Plant & Fungal Research (2020) 3(1): 61-65
http://dx.doi.org/10.29228/plantfungalres.70

June 2020

Chemical content of *Lactuca serriola* L.: fatty acid esters and triterpene compounds from the roots

Emil N. Shukurlu
Institute of Botany, Azerbaijan National Academy of Sciences, Badamdar 40, Baku, AZ1004, Azerbaijan

Abstract: This work aimed to study the chemical composition of the crystalline mass obtained from the acetone extract of the roots of *Lactuca serriola* L. Its characterization by gas chromatography-mass spectrometry (GC-MS) analyses led to the identification of 21 substances including palmitic acid, methyl ester, n–hexadecanoic acid, methyl-trans-oleate, 11-octadecenoic acid methyl ester, methyl stearate, oleic acid, 11-eicosenoic acid methyl ester, common in the most plant species. Furthermore, some triterpenoid compounds [olean-12-en-3-one, 13,27-cycloursan-3-one, ursa-9(11),12-dien-3-yl acetate, lupeol, germanicol, lup-20(29)-en-3-ol, acetate, (3β)] characteristic of the *L. serriola* were identified. Despite the richness of chemical composition and the wide availability in Azerbaijani flora, *L. serriola* is still uninvestigated. Therefore, the study of the qualitative and quantitative composition of this plant represent interest.

Key Words: *acetone extract, crystalline mass, GC-MS, Lactuca species, triterpenoids, lupeol acetate*

INTRODUCTION

The genus *Lactuca* (Asteraceae) is represented by a range of forms, including annual, biennial, and perennial, glabrous or pubescent herbs with abundant latex, rarely shrubs. The root system is rhizomatous, sometimes with underground stolons or with fusiform and/or tuberous roots. The distribution of *L. serriola* worldwide includes 17 species in Europe, 51 in Asia, 43 in Africa, and 12 in the Americas [Lebeda et al., 2004]. In the Caucasus, 15 species have been recognized. Ten of them are present in Azerbaijan [Askerova et al., 1961]. *L. serriola* L. is an annual or biennial plant, with needle-like roots, stems 30-100 cm high and vertical bluish-green leaves. Usually, it is found in mountainous places, mountain slopes, pebbly places, seashore and orchards [Askerova et al., 1961]. *L. serriola* has traditionally been used in folk medicine for the treatment of respiratory and gastrointestinal diseases, as sedative, hypnotic, expectorant, cough suppressant, purgative, demulcent, diuretic, antiseptic, vasorelaxant, and antispasmodic, as well as to cure bronchitis, asthma, pertussis, and several other diseases [Janbaz et al., 2013].

The methanol extract of *L. serriola* aerial parts was found to have spasmogenic, spasmolytic, bronchodilator and vasorelaxant activities. The spasmogenic activity could be due to some cholinergic constituents, whereas spasmolytic effect could be attributed to Ca^{++} channel blocking components able to relax gastrointestinal, tracheal, and aortic smooth muscles [Janbaz et al., 2013]. The leaves have beneficial effects as stomachic agent, in the treatment of biliousness, burning sensation, headache, troubles of the nose, bronchitis and cough, as well as in the purification of blood. The seeds are also used against headaches, ophthalmia and to relieve inflammation. Moreover, *L. serriola* is also used as analgesic, hypnotic and to prevent the fall of hair [Yadava, Jharbade, 2008]. The aqueous and methanolic leaf extracts of *L. serriola* demonstrated a significant dose-dependent antipseudomonal activity against multidrug-resistant *Pseudomonas aeruginosa* clinical isolates [Balogun et al., 2017].

Chemically, plants of the genus *Lactuca* can be characterized by the accumulation of sesquiterpene lactones, consisting mainly of guaianolides and germacranolides, and phenolic compounds (caffeic acid, ferulic acid, chlorogenic acid) [Terencio et al., 1992; Michalska, Kisiel, 2009]. Azerbaijani species are almost uninvestigated in terms of chemical composition.

