Azerbaijan Journal of Botany, 2021, 2(1): 66-70

INVESTIGATION OF CHEMICAL CONSTITUENTS FROM THE AERIAL PARTS OF *LACTUCA TATARICA* (L.) C.A. MEY. BY CHROMATOGRAPHY – MASS SPECTROMETRIC METHOD

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This article is devoted to the investigation of the chemical components of the aerial parts (stems and leaves) of *Lactuca tatarica*. The phytochemical study of the aerial parts of the species *L. tatarica* (320 g) revealed the presence of coumarin derivatives in its composition. In the acetonic extraction of plant raw material the total extractive contents is investigated by the Liquid chromatography–mass spectrometric (LC-MS) method and coumarin derivatives have been identified. Totally 10 compounds were obtained, of which three were identified. It was found that, of these, other three compounds belong to coumarins, derivatives of polyphenols and phenylpropanoids. LC-MS experiments were realised by a Shimadzu 20 A HPLC system and identification of the substances were performed by Analyst 1.6 software. Gluconic acid, glucose, di-hydroxycoumarin glucoside, are amongst those which were identified. The importance of gluconic acid is that it is a chelator at alkaline pH. Moreover, it is used as a food additive in the food industry. The plant is widely used in traditional Chinese and Indian folk medicine in the treatment of certain diseases. Thus, we consider it important to study the chemical composition of a plant in order to detect biologically active components with broad pharmacological activity.

Keywords: extractive compounds, LC-MS, Di-hydroxycoumarin glucoside, gluconic acid

INTRODUCTION

The discovery of the beneficial plant based substances has a significant role in healthcare. *Asteraceae* family have been shown to be of medical importance because of the pharmacologically active substances. Species of the genus *Lactuca* L. (*Asteraceae* Bercht. & J. Presl) have been shown to produce sesquiterpene lactones as their characteristic secondary metabolites [Michalska et al., 2009].

Previously α-amyrin, lactucin, lactucopicrin (lactucin-8-O-p-hydroxyphenylacetate) have been extracted from the aerial parts of *L. tatarica* [Akyev et al., 1990]. And of the flavonoid compounds apigenin, luteolin, quercetin-3-O-β-glucopyranoside, apigenin-7-O-β-glucopyranoside and kaempferol-3-O-β-glucopyranoside have been identified in its aerial parts [Kisiel, 1998].

11β-hydroxy-11, 13-dihydrolactucin; 2β-hydroxy-11β, 13-dihydrodouglanin were obtained from the whole plant [Wang et al., 2010]. *L. tatarica* is used as fodder plant for buffaloes and cows [Bhellum and Singh, 2015]. Ethnobotanical uses reported in Kibber Wildlife Sanctuary (India) that decoction of whole plant traditionally used for joint pains [Devi et al., 2013]. Traditionally its leaves used in treatment of headache, fever, internal wounds and vomiting in Amchi system of medicines in Skuru watershed of Karakoram wildlife sanctuary (India) [Namtak and Sharma, 2018]. In traditional medicine it has been used for treating skeleto-muscular (arthritis, bone fracture, joint problem) ailments in India with 100% fidelity [Thakur et al., 2020]. In Suru and Zanskar Valleys of India with its vernacular name Chamati the dried then powdered plant given to patient twice a day for treating vomiting [Rinchen and Pant, 2014]. Despite the fact that *L. tatarica* is in rich triterpenoic compounds, sesquiterpene lactones, flavanoids and widespread in Azerbaijan yet it is still uninvestigated in

Azerbaijani flora in terms of its chemical constituents. Therefore, the aim of this study is determination of chemical compounds of the aerial parts (stems and leaves) of *L. tatarica*.

MATERIAL AND METHODS

Plant material: As a research object the aerial parts (stems and leaves) of the *L. tatarica* are collected during the blossoming period, from the Shabran district (41°12'32.9"N 48°58'08.2"E; 54 m above sea level), on July, 2018. Plant material has been chopped into small pieces and dried at room temperature. Total weight of the raw material was 320 g.

Extraction: Dried stems and leaves (320g) are extracted 3 times with acetone (once in every three days) [Kurbanova and Serkerov, 2012]. Acetone is filtered off and expelled by rotary evaporator (evaporator model: ROVA-N2L; water bath model: WB-2000). The component analysis of the dry extract has been carried out by method.

LC-MS/MS Analysis of the Extract: LC-MS/MS analysis was carried out using an Absciex 3200 Q trap MS/MS detector. Experiments were performed with a Shimadzu 20A HPLC system coupled to an Applied Biosystems 3200 Q-Trap LC- MS/MS instrument equipped with an ESI source operating in negative ion mode. For the chromatographic separation, a GL Science Intersil ODS 250 × 4.6 mm, i.d., 5 µm particle size, octadecyl silica gel analytical column operating at 40º C has been used. The solvent flow rate was maintained at 0.5 mL/min. Detection was carried out with PDA detector.

