butylated Hydroxytoluene	28.011	0.11	$C_{15}H_{24}O$	
β-Bisabolene	28.090	0.22	$C_{15}H_{24}$	
Methanone, (4-methoxyphenyl)phenyl-	28.544	0.19	$C_{14}H_{12}O_2$	
(+) Spathulenol	29.185	0.54	$C_{15}H_{24}O$	
2,2,5-Trimethyl-piperidin-3-ol	29.533	0.62	$C_8H_{17}NO$	
2,6-Difluoro-3-methylbenzoic acid, tridecyl ester	29.746	15.87	$C_{21}H_{32}F_2O_2$	
1-[*p*-nitrophenyl]-3-[2-morpholinoethyl]urea	30.061	0.39	$C_{13}H_{18}N_4O_4$	
3,5-Heptanedione, 2,2,6,6-tetramethyl-	30.257	0.62	$C_{11}H_{20}O_2$	
Caryophyllene oxide	30.616	0.13	$C_{15}H_{24}O$	
Tetradecanoic acid	30.824	0.11	$C_{14}H_{28}O_2$	
Methylphosphonic acid, 2,2-dimethylcyclohexyl [(dimethyl)(tert-butyl)silyl] ester	30.998	0.74	$C_{15}H_{33}O_3PSi$	
2,3,5,6-Detetrahydrocyclohexanone, 2,6-di-t-butyl-4-hydroxymethylene	31.122	0.14	$C_{15}H_{22}O_2$	

Name	R_t	%	Molecular formula	Structure
Tetradecanoic acid, ethyl ester	31.240	0.14	$C_{16}H_{32}O_2$	
5,6-Epoxy-7-megastigmen-9-one	31.346	0.26	$C_{13}H_{20}O_2$	
p-Hydroxycinnamic acid, ethyl ester	31.706	0.14	$C_{11}H_{12}O_3$	
Phenanthrene	31.762	0.09	$C_{14}H_{10}$	
2-Pentadecanone, 6,10,14-trimethyl	31.801	0.09	$C_{18}H_{36}O$	
2,3-2H-Benzofuran-5-ol-2-one, 3,3-dimethyl-	31.841	0.20	$C_{10}H_{10}O_3$	
Pentadecanoic acid	31.914	0.11	$C_{15}H_{30}O_2$	
Cyclodecene, 1-methyl-	31.953	0.19	$C_{11}H_{20}$	
1,2-Benzenedicarboxylic acid, bis (2-methylpropyl) ester	32.082	0.62	$C_{16}H_{22}O_4$	
Morpholine, 4-octadecyl-	32.363	1.33	$C_{22}H_{45}NO$	
1-Hexadecanamine, N,N-dimethyl-	32.447	0.12	$C_{18}H_{39}N$	
trans-2-Hexadecenoic acid	32.773	0.37	$C_{16}H_{30}O_2$	
n-Hexadecanoic acid	32.958	3.74	$C_{16}H_{32}O_2$	
cis-3-Methyl-endo-tricyclo[5.2.1.0(2.6)]decane	33.132	0.28	$C_{11}H_{18}$	
Hexadecanoic acid, ethyl ester	33.301	1.13	$C_{18}H_{36}O_2$	
5-Phenyl-2,4-pyrimidinediamine	34.075	0.14	$C_{10}H_{10}N_4$	
2,4-Imidazolidinedione, 5-(2-methylpropyl)-, (S)-	34.418	0.16	$C_7H_{12}N_2O_2$	
Octadecanoic acid, methyl ester	34.581	0.14	$C_{19}H_{38}O_2$	
Oleic Acid	34.699	1.34	$C_{18}H_{34}O_2$	
2-Propenoic acid, 3-[(phenylmethyl)thio]-, methyl ester, (Z)-	34.800	0.21	$C_{11}H_{12}O_2S$	
Octadecanoic acid	34.895	3.61	$C_{18}H_{36}O_2$	
Linoleic acid ethyl ester	34.935	1.34	$C_{20}H_{36}O_2$	
7,10,13-Hexadecatrienoic acid, methyl ester	34.985	1.30	$C_{17}H_{28}O_2$	
Hexadecanoic acid, butyl ester	35.126	0.70	$C_{20}H_{40}O_2$	
Octadecanoic acid, ethyl ester	35.182	0.33	$C_{20}H_{40}O_2$	