In general, sesquiterpene lactones and their various derivatives have been extracted from *L. serriola* according to the world literature findings. From the aerial parts, 11β, 13-dihydrolactucin, deacetoxymatricarin (=leucodin, leucomisin), loliolide, melampolide glucoside [Alberto et al., 1992], quercetin-3-O-β-D-glycopyranoside, luteolin-7-O-β-D-glycopyranoside, luteolin, quercetin, kaempferol [Kim, 2001], 8-deoxylactucin, jacquinelin, crepidiaside B [Michalska et al., 2009] were obtained. In particular, as of guaianolide sesquiterpene lactones such as lactucopicrin, lactucin-15-oxalate, and 15-(4-hydroxyphenylacetyl)-lactucin-8-sulfate were isolated from the latex [Bushman et al., 2006]. In Poland, 8-deoxylactucin, jacquinelin,

Accepted for publication: 8 April 2020
E-mail: geneticsster@gmail.com

crepidiaside B, lactucin, 11β, 13-dihydrolactucin, lactucopicrin, vernoflexuoside (glucozaluzanin C) and lactuside A were isolated from the roots [Michalska et al., 2009]. In addition, it has been found that inulin-type substance and fructooligosaccharides were identified in the taproots of *L. serriola* [Petkova, Denev, 2013], making it a new source of prebiotics in human and animal nourishment.

Therefore, the aim of this work was to characterize, both from the qualitative and quantitative point of view, the chemical compounds present in the roots of *L. serriola*, a species widespread in the southern Caucasus region.

MATERIAL AND METHODS

Plant material. Roots of *L. serriola* were collected during the blooming period from the Vilash village (38°59'23.4" N; 48°34'49.9" E) located in Masally region in the south of Azerbaijan. They were chopped into small pieces and dried at room temperature.

Extraction. The roots (146.5 g) were extracted 3 times with acetone (once every three days). The obtained extracts were filtered to remove residues and evaporated to dryness by using a rotary evaporator. During this process, a crystalline mass is separated from the total extract. It was filtered and rinsed twice with acetone.

TLC. Benzene was used as a solvent for TLC analysis. Visualization of compounds was obtained via chromatoscope. TLC plates (Silufol-UV-254) were observed under UV-366 nm light.

GS-MS analysis. Fatty acid methyl esters (FAMEs) and triterpene compounds were separated by GC-MS (Agilent Technologies 6890N Network CG System, 5975 inert Mass Selective Detector mass-spectrometer with chromatograph) using a capillary column" HP-5MS 5% Methyl Siloxane" (30 m length, 0.25 mm internal diameter, 0.25μ thickness of inactive phase). The temperature program was as follows: the initial temperature of 50° C was held for 2 min, followed by temperature increase from 15° C to 200° C - 2 minutes constant; temperature increase from 15° C to 280° C – 10 minutes constant with helium as the carrier gas (constant flow rate of 1 ml min^{-1}).

The compounds were identified by comparasion with the NIST mass spectral database (The NIST Mass Spectral Seach Program for the NIST/EPA/NIH/Mass Spectral Library. Version 2.0.g.build May 19, 2011).

RESULTS AND DISCUSSION

A crystalline mass (2.16 g) was precipitated from the total acetone extract (8.96 g) of the roots of *L. serriola.* At first, TLC analysis of the sample showed several spots that were indicative of a polycomponent mixture, subsequently characterized by GC-MS method. In total, 21 components were identified (Fig.; Table). Among them, 9 were triterpenoid compounds, whereas 8 were described as fatty acid esters. In addition, 2 fatty acids and 2 dicarboxylic acid esters were identified.

According to the table, decanedioic acid, bis (2-ethylhexyl) ester and 11-eicosenoic acid methyl ester represented the least abundant compounds, making up 0.18% and 0.16% of the total, respectively. Among fatty acids, methyl-trans-oleate (7.17%) was the predominant component, followed by palmitic acid methyl ester (3.10%) and methyl linoleate (2.47%), although with concentrations two to three times lower. The ratio of unsaturated to saturated fatty acid esters was 6:2.

The triterpene profile of *L. serriola* was characterized by the high concentrations of lup-20(29)-en-3-ol, acetate, 3β (lupeol acetate) (37.50%) and germanicol (27.20%), while the lowest amounts were detected for methyl ursolate (0.67%) and lupeol (0.30%). Some of the identified triterpenes such as lupeol, lupeol acetate and germanicol, in addition to α-amyrin, β-amyrin, and olean-18-ene (germanicen), were previously isolated from the methanol extract of *L. serriola* aerial parts [Elsharkawy, Alshathly, 2013]. Our results also confirmed the presence of methyl linoleate, methyl palmitoleinate and palmitic acid methyl esters in *Lactuca* genus in accordance with Abd El-Fattah and collaborators [1992], who isolated them in the flowering parts of *L. saligna* L.

