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/10.32014/2018.2518-1491.38**
Volume 6, Number 432 (2018), 156 – 162

L.A.Utegenova[1], A.K.Nurlybekova[1], Hajiakber Aisa[2,3], J. Jenis[1]

[1]Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan;
[2]Xinjiang Technical Institutes of Physics and Chemistry, Central Asian of Drug Discovery and Development;
[3]Xinjiang Key Laboratory of Plant Resources and Natural Product Chemistry, XTIPC CAS, R. P. China
E-mail: lyazzat.utegenova@list.ru

LIPOSOLUBLE CONSTITUENTS OF *FRITILLARIA PALLIDIFLORA*

Abstract: Chemical constituents of the roots of *Fritillaria pallidiflora* collected in Kazakhstan were investigated for the first time. The quantitative and qualitative analysis of bioactive constituents of the medicinal plant have been made. The liposoluble constituents of hexane extract were obtained from the root parts of *F.pallidiflora* and analyzed by GC-MS method. More than thirty compounds were separated. Their relative contents were determined by area normalization in which 30 liposolubles were identified. The major liposoluble constituents of n-hexadecanoic acid (28.97%), linoelaidic acid (16.68%), oleic acid (11.30%), octadecanoic acid (6.95%), silanamine, n-phenyl- (4.41%), trans,trans-Dibenzylideneacetone(3.85%), gamma.-sitosterol (3.51%), ethyl 9.cis.,11.trans.-octadecadienoate (2.91%), hexadecanoic acid, ethyl ester (2.45%).

Key words: *Fritillaria pallidiflora,* GC-MS, liposoluble constituents.

Introduction

Fritillaria– is a genus of perennial herbaceous plants of the family Liliaceae, which in Latin translates into a glass for throwing out dice, in the shape of a corolla. One hundred and fifty species of hazel grouse, wildly growing in the temperate climate of the Northern Hemisphere, are known. Some species are found in the forests of East Asia, many in Western Asia. In the steppe zones, meadow places, on the slopes of the alpine and subalpine belt of Kazakhstan, there are 5 different species of *Fritillaria* growing[2]. Virtually all species of grouse contain alkaloids: peymin, verticin, peyminin, propymine, peymidine, peymifin, peymizin, peymithidin. They also include glycosides: peyminoside and zebaininoside. In addition, the bulbs contain organic acids, terpenoids, phytosterols and some vitamins. In small doses, the alkaloids contained in the bulbs have a therapeutic effect. Thus, in Chinese medicine, on the basis of the alkaloids contained in the bulbs, expectorants and soothing agents are made. In large doses of hazelnut bulbs are dangerous to health [4]. According to traditional descriptions, *Fritillaria* is slightly cold, and affects the lungs (to clear heat and moisten dryness, and used for hot-type bronchitis with dry cough) and the heart (to calm heart fire). *Fritillaria* is also used for treating lumps beneath the skin, such as scrofulous swellings and breast lumps. *F.pallidiflora* widely distributed in China and finds widespread applications as antitussive, antiasthmatic and expectorant medicine. Base on references, the main chemical constituents of *F. pallidiflora* be regarded as steroidal saponins and alkaloids [5].

In our continuously study of the plant, thirty liposoluble constituents in hexane part from medicinal plant, *F.pallidiflora* have been identified by GC-MS methods which grown in Almaty region of Kazakhstan for the first time.

Materials and Methods

Plant material. The root part of *F.pallidiflora* was collected in Almaty region of Kazakhstan, in May 2017 and identified by Dr. Alibek Ydyrys. Medicinal herbs were deposited in the Herbarium of Laboratory Plant Biomorphology, Faculty of Biology and Biotechnology, Al-Farabi Kazakh National

University, Almaty, Kazakhstan. The air dried roots of *F.pallidiflora* were cut into small pieces and stored at room temperature.

