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CHEMICAL CONSTITUENTS OF *LIGULARIA NARYNENSIS*

Abstract. In this work, the quantitative and qualitative analysis of phytochemical constituents of medicinal plant *Ligularia narynensis* from Kazakhstan have been made for the first time. Total bioactive components of *L. narynensis* such as organic acids (0.58 %), flavonoids (0.64 %) and together with moisture content (5.98 %), total ash (7.58 %), and extractives content (25.1 %) were determined. Eleven macro-, microelements from the ash of plant were identified, main contents of them were K (1308.25 µg/ml), Ca (1312.77 µg/ml), and Mg (231.18 µg/ml) by using method of multi-element atomic emission spectral analysis. In addition, the ethyl acetate extract from the aerial part of *L. narynensis* was analyzed by Liquid Chromatography-Mass Spectrometry (LC-MS).

Key words: *Ligularia narynensis*, bioactive constituents, macro-, microelements, LC-MS.

Introduction

Ligularia is a medicinally important genus of the family Compositae that comprises about 180 Eurasian species, 17 species growing in mountains of Kazakhstan [1]. They grow in a great variety of habitats from riverine to high-mountain rocky places, ranging from sea level to 5000 m altitude [2]. More than 27 *Ligularia* species have been used as traditional Kazakh and Chinese medicinal herbs for the treatment of fever, pain, inflammation, intoxication, cough phlegm, removing [blood stasis](#), emetic, [diuresis](#), cholagogue and removing jaundice [3-10]. Phytochemical investigations of various *Ligularia* species showed the presence of monoterpenes, sesquiterpenes, diterpenes, triterpenes, alkaloids, steroids, flavonoids, lignans, and other skeleton type compounds, as well as some of these compounds showed various biological activities such as anticancer, antibacterial, antihepatotoxicity, antioxidant, and antithrombus [11-13].

L. narynensis is a [perennial](#) herb growing in Almaty region of Kazakhstan and in Xinjiang province of China. Scientist Xue Gao determined the structures of oplopane-type sesquiterpenes, a new 8-O-4'-type neolignan, oplopane and guaiane type sesquiterpenoids, monoterpenoids from the roots of *L. narynensis* [3, 9, 14, 15].

Our previous phytochemical investigations have reported the total bioactive components from the root part of *L. narynensis* such as organic acids, flavonoids, moisture content, total ash, and extractives content. By using method of multi-element atomic emission spectral analysis eleven macro-, microelements from the ash of plant were determined. Concurrently, twenty amino and eight fatty acids were analyzed from this plant [16]. Additionally, fifty nine liposoluble constituents in chloroform extract from the root part of *L. narynensis* have been identified by GC-MS method [17].

In present study has been made the investigation of the chemical constituents for the aerial part of medicinal plant *L. narynensis* grown in Almaty region of Kazakhstan for the first time. Total bioactive components of *L. narynensis* such as organic acids, flavonoids together with moisture content, total ash, and extractives content were determined. Eleven macro-, microelements from the ash of plant were identified by using method of multi-element atomic emission spectral analysis. In addition, the ethyl acetate extract from the aerial part of *L. narynensis* has been analyzed by Liquid Chromatography-Mass Spectrometry (LC-MS).

Materials and methods

Plant material. The aerial part of plant *L. narynensis* was collected in September 2018 from the Zailiysky Alatau Mountains of Almaty region and identified by Dr. Alibek Ydyrys. Specimens (1217-BH-17) were deposited in the Herbarium of Laboratory Plant Biomorphology, Faculty of Biology and Biotechnology, Al-Farabi Kazakh National University, Almaty, Kazakhstan. The air dried aerial part of *L. narynensis* were cut into small pieces and stored at room temperature.

Extraction. The air-dried plant *L. narynensis* (8.5 kg) were pulverised and extracted with 95% ethanol (EtOH) three times (seven days each time) at room temperature. After evaporation of the solvent under reduced pressure, 420 g of the residues were mixed and suspended in water and then successively partitioned with petroleum ether (PE), dichloromethane (DCM), and ethyl acetate (EA) to afford the corresponding extracts.

Experimental part

The quantitative and qualitative analysis. The quantitative and qualitative contents of biologically active constituents from the aerial part of the plant were determined according to methods reported in the State Pharmacopeia XI edition techniques [18].

Analysis of macro-, microelements. In the «Center of Physico-Chemical methods and analysis», Republican State Enterprise Kazakh National Al-Farabi University, MON RK using the method of multi-element atomic emission spectral analysis in the ash of *L. narynensis* was analyzed elemental constituents. To determine the mineral composition of ashes was used Shimadzu 6200 series spectrometer [16].