The elution gradient consisted of mobile phases (A) acetonitrile:water:formic acid (10:89:1, v/v/v) and (B) acetonitrile:water:formic acid (89:10:1, v/v/v). The composition of B was increased from 10% to 100% in 40 min.

LC-ESI-MS/MS data were collected and processed by Analyst 1.6 software [https://sciex.com/products/software/analyst-software].

RESULTS AND DISCUSSION

As a result of the total extract mass was 9.36 g, therefore extraction ratio was 2.92 %. The qualitative composition of the substances obtained from the aerial parts of the *Lactuca tatarica* (L.) C.A. Mey. species has been identified by the LC-MS method. According to the table, totally 10 compounds acquired and 3 were identified. Gluconic acid, glucose, dihydroxycoumarin glucoside are amongst those which are identified. Compounds that are found similar to the caffeic acid derivative and caffeoylquinic acid consist of 1 per each. 1 compound was found to be similar to dihydroxycoumarin.

Several authors have also found compounds that belongs to the same group as ours. 5-caffeoylquinic acid (5-CaQA), p-coumaroylcaffeoyltartaric acid (CoCaTA) and di-p-coumaroyltartaric acid (DiCoTA) have been derived from the *L. sativa* L.) [Agustí et al., 2011]. These substances have similarities with compound №8 and compound №5, respectively (Tab.).

Another identified component is a gluconic acid, which is a carboxylic acid, is a good chelator at alkaline pH; its action is relatively better than EDTA, NTA and other chelators. In the European Parliament and Council Directive No. 95/2/EC, gluconic acid is listed as a generally permitted food additive (E 574) [eurlex.europa.eu].

Gluconic acid is plentifully available in plants, fruits and other aliments such as meat, rice, dairy products, wine (up to 0.25 %), honey (up to 1 %), and vinegar. Mainly, gluconic acid and its salts are utilized in the formulation of food, pharmaceutical and hygienic products [Ramachandran et al., 2006].

Next identified compound is a glucose that has found in the ethanol extracts acquired from the roots of *L. serriola* L. [Petkova and Denev, 2013].

With regards to the Di-hydroxycoumarin glucoside, esculin (6,7-Dihydroxycoumarin-6-glucoside) has been obtained from the leaves of *L. sativa* L. [Qin et al., 2018]. From the heads of butterhead lettuce dihydroxycoumarin has also been identified [Viacava et al., 2018].

Dried acetonic extract of the aerial parts of *L. tatarica* (L.) C.A.Mey. has been passed

Table. Summary of the components identified by LC-MS/MS method from extract of the aerial parts of *L. tatarica*

№ of peak	RT, min	M-H	Fragments	Identified component
1	3.413	195	177, 159,129	Gluconic acid
2	6.043	198	163	Glucose
3	10.188	339	177,133	Di-hydroxycoumarin glucoside
4	11.902	485	439, 421, 377, 277, 215, 197	Unknown
5	14.115	277	215, 177, 133	Similar to caffeic acid derivative
6	14.331	362	335, 307, 291, 263, 227, 203, 175	Unknown
7	15.249	179	135	Similar to Dihydroxycoumarin
8	15.760	353	335, 309, 281, 177	Smilar to caffeoylquinic acid
9	21.789	356		Unknown
10	27.516	257	242, 227, 213, 198, 195, 185, 169, 167, 157, 129, 121	Unknown