Extraction and isolation. The air-dried roots of *F. pallidiflora* (100 g) were pulverised then extracted with 70% ethyl alcohol (1:1) three times (seven days each time) at room temperature. After evaporation of the solvent under reduced pressure, the residues were mixed and suspended in water and then successively partitioned with hexane, EtOAc, and n- BuOH to afford the corresponding extracts. The obtained hexane extract was analyzed by GC-MS method.

Experimental part. The liposoluble constituents of from hexane extract of the medicinal plant were analyzed by using GC-MS method. GC-MS analysis: Electron Impact Ionization (EI) method on Agilent 7890A-5975C GC-MS (Gas Chromatograph coupled to Mass Spectrometer) fused silica capillary column (30m x 2.5mm; 0.25 μm film thickness), coated with HP-5MS were utilized. The carrier gas was helium (99.999%). The column temperature was programmed from 50°C (held for 10min), at 10°C/min rate program to increase temperature to 300°C. The latter temperature maintained for 40min (Acquisition parameters full scan; scan range 30-1000 amu). The injector temperature was 310°C. Injection: with a 1ul: detector ion source (EI-70eV). Samples were injected by splitting with the split ratio 5:1.

Identification of the compounds: identification of compounds was done by comparing the NIST and Wiley library data of the peaks and mass spectra of the peaks with those reported in literature. Percentage composition was computed from GC peak areas on HP-5MS column without applying correction factors.

Results and discussion

The liposoluble constituents of hexane extract from the root parts of *F.pallidiflora* were analyzed by GC-MS. Thirty compounds were separated. Their relative contents were determined by area normalization. Table 1 showed the liposolubles contents of the root parts of *F.pallidiflora.* The liposoluble contents of *F.pallidiflora* have been identified in which the major constituents are n-hexadecanoic acid (28.97%), linoelaidic acid (16.68%), oleic Acid (11.30%), octadecanoic acid (6.95%), silanamine, n-phenyl- (4.41%), trans,trans-dibenzylideneacetone (3.85%), .gamma.-sitosterol (3.51%), ethyl 9.cis.,11.trans.-octadecadienoate (2.91%), hexadecanoic acid, ethyl ester (2.45%).

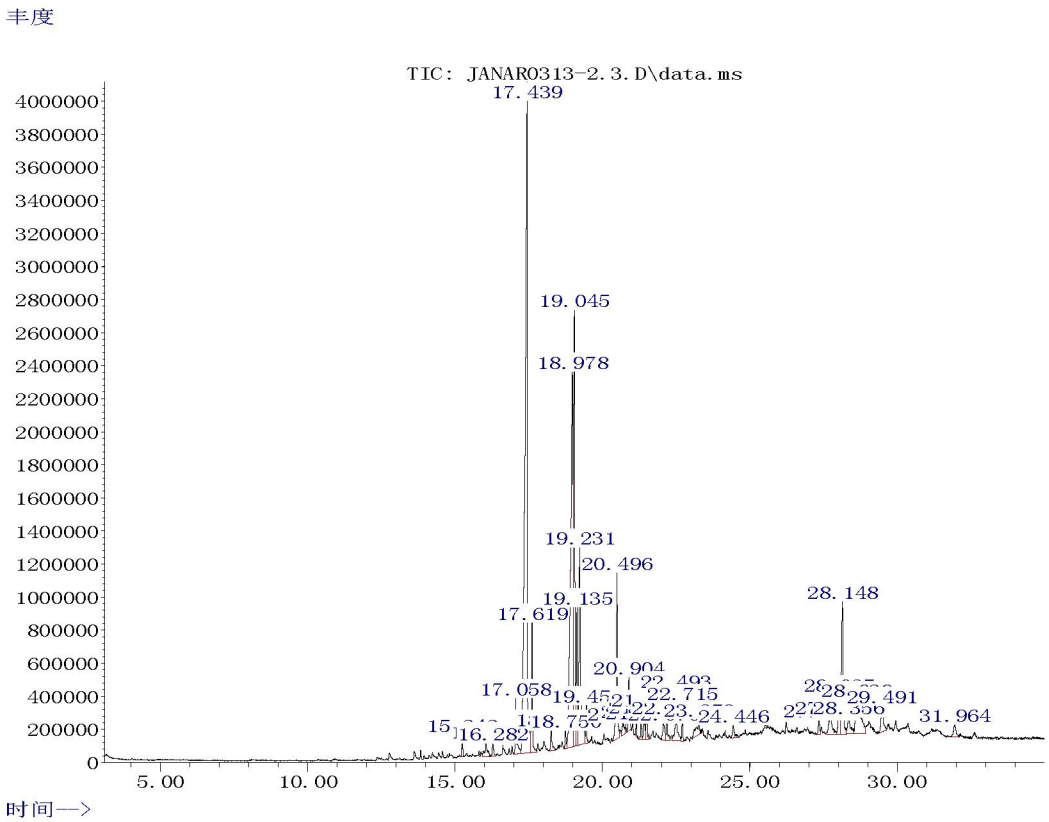
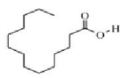
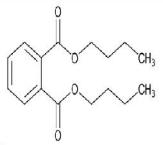
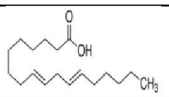


