ОРГАНИКАЛЫҚ ХИМИЯ
ОРГАНИЧЕСКАЯ ХИМИЯ
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Study of the chemical composition of dichloromethane extract *Tamarix hispida*

In this article, first time there was observed dichloromethane extract from the aerial part of the *Tamarix hispida (Tamaricaceae)* harvested in the Almaty region of the Republic of Kazakhstan. The extraction of the previously dried and crushed vegetable raw material was carried out with dichloromethane in a Soxhlet apparatus. The extract was investigated by gas chromatography with mass spectrometry module under the following conditions: SHP-5MS gas chromatography column (30 m × 250 mm × 0.25 mm) temperature at 40 ºC for 5 minutes. As the carrier gas we used helium at a flow rate of 1 ml/min; with temperature programming up to 250 ºC and a temperature change of 50 ºC/min. Sample 0,2 µl was taken for assay. The compounds were identified by mass spectra and retention times, using the NIST library and Wiley GC/MS. As a result 25 compounds were identified in the dichloromethane extract which the highest contents were: picheol; methyl 3-(acetoxy)-20-hydroxy-12-en-28-oate; 6,10,14-trimethyl-2-pentadecanone; 2-hydroxy-1,1,10-trimethyl-6,9-epidioxydecalin, respectively. The presence of halogen-organic compounds: heptadecyl ester of 3-chloropropionic acid, 2-chlorophenylethyl ester of fumaric acid and 1,54-dibromo tetrapentacontane were detected in the extract. Halogen-containing compounds were firstly detected in the genus *Tamarix*.

Keywords: dichloromethane extract, *Tamaricaceae*, *Tamarix hispida*, aerial mass, halogenorganic compounds, dichloromethane, chromatography-mass spectrometry, Soxhlet method.

Tamarix are decorative bushes or trees, mostly evergreen, with pink or white flowers. They are relatively long-lived plants that can tolerate a wide range of environmental conditions and withstand abiotic stresses, such as high temperatures, salt and drought. *Tamarix* withstands saline soils, regulating the balance of salt through the release of secret salts through the deciduous glands and consuming large amounts of water from underground sources [1, 2].

Tamarix is widespread in Central Asia, India, Pakistan, and Southern Europe in the Caucasus, the Crimea and even in some regions of North America. Plant *Tamarix hispida* Willd. belongs to the genus *Tamarix* family *Tamaricaceae*. In folk medicine the plant is used for treating rheumatism, syphilis, infertility, and as an astringent for gastrointestinal diseases and bleeding [3]. *Tamarix hispida* Willd. is characterized by the diversity of the composition of natural metabolites, which have a wide range of biological effects. Currently there are studies on biologically active substances of polyphenolic nature (tannins, flavonoids and their glycosides, phenolic acids) [3–6]. In the aspect we investigated the data on the study of the lipophilic extract having the most interest.

Continuing the study of the chemical composition we studied the dichloromethane extract obtained from the aerial part of *Tamarix hispida* Willd. raw plant materials harvested in the Almaty region during the flowering phase in 2016.

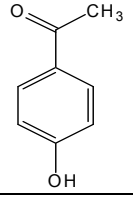
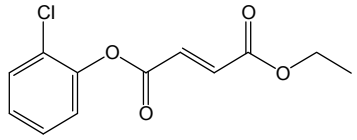
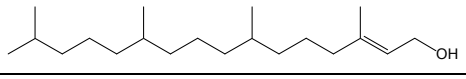
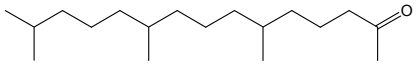
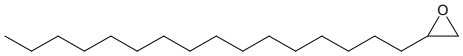
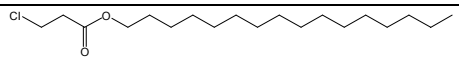
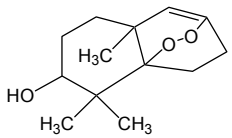
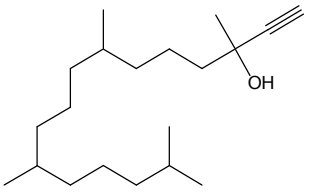
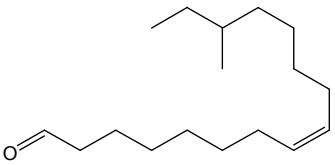
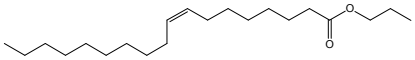
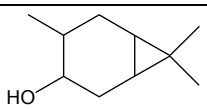
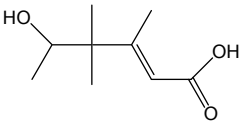
The extraction of the previously dried and crush vegetable raw material was carried out by dichloromethane in a Soxhlet apparatus. The extract was examined by gas chromatography using a gas chromatograph with an Agilent Technologies 7000 GS / MS mass-selective detector under the following conditions: a SHP-5MS column (30 m × 250 mm × 0.25 mm) was used, the gas velocity of the helium carrier was