Most of the identified metabolites of *L. serriola* exhibited certain pharmaceutical properties. For example, lupeol was found to have anti-cancer and anti-inflammatory properties [Saleem, 2009]. Methyl ursolate displayed *in vitro* cytotoxic and leishmanicidal activities, while in vivo anti-inflammatory and antioxidative abilities [Fabri et al., 2014]. Lupeol acetate showed to slow down the progression of rheumatoid arthritis by inhibiting the activation of macrophages and osteoclastogenesis [Wang et al., 2016]. Furthermore, lupeol acetate remarkably was able to reduce rheumatoidal arthritis symptoms by inhibition of inflammatory cytokine expression. This anti-inflammatory activity is very important for skin regeneration process [Malinowska et al., 2019]. Olean-12-en-3-yl acetate had antimicrobial, anti-diabetic, anti-amylase inhibitor effects [Venkata et al., 2012].

Due to the highest level of lupeol acetate in *L. serriola*

roots and its numerous pharmacological activities, this plant part can be recommended as a source of this potentially interesting molecule.

Table. Summary of the components identified by GC-MS method in the crystalline mass obtained from *Lactuca serriola*.

№	RT, min	Fragments	Molecular weight	Chemical formula	Name	% of total
			Fatty acid esters and fatty acids			
1	16.822	99, 97, 88, 84, 75, 70, 56, 42	268 g/mol	$C_{17}H_{32}O_2$	Methyl palmitoleinate	0.25
2	17.147	227, 143, 88, 75, 69, 57, 55, 43, 41	270 g/mol	$C_{17}H_{34}O_2$	Palmitic acid, methyl ester	3.10
3	17.660	129, 83, 74, 71, 61, 58, 56, 44, 42	256 g/mol	$C_{16}H_{32}O_2$	*n*-Hexadecanoic acid	0.21
4	19.815	109, 96, 83, 82, 79, 68, 56, 41	294 g/mol	$C_{19}H_{34}O_2$	Methyl linoleate	2.47
5	19.935	97, 96, 87, 84, 83, 74, 70, 56, 44, 42	296 g/mol	$C_{19}H_{36}O_2$	Methyl-trans- oleate	7.17
6	20.022	97, 96, 87, 84, 83, 74, 69, 56, 41	296 g/mol	$C_{19}H_{36}O_2$	11-Octadecenoic acid, methyl ester	1.45
7	20.325	298, 143, 88, 75, 69, 57, 55, 43, 41	298 g/mol	$C_{19}H_{38}O_2$	Methyl stearate	1.51
8	20.487	98, 97, 96, 84, 83, 70, 57, 56, 43	282 g/mol	$C_{18}H_{34}O_2$	Oleic Acid	0.37
9	21.285	109, 96, 95, 82, 81, 79, 69, 68, 55	294 g/mol	$C_{19}H_{34}O_2$	Methyl 9-cis, 11-trans-octadecadienoate	0.39
10	22.973	292, 98, 97, 96, 84, 83, 74, 69, 67, 55	324 g/mol	$C_{21}H_{40}O_2$	11-Eicosenoic acid, methyl ester	0.16
			Dicarboxylic acid esters			
11	26.161	279, 167, 150, 71, 70, 57, 55, 43, 41	390 g/mol	$C_{24}H_{38}O_4$	Bis(2-ethylhexyl) phthalate	2.96
12	29.504	186, 112, 98, 83, 71, 70, 57, 55, 43, 41	426 g/mol	$C_{26}H_{50}O_4$	Decanedioic acid, bis(2-ethylhexyl) ester	0.18
			Triterpene compounds			
13	37.086	219, 203, 135, 95, 81, 69, 55, 43, 41	424 g/mol	$C_{30}H_{48}O$	Olean-12-en-3-one	1.08
14	37.257	425, 206, 139, 124, 122, 110, 96, 82, 70, 56	424 g/mol	$C_{30}H_{48}O$	13,27-Cycloursan-3-one	0.70
15	37.887	467, 392, 255, 96, 82, 70, 56, 45, 43	466 g/mol	$C_{32}H_{50}O_2$	Ursa-9(11),12-dien-3-yl acetate	1.21
16	38.795	110, 96, 94, 82, 70, 69, 68, 56, 44, 42	426 g/mol	$C_{30}H_{50}O$	Lupeol	0.30
17	39.863	219, 203, 189, 136, 110, 96, 82, 69, 44	468 g/mol	$C_{32}H_{52}O_2$	Olean-12-en-3-yl acetate	5.383
18	40.225	218, 205, 190, 178, 132, 121, 109, 95	426 g/mol	$C_{30}H_{50}O$	Germanicol	27.20
19	41.224	190, 122, 110, 108, 96, 94, 82, 70, 56, 44	468 g/mol	$C_{32}H_{52}O_2$	Lup-20(29)-en-3-ol, acetate, 3β (lupeol acetate)	37.50
20	42.609	263, 207, 204, 119, 81, 70, 57, 56, 44, 42	470 g/mol	$C_{31}H_{50}O_3$	Methyl ursolate	0.67
21	43.466	469, 206, 139, 136, 124, 122, 110, 96, 70, 44	468 g/mol	$C_{32}H_{52}O_2$	13,27-Cycloursan-3-ol, acetate, (3 β, 13 β, 14 β)-	5.73