Fig. 1 Total ionization chromatogram of liposoluble contents hexane part from roots of *F.pallidiflora*

According to the report n-hexadecanoic acid (28.97%) is used in the production of stearin (a mixture with stearic acid), napalm, detergents and cosmetics, lubricating oils and plasticizers. And second major liposoluble constituents Linoelaidic acid (16.68%) showed rejuvenatingand anti-inflammatory activates. Oleic Acid (11.30%) and its esters are used for the production of paint and varnish materials, as plasticizers. It is used in soap making, oleic acid and its salts are widely used as emulsifiers. It is part of cosmetic products [13].

Most of these constituents have been found to show interesting biological activity against certain illnesses and pathogens. For instance, the anti-inflammatory, antioxidant, hypocholesterolemic [14], antibacterial [15], activities reported for n-hexadecanoic acid (28.97%), may suggest the rationale for the traditional use of the species. Linoelaidic acid (16.68%) showed anti-inflammatory activity,oleic Acid (11.30%), and octadecanoic acid (6.95%) have antibacterial,antimicrobial activity [16], hexadecanoic acid, ethyl ester (2.45%) possessantioxidant, hypocholesterolemic, nematicide, pesticide, antiandrogenic flavor, and hemolytic activities [17].

Table 1 - The liposoluble constituents of root parts of *F.pallidiflora*

Peak No.	Constituents	t_R (min)	Molecular Formula	Structure	MW	Content (%)
1	Tetradecanoicacid	15,244	$C_{14}H_{28}O_2$		228,209	0.43
2	9-Methyl-Z,Z-10,12-hexadecadien-1-ol acetate	16,051	$C_{19}H_{34}O_2$		294,256	0.69
3	12-Bromododecanoic acid	16,28	$C_{12}H_{23}BrO_2$		279,088	0.33
4	Dibutylphthalate	17,062	$C_{16}H_{22}O_4$		278,152	1.44
5	n-Hexadecanoicacid	17,435	$C_{16}H_{32}O_2$		256,24	28.97
6	Hexadecanoicacid, ethylester	17,622	$C_{18}H_{36}O_2$		284,272	2.45
7	n-Decanoicacid	18,259	$C_{10}H_{20}O_2$		172,146	0.62
8	Styrene	18,752	C_8H_8		104,063	0.37
9	Linoelaidicacid	18,982	$C_{18}H_{32}O_2$		280,24	16.68
10	OleicAcid	19,05	$C_{18}H_{34}O_2$		282,256	11.30
11	Ethyl 9.cis.,11.trans.-octadecadienoate	19,135	$C_{20}H_{36}O_2$		308,272	2.91