Liquid chromatography-mass spectrometry. Analytical LC-MS spectra perform on a Waters 2695 instrument coupled with a Waters 2998 PAD, a Waters 2424 ELSD and a Waters 3100 SQDMS detector [19]. The EA fraction were analyzed by LC-MS using water-acetonitrile in increasing non-polarity until 100% acetonitrile (Table 1).

Table 1 – The method of LC-MS

H ₂ O, %	ACN, %	Time, min
90	8	5
90	10	5
80	20	7
70	30	8
5	95	10
0	100	10

Results and discussion

Extraction. Powdered the aerial part of *L. narynensis* plant (8.5 kg) was extracted (30 L x 3) for twenty one days in total at room temperature. The combined extract was evaporated under reduced pressure to give a residue (420 g) which was dissolved in water and partitioned with solvents of increasing polarity to give PE (195 g), DCM (20 g), and EA (11 g) (Figure 1).

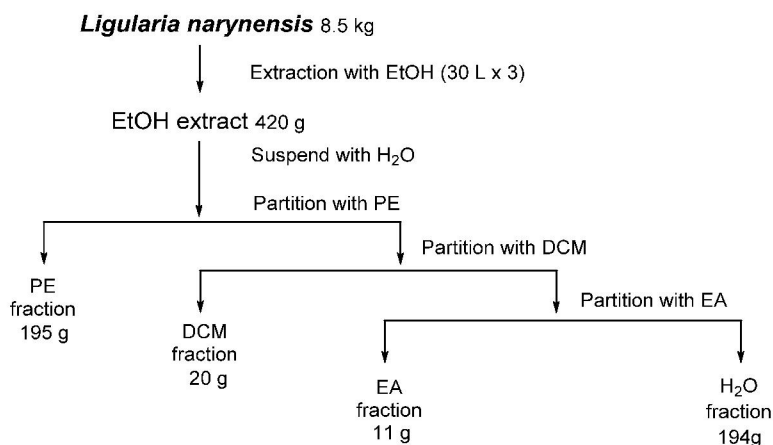


Figure 1 – Flow-chart of partition of the aerial part of *L. narynensis*

The quantitative and qualitative analysis. The quantitative and qualitative analysis of biologically active constituents together with moisture content, total ash, and extractives contents were determined from the aerial part of *L. narynensis*. The results shown in Table 2.

Table 2 – Quantitative analysis of bioactive constituents of *L. narynensis*

		Content, %		
Moisture content	Ash	Extractives	Organic acids	Flavonoids
5.98	7.58	25.1	0.58	0.64

Analysis of macro-, microelements. In «Center of Physico-Chemical methods of analysis», Republican State Enterprise Kazakh National Al-Farabi University, MON RK using the method of multi-element atomic emission spectral analysis in the ash of *L. narynensis* were determined eleven macro- and microelements, showed in Table 3 and major of them was K (2214.13 µg/ml), Ca (391.31 µg/ml), Mg (231.18 µg/ml), Fe (80.61 µg/ml). Potassium, magnesium and calcium are macroelements. Typically, each of the macroelements performs several functions.

Potassium is the main intracellular ion, while the main extracellular ion is sodium. The interaction of these ions is important in maintaining cell isotonicity. Potassium contributes to better brain activity, improving its oxygen supply. It has a positive effect in many allergic conditions.

Calcium is the most common macroelement in the human body. Being one of the main components of bones, calcium is necessary for mineralization of new bone tissue. It is also a cofactor for the activation of many enzymes or the formation of a number of enzyme complexes in multi-stage blood clotting processes.

Magnesium is a universal regulator of biochemical and physiological processes in the body, participating in energy, plastic and electrolyte metabolism. As a cofactor of many enzymes, magnesium is related to more than 300 biochemical reactions.

Iron is the most important microelement, which is necessary for the normal functioning of the body. It plays a very important role in the oxidation and reduction processes. Iron is part of the red blood cell hemoglobin, myoglobin and many enzymes involved in hematopoiesis. Consequently, iron provides reversible binding of oxygen to red blood cells and its transport to all organs and tissues of the human body [20].

Table 3 – Composition of macro-micro elements in the ash of plant *L. narynensis*

Element	Cu	Zn	Cd	Pb	Fe	Ni	Mn	K	Na	Mg	Ca
µg/ml	0.90	2.34	0.15	1.54	80.61	0.10	6.39	1308.25	20.98	231.18	1312.77

Liquid Chromatography-Mass Spectrometry. The results of the spectral analysis of the studied extract of *L. narynensis* obtained by LC-MS are shown in Figures 2. On UV spectra of the fraction has an intense absorption bands, which supposedly indicates the presence in the extract of flavonoids and flavonoid glycosides. These components can be identified with the peaks at retention time of 7.31 min, 383 m/z, 8.39 min, 447 m/z, 9.11 min, 427 m/z, 9.58 min, 535 m/z, 12.55 min, and 327 m/z, respectively.