1 ml/min. The gas chromatography column temperature at 40 ºC for 5 minutes; with temperature programming up to 250 ºC with a temperature change rate of 5 ºC/min. For assay 0,2 µl sample was taken.

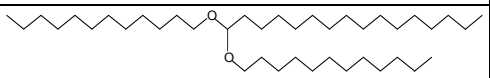
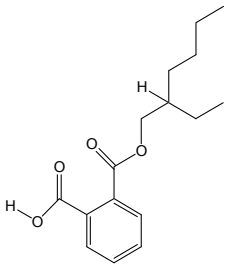
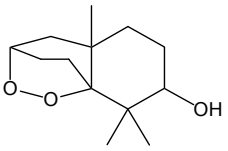
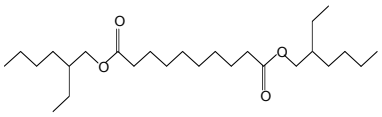
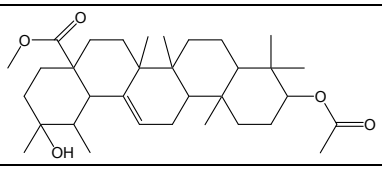
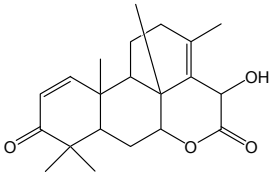
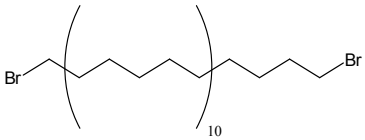
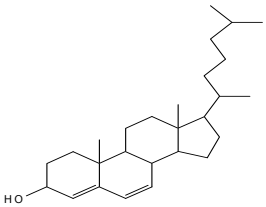
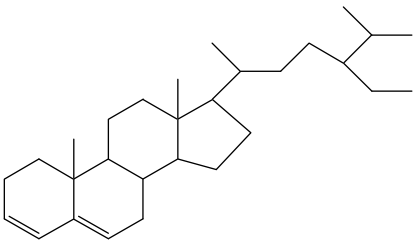
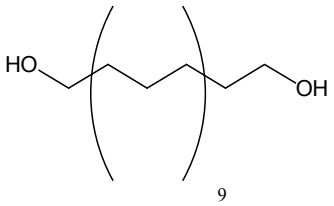
The components were identified by mass spectra and retention times, using the NIST library and Wiley GC / MS. The results are shown in Table.

T a b l e

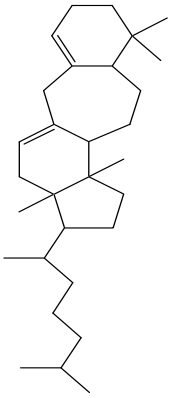
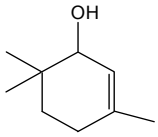
Component composition of the dichloromethane extract of the aerial mass *Tamarix hispida* Willd.