Note: RT - retention time.

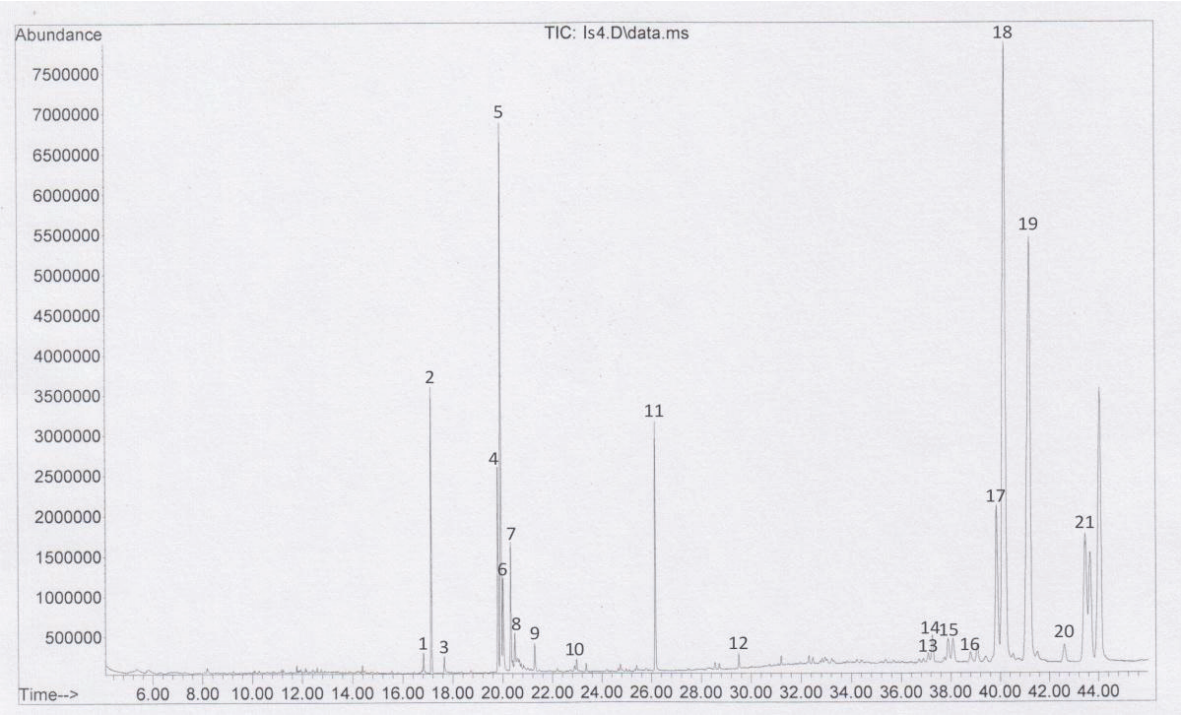

Figure. GC-MS chromatogram of crystalline mass obtained from the acetone extract of the roots of *Lactuca serriola*: (1) methyl palmitoleinate; (2) palmitic acid, methyl ester; (3) n-hexadecanoic acid; (4) methyl linoleate; (5) methyl-trans- oleate; (6) 11-octadecenoic acid, methyl ester; (7) methyl stearate; (8) oleic acid; (9) methyl 9-cis, 11-trans-octadecadienoate; (10) 11-eicosenoic acid, methyl ester; (11) bis(2-ethylhexyl) phthalate; (12) decanedioic acid, bis(2-ethylhexyl) ester; (13) olean-12-en-3-one; (14) 13,27-cycloursan-3-one; (15) ursa-9(11),12-dien-3-yl acetate; (16) lupeol; (17) olean-12-en-3-yl acetate; (18) germanicol; (19) lup-20(29)-en-3-ol, acetate, 3β (lupeol acetate); (20) methyl ursolate; (21) 13,27-cycloursan-3-ol, acetate, (3 β, 13 β, 14 β) -.