Name	R_t	%	Molecular formula	Structure
Acetic acid, octadecyl ester	35.311	0.17	$C_{20}H_{40}O_2$	
2,5-Piperazinedione, 3-(phenylmethyl)-	35.384	0.15	$C_{11}H_{12}N_2O_2$	
5-Ethyl-2-formylpyridine thiosemicarbazone	36.063	0.27	$C_9H_{12}N_4S$	
Kaur-16-ene, (8β,13β)-	36.249	0.32	$C_{20}H_{32}$	
1-Formylanthraquinone	36.608	0.38	$C_{15}H_8O_3$	
Hexanedioic acid, bis(2-ethylhexyl)ester	36.934	38.26	$C_{22}H_{42}O_4$	
Acetamide, 2-[2-(2H-1,2,3-benzotriazol-2-yl)-4-methylphenoxy]-N-(2-pyridinyl)-	37.074	0.13	$C_{20}H_{17}N_5O_2$	
Esculetin	37.742	0.27	$C_9H_6O_4$	
Benzonitrile, *m*-phenethyl-	37.855	0.27	$C_{15}H_{13}N$	
1,2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester	38.366	0.26	$C_{16}H_{22}O_4$	
Chola-5,22-dien-3-ol, (3β,22Z)-	41.729	0.14	$C_{24}H_{38}O$	

Conclusion. In this study, it proved that hydrodistillation with solvent-extraction could be a successfully developed method to identify and determine the volatile oils in the aerial parts of *Camphorosma lessingi*. A total of 70 constituents have been identified and this is the first report about identification of oil from this genus.

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Резюме

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CAMPHOROSMA LESSINGII ЭФИР МАЙЛАРЫНЫҢ ҚҰРАМДАСТАРЫН ЗЕРТТЕУ

Алматы аймағында жиналған *Camphorosma lessingii* өсімдігінің жерүсті бөлігінен гидродистилляция арқылы эфир майлары бөлініп алынды. Газды хроматография әдісі көмегімен 70 қосылыс анықталды, олардың ішінде ең көп мөлшерді гексадио қышқылының бис-2-этилгексил эфирі (38.26%); бензой қышқылының тридецил эфир-2,6-дифтор-3-метилі (15.87%); н-гексадекан қышқылы (3.74%); монотерпеноидтар – вербенол (1.3%) и α-пинен (1.13%); сесквитерпеноид – спатуленол (0.54%) құрайды.

Тірек сөздер: эфир майлары, газды хроматография, *Camphorosma lessingii*, *Chenopodiaceae*, гидродистилляция.

Резюме

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ИССЛЕДОВАНИЕ КОМПОНЕНТОВ ЭФИРНЫХ МАСЕЛ *CAMPHOROSMA LESSINGII*

Из надземной массы *Camphorosma lessingii* заготовленной в Алматинском регионе гидродистилляцией выделены эфирные масла. Методом газовой хроматографии идентифицировали 70 соединений, из которых наибольшее количество составили бис-2-этилгексиловый эфир гексадиовая кислота (38.26%); тридециловый эфир-2,6-дифтор-3-метил бензойная кислота (15.87%); н-гексадекановая кислота (3.74%); монотерпеноиды – вербенол (1.3%) и α-пинен (1.13%); сескивтерпеноид –спатуленол (0.54%).

Ключевые слова: эфирные масла, газовая хроматография, *Camphorosma lessingii*, *Chenopodiaceae*, гидродистилляция.

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