No.	Compound	Structure	M, g/mol	RT, min	W, %
1	2	3	4	5	6
1	4'-Hydroxy acetophenone (Piceol) $C_8H_8O_2$		136	3.61	36.91
2	Fumaric acid 2-chlorophenylethyl ester $C_{12}H_{11}ClO_4$		254	24.38	1.33
3	3,7,11,15-Tetramethyl-2-hexadecen-1-ol $C_{20}H_{40}O$		296	26.74	2.30
4	6,10,14-Trimethyl -2-pentadecanone $C_{18}H_{36}O$		268	33.56	7.82
5	1,2-Epoxyoctadecane $C_{18}H_{36}O$		268	34.51	1.31
6	3-Chloropropionic acid, heptadecyl ether $C_{20}H_{39}ClO_2$		346	35.35	2.75
7	2-Hydroxy-1,1,10-trimethyl-6,9-epidioxydecalin $C_{13}H_{22}O_3$		226	42.04	0.56
8	3,7,11,15-Tetramethyl-1-hexadecyn-3-ol $C_{20}H_{38}O$		294	42.41	0.46
9	(8*Z*) -14-Methyl-8-hexadecenal $C_{17}H_{32}O$		252	42.52	0.59
10	Izopropyl 9-octadecenoate $C_{21}H_{40}O_2$		324	43.19	1.30
11	4,7,7-Trimethylbicyclo[4.1.0]hepta-3-ol $C_{10}H_{18}O$		154	44.08	0.96
12	(2*E*)-5-hydroxy-3,4,4-trimethyl-2-hexenoic acid $C_9H_{16}O_3$		172	45.13	0.48

Continuation of Table

1	2	3	4	5	6
13	Ethyleneglycol monododecyl ether $C_{40}H_{82}O_2$		594	47.22	1.85
14	Monoethylhexylphthalate $C_{16}H_{22}O_4$		278	48.06	0.39
15	2-Hydroxy-1,1,10-trimethyl-6,9-epidioxydecalin $C_{13}H_{22}O_3$		226	48.73	7.04
16	Decanedioic acid *bis*(2-ethylhexyl) ester $C_{26}H_{50}O_4$		426	49.55	0.63
17	Methyl 3-(acetyloxy)-20-hydroxyurs-12-en-28-oate $C_{33}H_{52}O_5$		528	51.38	22.26
18	15-Hydroxy-4-methylpicrasa-1,13-diene-3,16-dione $C_{21}H_{28}O_4$		344	52.24	1.71
19	1,54-Dibromo-tetrapentacontane $C_{54}H_{108}Br_2$		914	52.91	1.16
20	4,6-Cholestadien-3β-ol $C_{27}H_{44}O$		384	54.96	1.25
21	Stigmastan-3,5-diene $C_{29}H_{48}$		396	55.20	0.96
22	1,30-Triacontanediol $C_{30}H_{62}O_2$		454	55.53	0.89

Continuation of Table

1	2	3	4	5	6
23	3-(5,5-dimethyl-hexyl)-3a,10,10,12b-tetramethyl-1,2,3,3a,4,6,8,9,10,10a,11,12,12a,12b-tetradecahydro-benzo[4,5]cyclohepta[1,2-E]indene $C_{30}H_{50}$		410	57.77	2.54
24	3,6,6-Trimethyl-2-cyclohexen-1-ol $C_9H_{16}O$		140	60.32	2.60

Note. W is the content of the components; RT is the retention time; M is molar mass.

In the dichloromethane extract, 25 compounds were identified, of which the most abundant were: piceol (36.91 %); methyl 3-(acetyloxy)-20-hydroxyurs-12-en-28-oate (22.26 %); 6,10,14-trimethyl-2-pentadecanone (7.82 %); 2-hydroxy-1,1,10-trimethyl-6,9-epidioxydecalin (7.04 %), respectively.

In the extract halogen-organic compounds were detected in small amounts: 3-chloropropionic acid, 2.75 % heptadecyl ester, 2 fumaric acid 2-chlorophenylethylester (1.33 %) and 1,54-Dibromo tetrapentacontane (1.16 %). Halogen-organic compounds were first identified in the genus *Tamarix*.

From the literature data it is known that halogenated derivatives are rarely found in plants, but to date, chlorine and bromine containing mono-, di-, tri-, sesquiterpenoids, iridoids, alkaloids, phenolic compounds, fatty acids and other compounds isolated from plant material are known [6, 7].

It should be noted that previously we isolated some terpenoids, steroids and limiting alcohols from the native species of *Tamarix* plants, and some terpenoids were identified and characterized by physicochemical data [6–9]. The chemical composition of the dichloromethane extract from *Tamarix hispida* was firstly analyzed by gas chromatography.