REFERENCES

Abd El-Fattah H., Khalil A.T., Mansour E.S., Waight E.S. (1992) Triterpenes and triterpene esters from *Lactuca saligna*. *Int. J. Pharmacognosy*, 30(1): 21-26.

Alberto M.J., Sanz J.F., Albiach R. (1992) A sesquiterpene ester from *Lactuca serriola*. *Phytochemistry*, 31(7): 2539-2540.

Balogun S.T., Stephenson C., Akanmu A.O., Gamache S., Jibrin J. (2017) Antipseudomonal activity of aqueous and methanolic leaf extracts of *Lactuca serriola* Linn. (Astereceae). *IJAPBC*, 6(1): 1-6.

Bushman B.S., Scholte A.A., Cornish K., Scott D.J., Brichta J.L., Vederas J.C., Ochoa O., Michelmore R.W., Shintani D.K., Knapp S.J. (2006) Identification and comparison of natural rubber from two *Lactuca* species. *Phytochemistry*, 67: 2590-2596.

Elsharkawy E., Alshathly M. (2013) Anticancer activity of *Lactuca serriola* growing under dry desert condition of northern region in Saudi Arabia. *J. Nat. Sci. Res*, 3: 5-19.

Fabri R.L., Garcia R.A., Florêncio J.R., Carvalho L.O., Castro Campos Pinto N., Coimbra E.S., Souza-Fagundes E.M., Ribeiro A., Scio E. (2014) Pentacyclic triterpenoids from *Mitracarpus frigidus* (Willd. ex Roem. & Schult.) K. Shum: *in vitro* cytotoxic and leishmanicidal and in vivo anti-inflammatory and antioxidative activities. *Med. Chem. Res.*, 23: 5294-5304.

Flora Azerbaidjana (1961) Ed.: R.K. Askerova, G.F. Akhundov, Y.M. Isaev, I.I. Karyagin, L.I. Irilipko, R.M. Sofieva. Baku: AN Azerb. SSR, 8: 551-557. [Флора Азербайджана (1961) Под ред. Р.К. Аскерова, Г.Ф. Ахундов, Я.М. Исаев, И.И. Карягин, Л.И. Ирилипко, Р.М. Софиева. Баку: АН Азербайджан. ССР, 8: 551-557]

Janbaz K.H., Latif M.F., Saqib F., Imran I., Zia-Ul-Haq M., De Feo V. (2013) Pharmacological effects of *Lactuca serriola* L. in experimental model of gastrointestinal, respiratory, and vascular ailments. *Evid Based Complement Alternat Med*, Article ID 304394

Kim D.K. (2001) Antioxidative components from the aerial parts of *Lactuca scariola* L. *Korean Arch. Pharm. Res*., 24(5): 427-430.

Lebeda A., Dolezalová I., Feráková V., Astley D. (2004) Geographical distribution of wild *Lactuca* species (Asteraceae, Lactuceae) *Bot. Rev.*, 70(3): 328-356.

Malinowska M., Miroslaw B., Sikora E., Ogonowski J., Wojtkiewicz A.M., Szaleniec M., Pasikowska-Piwko M., Eris I. (2019) New lupeol esters as active substances in the treatment of skin damage. *PLOS ONE*, 14(3): e0214216.

Michalska K., Kisiel W. (2009) Root constituents of *Lactuca sibirica* and a comparison of metabolite profiles of *L. sibirica* and *L. tatarica*. *Acta Soc. Bot. Pol*., 78(1): 25-27.

Michalska K., Stojakowska A., Malarz J., Dolezalova I., Lebeda A., Kisiel W. (2009) Systematic implications of sesquiterpene lactones in *Lactuca* species. *Biochem. Syst. Ecol.*, 37: 174-179.

Petkova N., Denev P. (2013) Evaluation of fructan contents in the taproots of plants *Lactuca serriola* L. and *Sonchus sleraceus* L. *Scientific Bulletin. Series F. Biotechnologies*, XVII: 117-122.