Продолжение таблицы 1

Peak No.	Constituents	t_R (min)	Molecular Formula	Structure	MW	Content (%)
12	Octadecanoicacid	19,228	$C_{18}H_{36}O_2$		284,272	6.95
13	Octadecanoicacid, ethylester	19,457	$C_{20}H_{40}O_2$		312,303	0.68
14	trans,trans-Dibenzylideneacetone	20,494	$C_{17}H_{14}O$		234,104	3.85
15	11-(2-Cyclopenten-1-yl)undecanoicacid, (+)-	20,698	$C_{16}H_{28}O_2$		252,209	0.47
16	Eicosanoicacid	20,902	$C_{20}H_{40}O_2$		312,303	1.26
17	Ethyl 14-methyl-hexadecanoate	21,148	$C_{21}H_{42}O_5$		298,287	0.25
18	Oxirane, 2,3-diphenyl-	21,318	$C_{14}H_{12}O$		196,089	0.35
19	1,2-Propanedione, 1-phenyl-, 2-oxime	21,42	$C_9H_9NO_2$		163,063	0.62
20	1,2-Propanedione, 1-phenyl-, 2-oxime	21,513	$C_9H_9NO_2$		163,063	0.76
21	Octadecylpropylether	22,074	$C_{21}H_{44}O$		312,339	0.67
22	Phthalicacid, monodecylester	22,193	$C_{18}H_{26}O_4$		306,183	0.61
23	Docosanoicacid	22,49	$C_{22}H_{44}O_2$		340,334	1.81

Окончание таблицы 1

Peak No.	Constituents	t_R (min)	Molecular Formula	Structure	MW	Content (%)
24	Octadecanoic acid, 17-methyl-, methyl ester	22,711	$C_{20}H_{40}O_2$		312,303	0.61
25	3,3,3-Trifluoroprop-1-en-1-yl fluorosulfate	23,28	$C_3H_2F_4O_3S$		193,966	0.89
26	2-Benzoyl-1,2,3,4-tetrahydro-isoquinoline-3-carboxylic acid	24,444	$C_{17}H_{18}N_2O$		281,105	0.47
27	Azete, 2,3-dihydro-4-phenyl-	27,349	C_9H_9N		131,073	0.38
28	Acetamide, N-[4-[[2-(6-chloro-3-cyano-4-methyl-2-pyridinyl)-2-ethylhydrazono]methyl]phenyl]-	28,038	$C_{20}H_{24}N_2O_5$		355,12	1.32
29	Silanamine, N-phenyl-	28,148	C_6H_6NSi		123,05	4.41
30	Gamma.-Sitosterol	28,641	$C_{29}H_{50}O$		414,386	3.51

Conclusion

The liposoluble constituents were extracted by hexane from the root parts of *F.pallidiflora* which analyzed by GC-MS method. More than thirty compounds were separated. Their relative contents were determined by area normalization in which 30 liposolubles were identified. Active principles of hexane extract of the medicinal plant (*F.pallidiflora*) which collected from Almaty region of Kazakhstan were determined for the first time. While the major liposoluble constituents are n-hexadecanoic acid (28.97%), linoelaidic acid (16.68%), and oleic acid (11.30%) that possessing antifungal, insecticidal, larvicidalanti – inflammatory and analgesic activities separately.

Acknowledgement

The work was supported by grants from Ministry of Education and Science of Kazakhstan (0118PK00458).

REFERENCES

[1] M.S. BaitenovFlora of Kazakhstan,Gylym, Almaty, 2001. - Vol. 2

[2] *Brickell, Christopher, ed. (2016). RHS: A–Z Encyclopedia of garden plants (4th ed.).* Dorling Kindersley. ISBN 978-0-241-23912-4.