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Tamarix hispida өсімдігінің дихлорметандық экстрактының химиялық құрамы

Мақалада алғаш рет Қазақстанның Алматы аймағынан жиналған *Tamarix hispida* Willd. (*Tamaricaceae)* өсімдігінің жер үсті бөлігінен алынған дихлорметан экстрактының химиялық құрамы қарастырылған. Алдын ала кептіріліп, ұнтақталған өсімдік шикізатының экстракциясы Сокслет аппаратында дихлометан ерітіндісімен жүргізілді. Алынған экстракт газды хроматография және масс-спектрометрия әдісімен келесі шарт бойынша зерттелді: 40 ºС температурада 5 мин аралығында SHP-5MS (30 м × 250 мм × 0.25 мм) газхроматографиялық бағанасында ұсталынды; тасушы газ — гелий ағынының жылдамдығы 1 мл/мин; бағдарламалау температурасы 250 ºС дейін және температураның өзгеруі 5 ºС/мин. Сынама көлемі 0,2 мкл. NIST және Wiley GC/MS кітапханасын қолдана отырып, масс-спектрі және ұстау уақыты бойынша сәйкестендірілді. Дихлорметан экстрактысында 25 қосылыс анықталды, оның ішінде сәйкесінше пицеол; метил 3-(ацетокси)-20-гидроксиурс-12-ен-28-оат; 6,10,14-триметил-2-пентадеканон, 2-гидрокси-1,1,10-триметил-6,9-эпидиоксидекалин көп мөлшерде байқалды. Зерттелген экстрактыда галогенорганикалық қосылыстар аз мөлшерде кездеседі: 3-хлорпропион қышқылының гептадецил эфирі, фумар қышқылының 2-хлорфенилэтил эфирі және тетрапентаконтанның 1,54-дибромы. Алғаш рет *Tamarix* өсімдік түрінде галоген туындылары табылды.

Кілт сөздер: дихлорметан экстракт, *Tamaricaceae, Tamarix hispida*, өсімдігінің жер үсті бөлігінен, галогенорганикалық қосылыстар, хромато-масс-спектрометрия, Сокслет әдісі.

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Исследование химического состава дихлорметанового экстракта *Tamarix hispida*

В статье впервые рассмотрен химический состав дихлорметанового экстракта, полученного из надземной массы растения *Tamarix hispida* Willd. (*Tamaricaceae)*, заготовленного в Алматинском регионе Республики Казахстан. Экстракцию предварительно высушенного и измельчённого растительного сырья проводили дихлорметаном в аппарате Сокслета. Полученный экстракт исследовали методом газовой хроматографии с масс-спектрометрией при следующих условиях: газохроматографическую колонку SHP-5MS (30 м × 250 мм × 0.25 мм) выдерживали при температуре 40 ºС в течение 5 мин; газ носитель — гелий со скоростью потока 1 мл/мин; с программированием температуры до 250 ºС и скоростью изменения температуры 5 ºС/мин. Объем аликвоты 0,2 мкл. Соединения идентифицировали по масс-спектрам и времени удерживания, с использованием библиотеки NIST и Wiley GC/MS. В дихлорметановом экстракте идентифицировали 25 соединений, из которых в наибольшем количестве составили: пицеол; метил 3-(ацетокси)-20-гидроксиурс-12-ен-28-оат; 6,10,14-триметил-2-пентадеканон; 2-гидрокси-1,1,10-триметил-6,9-эпидиоксидекалин соответственно. В исследуемом экстракте выявили присутствие галогенорганических соединений в небольших количествах: гептадециловый эфир 3-хлорпропионовой кислоты, 2-хлорфенилэтиловый эфир фумаровой кислоты и 1,54-дибром тетрапентаконтан. Галогенопроизводные соединения впервые обнаружены в растениях рода *Tamarix*.

Ключевые слова: дихлорметановый экстракт, *Tamaricaceae, Tamarix hispida*, надземная масса, галогенорганические соединения, дихлорметан, хромато-масс-спектрометрия, метод Сокслета.

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