Saleem M. (2009) Lupeol, a novel anti-inflammatory and anti-cancer dietary triterpene. *Cancer Letters*, 285: 109-115.

Terencio M.C., Sanz M.J., Fonseca M.L., Máñez S. (1992) Phenolic compounds from *Lactuca viminea* L. *Zeitschrift für Naturforschung C*., 47(1-2): 17-20.

Venkata R.B., Samuel L.A., Pardha S.M., Narashimha R.B., Naga V.K.A., Sudhakar M., Radhakrishnan T.M. (2012) Antibacterial, antioxidant activity and GC-MS analysis of *Eupatorium odoratum*. *AJPCR*, 5(2): 99-106

Wang W.H., Chuang H.Y., Chen C.H., Chen W.K., Hwang J.J. (2016) Lupeol acetate ameliorates collagen-induced arthritis and osteoclastogenesis of mice through improvement of microenvironment. *Biomed. Pharmacother*, 79: 231-240.

Yadava R.N., Jharbade J. (2008) New antibacterial triterpenoid saponin from *Lactuca scariola*. *Fitoterapia*, 79(4): 245-249.

Lactuca serriola L. növünün kimyəvi tərkibi: köklərdən alınan yağ turşularının efirləri və triterpen birləşmələri

Emil N. Şükürlü
AMEA Botanika İnstitutu, Badamdar şossesi 40, Bakı, AZ1004, Azərbaycan

Tədqiqat işi *Lactuca serriola* L. növü köklərinin asetonlu ekstraktından alınan kristallik kütlənin kimyəvi tərkibinin öyrənilməsinə həsr edilmişdir. Kristallik kütlə qaz xromatoqrafiya-mass spektrometriya (QX-MS) üsulu ilə analiz edilərək əksər bitki növlərində rast gəlinən (palmitin turşusunun metil efiri, n-heksadekan turşusu, trans-metiloleat, 11-oktadesen turşunun metil efiri, metil stearat, olein turşusu, 11-eikosen turşusunun metil efiri də daxil olmaqla) 21 komponent identifikasiya olunmuşdur. Bundan başqa, *L. serriola* növü üçün xarakterik bəzi triterpen birləşmələri [olean-12-en-3-on, 13,27-tsikloursan-3-on, ursa-9(11),12-dien-3-ol asetat, lupeol, germanikol, lup-20(29)-en-3-ol, asetat, (3β)] də təyin edildi. Azərbaycan florasında onun olduqca geniş ehtiyatının olmasına və kimyəvi tərkibinin zənginliyinə baxmayaraq *L. serriola* hələ də tədqiqat obyekti olmamışdır. Bu səbəbdən, bitkinin keyfiyyət və kəmiyyət tərkibinin tədqiqi əhəmiyyət kəsb edir.

Açar sözlər: *asetonlu ekstrakt, kristallik kütlə, QX-MS, Lactuca növləri, triterpenoidlər, lupeol asetat*

Химический состав *Lactuca serriola* L.: эфиры жирных кислот и тритерпеновые соединения корней

Эмиль Н. Шукюрли
Институт Ботаники НАНА, Бадамдарское шоссе 40, Баку, AZ1004, Азербайджан

Данная работа посвящена изучению химического состава кристаллической массы, полученной из ацетонового экстракта корней *Lactuca serriola* L. Кристаллическая масса была проанализирована с помощью газовой хромато-масс-спектрометрии (ГХ-МС) по результатам которой было идентифицировано 21 веществ (включая метиловый эфир пальмитиновой кислоты, н-гексадекановая кислота, метил-трансолеат, метиловый эфир 11-октадеценовой кислоты, метилстеарат, олеиновая кислота, метиловый эфир 11-эйкозеновой кислоты), встречающиеся в составе большинства видов растений. Кроме того, были определены характерные для *L. serriola* некоторые тритерпеновые соединения [олеан-12-ен-3-он, 13,27-циклоурсан-3-он, урса-9(11),12-диен-3-ол ацетат, люпеол, германикол, люп-20(29)-ен-3-ол, ацетат (3β)]. Несмотря на богатый химический состав и наличие большого запаса данного вида во флоре Азербайджана, *L. serriola* до сих пор не исследован. В этой связи представляет интерес исследование качественного и количественного состава растения.

Ключевые слова: *ацетоновый экстракт, кристаллическая масса, ГХ-МС, виды Lactuca, тритерпеноиды, люпеол ацетат*