[3] Nysanbaev A (1998) «Kazakhstan» National Encyclopedia, I: 328. Kazakh Encyclopediareduction, Almaty. ISBN 5-89800-123-9

[4] Lozina-Lozinskaya A.S.Ryabchik - Fritillaria // Flora of the USSR / Botanical Institute of the USSR Academy of Sciences; Editor-in-chief and editor of the fourth volume of Acad. VL Komarov. - L.: Publishing House of the USSR Academy of Sciences, 1935. - T. IV. - P. 302-320.

[5] Shuo Shen, Guoyu Li, Jian Huang, Chaojun Chen, Bu Ren, Ga Lu, Yong Tan, Jiaxu Zhang ,

Xian Li, Jinhui Wang. Steroidal saponins from Fritillaria pallidiflora Schrenk // Fitoterapia 83 (2012) 785–794

[6] Dorni C, Sharma P, Saikia G, Longvah T. (2018) Fatty acid profile of edible oils and fats consumed in India, Food Chemistry, 238: 9-15.DOI:10.1016/j.foodchem.2017.05.072

[7] Szymczycha-Madeja A, Welna M, Pohl P. (2012) Elemental analysis of teas and their infusions by spectrometric methods,TrAC Trends in Analytical Chemistry, 5: 165-181.DOI: 10.1016/j.trac.2011.12.005.

[8] Yang B, Chen H, Stanton C, Ross RP, Zhang H, Chen YQ, Chen W. (2015) Review of the roles of conjugated linoleic acid in health and disease, Journal of Functional Foods, 15: 314-325.DOI: 10.1016/j.jff.2015.03.050

[9] Bowen KJ, Kris-EthertonaPM,SheareraGS, Westa ShG, ReddivaricL, Jones PJ.(2017)Oleic acid-derived oleoylethanolamide: A nutritional science perspective,Progress in Lipid Research, 67: 1-15.DOI: 10.1016/j.plipres.2017.04.001

[10] Maechler P. (2017) Glutamate pathways of the beta-cell and the control of insulin secretion,Diabetes Research and Clinical Practice, 131:149-153.DOI: 10.1016/j.diabres.2017.07.009

[11] Katane M, Kanazawa R, Kobayashi R, Oishi M, Nakayama K,Saitoh Y, Miyamoto T, Sekine M, Homma H. (2017) Structure–function relationships in human D-aspartate oxidase: characterisation of variants corresponding to known single nucleotide polymorphisms, BBA - Proteins and Proteomics, 1865: 1129-1140.DOI:10.1016/j.bbapap.2017.06.010

[12] Liu L, Chen Y, Yang L. (2014) Inhibition study of alanine amino transferase enzyme using sequential online capillary electrophoresis analysis, Analytical Biochemistry, 467: 28-30.DOI: 10.1016/j.ab.2014.08.035

[13] https://pubchem.ncbi.nlm.nih.gov/

[14] Kumar P.P., Kumaravel S., Lalitha C. Screening of antioxidant activity, total phenolics and GC-MS study of Vitexnegundo. Afr. J. Biochem. Res. 2010, 4, 191-195.

[15] Rahuman A.A., Gopalakrishnan G., Ghouse B.S., Arumugam S., Himalayan B. Effect of Feronialimonia on mosquito larvae. // Fitoterapia 2000, 71, 553-555.

[16] Mustapha N. Abubakar, Runner R. T. Majinda. GC-MS Analysis and Preliminary Antimicrobial Activity of Albiziaadianthifolia (Schumach) and Pterocarpusangolensis (DC) // Medicines 2016, 3, 3

[17] Sudha T, Chidambarampillai S., Mohan V.R. GC-MS Analysis of Bioactive Components of Aerial parts of FluggealeucopyrusWilld. (Euphorbiaceae) // Journal of Applied Pharmaceutical Science 3 (05); 2013: 126-130.