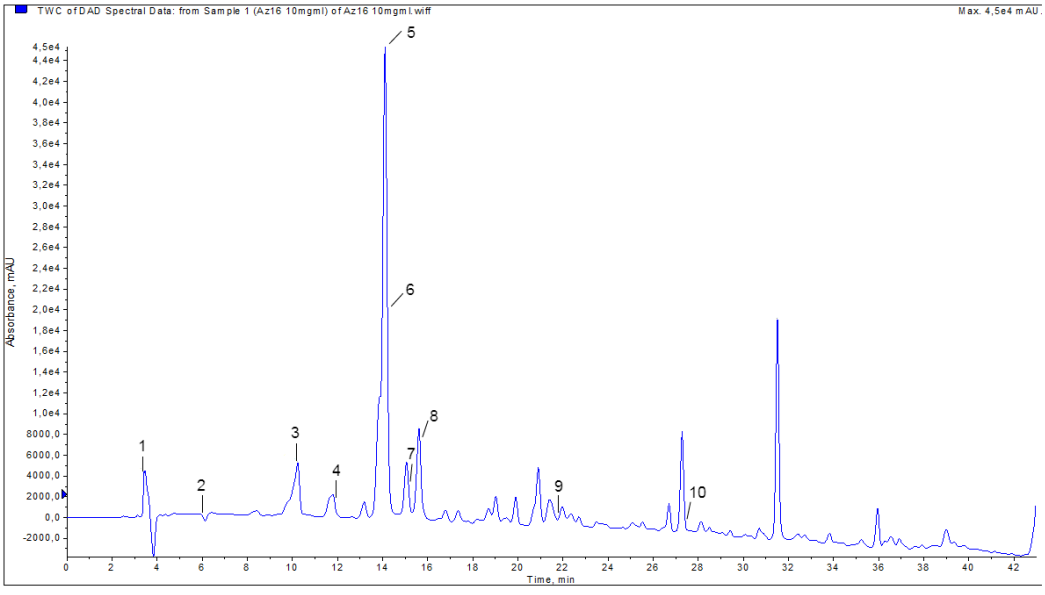

Figure. LC-MS chromotogram of acetonic extract of aerial parts of *L. tatarica*

through LC-MS for its chemical substance investigation. Totally 10 compounds obtained. Those belong to carboxylic acids, monosaccharide, coumarins, polyphenol derivatives and phenylpropanoids. Due to the wide range of pharmacological activity of the components identified in the plant, we consider it expedient to use the plant in the production of drugs and food additives.

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Lactuca tatarica (L.) C.A. Mey. növünün yerüstü hissələrinin xromato-mass spektrometriya üsulu ilə kimyəvi tərkibinin tədqiqi

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Məqalə *Lactuca tatarica* növünün yerüstü hissələrinin (gövdə və yarpaqlar) kimyəvi komponentlərinin tədqiqinə həsr edilmişdir. *L. tatarica* növünün yerüstü hissələrinin (320 qr) fitokimyəvi tədqiqi kumarin birləşmələrinin mövcudluğunu ortaya çıxardı. Bitki xammalının asetonlu ekstraksiyasında ümumi ekstraktiv tərkib maye xromatoqrafiya-kütlə spektrometriya (MX-KS) üsulu ilə tədqiq edilərək orada kumarin törəmələrinin olması müəyyən edilmişdir. Ümumilikdə 10 maddə əldə edilmişdir və

bunlardan 3-ü identifikasiya edilmişdir. Digər 3 maddənin isə kumarinlər, polifenol törəmələri və fenilpropanoidlərə aid olduğu müəyyən edilmişdir. LC-MS prosesi Shimadzu 20 A HPLC sistemi ilə, maddələrin identifikasiyası isə Analyst 1.6 proqramı tərəfindən həyata keçirildi. Qlükon turşusu, qlükoza, di-hidroksikumarin qlükozid, identifikasiya edilən birləşmələr arasındadır. Qlükon turşusunun əhəmiyyəti, qələvi pH-da xelator olmasıdır. Üstəlik qida sənayesində qida qatqısı olaraq istifadə olunur. Bitki bütöv olaraq, müəyyən xəstəliklərin müalicəsi üçün Çin və Hindistanda ənənəvi xalq təbabətində geniş istifadə olunur. Beləliklə, geniş farmakoloji aktivliyə malik bioloji aktiv komponentləri aşkar etmək üçün bitkinin kimyəvi komponentlərini öyrənilməsi əhəmiyyətlidir.

Açar sözlər: ekstraktiv birləşmələr, MX-KS, dihidroksikumarin qlükozid, qlükon turşusu

Исследование химического состава надземных частей *Lactuca tatarıca* (L.) C.A. Mey. с применением метода Хромато-Масс-Спектрометрии

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Статья посвящена изучению химических компонентов надземной части (стеблей и листьев) *Lactuca tatarica*. Фитохимические исследования надземной части *Lactuca tatarica* (320 г) выявили присутствие в его составе соединений кумарина. При ацетонной экстракции растительного сырья общее экстрактивное содержание исследовали методом жидкостной хромато - масс-спектрометрии (ЖХ-МС) и в результате определили присутствие производных кумарина. Всего было получено 10 соединений, из них три идентифицированы. Установлено что, из них еще три соединений относятся к кумаринам, производным полифенолов и фенилпропаноидам. Эксперименты ЖХ-МС проводены с помощью системы Shimadzu 20 A HPLC, а идентификацию веществ выполняли с помощью программного обеспечения Analyst 1.6. Глюконовая кислота, глюкоза, дигидроксикумарин глюкозид, входит в число идентифицированных соединений. Важность глюконовой кислоты заключается в том, что она является хелатором при щелочном pH. Более того, она используется в пищевой промышленности как пищевая добавка. Растение широко используется в традиционной народной медицине Китая и Индии при лечении некоторых заболеваний. Таким образом, считаем необходимым, изучить химический состав растения в целях обнаружения в его составе биологически активных компонентов, обладающих широкой фармакологической активностью.

Ключевые слова: экстрактивные соединения, ЖХ-МС, дигидроксикумарин глюкозид, глюконовая кислота.