[18] G.O. Kantureeva, E. Defrancesco, R.S. Alibekov, K.A. Urazbayeva, I.E. Efimova. New trends in the identification of the traditionalfood products of Kazakhstan. **News of NAS RK. Series of Chemistry and technology.** Volume 5, Number 431 (2018), 6 – 12. https://doi.org/10.32014/2018. 2518-1491.1 ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

[1]Л.А. Утегенова, [1]А.К. Нурлыбекова, [2,3]Хажиакбер Аиса, [1]Ж. Жеңіс *

[1]Әл-Фараби атындағы ҚазҰУ, Химия және Химиялық Технология Факультеті, Алматы, Қазақстан;
[2]Шыңжаң физика және химия техникалық институты, Қытайғылымдар академиясы;
[3]Шыңжаң табиғи ресурстар мен табиғи өнімдер химиясы зертханасы, Қытайғылымдар академиясы, Қытай

АҚШЫЛСЕПКІЛГҮЛӨСІМДІГІНІҢМАЙДА ЕРИТІНҚҰРАМЫНЗЕРТТЕУ

Аннотация: Алматы өңірінен жиналған *Fritillaria pallidiflora*өсімдігі тамырының химиялық құрамы алғаш рет зерттелді. Дәрілік өсімдіктің биологиялық белсенді құрамының сандық және сапалық талдаулары

жасалды. *F.pallidiflora*өсімдігі тамырынанмайда ергішзаттарданқұрам тапқан гександіэкстракті алындыжәне GC-MS әдісімен талданды. Соныменгександы бөліктен отызқосылыссарапталды.Олардың салыстырмалы құрамы қалыпты аймақ көмегімен есептеліп, нәтижесінде гександы бөліктегі негізгі қосылыстар:n-гексадекан қышқылы (28,97%), линолейн қышқылы (16,68%), олеин қышқылы (11,30%), октадекан қышқылы (6,95%), силанамин, n -фенил- (4,41%), транс, транс-Дибензилиденацетон (3.85%), гамма-ситостерол (3.51%), этил9.цис, 11. транс-октадекадиеноат (2.91%) және гексадекан қышқылдың этил эфирі (2.45%) болып табылды.

Түйін сөздер: *Fritillaria pallidiflora*, GC-MS, майда ергішзаттар

[1]Л.А. Утегенова, [1]А.К. Нурлыбекова, [2,3]Хажиакбер Аиса, [1]Ж. Жеңіс *

[1]Факультет химии и химической технологии, Казахский национальный университет им. Аль-Фараби, Алматы, Казахстан

[2]Синьцзянскийтехническийинститутфизикиихимии, Китайская академия наук

[3]ЛабораторияСиньцзянрастительныхресурсовихимииприродныхсоединений,Китайская академия наук, Китай

ИССЛЕДОВАНИЕ ЖИРОРАСТВОРИМОГО СОСТАВА РЯБЧИКА БЛЕДНОЦВЕТКОГО

Аннотация:Впервые был исследован химический состав корней *Fritillaria pallidiflora*, собранных в Алматинской области. Сделан количественный и качественный анализ биологически активных компонентов лекарственного растения. Жирорастворимые компоненты гексанового экстракта были получены из корневой части *F.pallidiflora* и проанализированы методом GC-MS. Было разделенотридцать соединений.Их относительное содержание было определено по нормализации площади, среди которыхосновными компонентами являютсяn-гексадекановая кислота (28,97%), линолеиновая кислота (16,68%), олеиновая кислота (11,30%), октадекановая кислота (6,95%), силанамин, n -фенил- (4,41%), транс, транс-Дибензилиденацетон (3,85%), гамма-ситостерол (3,51%), этил-9.цис., 11.trans.-октадекадиеноат (2,91%), этиловый эфир гексадекановой кислоты (2,45%).

Ключевые слова: *Fritillaria pallidiflora*, GC-MS, жирорастворимые компоненты.