Variety of flavonoids found in the nature possesses their own physical, chemical, and physiological properties. Structure function relationship of flavonoids is epitome of major biological activities. Medicinal efficacy of many flavonoids as antibacterial, hepatoprotective, anti-inflammatory, anticancer, and antiviral agents is well established [21]. A wide spectrum of biological activities has been documented for flavonoid glycosides, including [antioxidant](#), immunomodulatory, [anticancer activities](#) [22].

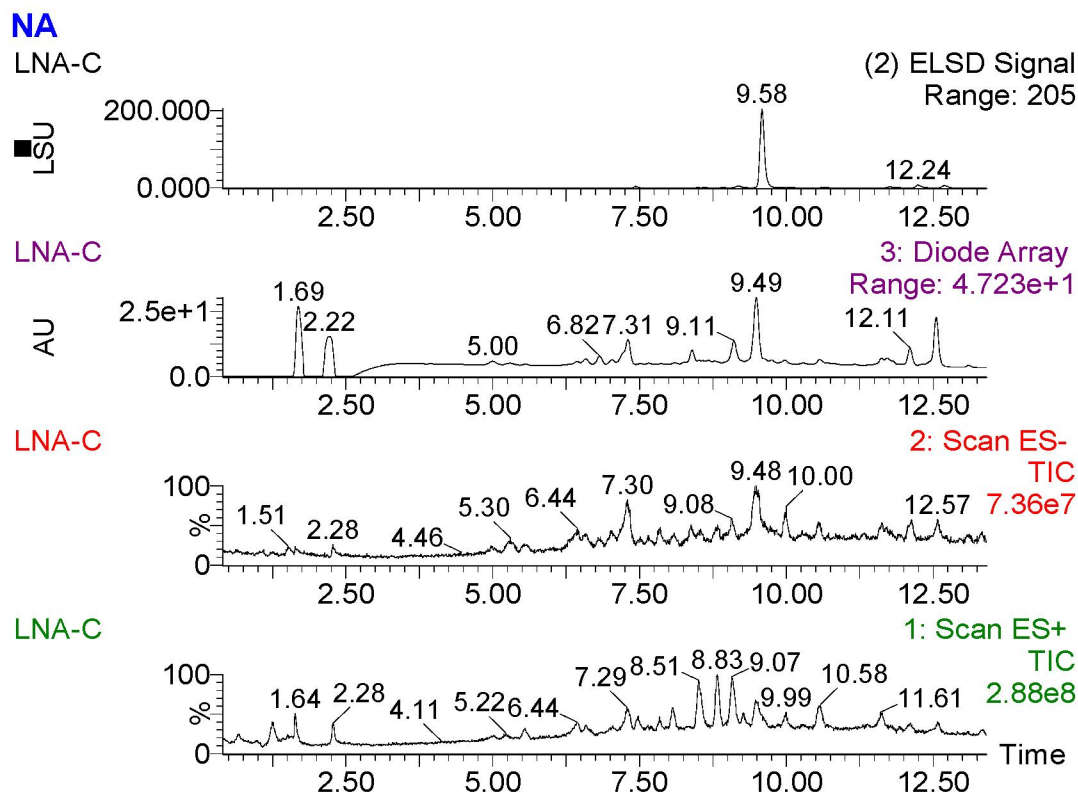


Figure 2 – LC-MS chromatogram of the EA fraction from the aerial part of *L. narynensis*

Comparative review. The contents of the investigated biological active compounds and macro-, microelements from the aerial and the root parts of the *L. narynensis* are similar [16].

Conclusion

In summary, the quantitative and qualitative analysis of phytochemical constituents from the aerial part of *L. narynensis* of Kazakhstan have been made for the first time. As the results of this study, the dried and powdered plant was extracted three times with 95% ethanol, the extract was evaporated in vacuo to give a residue, which was suspended in water and partitioned successively with petroleum ether, dichloromethane, ethyl acetate; total bioactive components of *L. narynensis* were determined; eleven macro-, microelements from the ash of plant were identified; the ethyl acetate fraction of the aerial part presumably rich by flavonoids and flavonoid glycosides was analyzed by LC-MS. Flavonoids and flavonoid glycosides have important pharmacological activities such as anticancer, antibacterial, hepatoprotective, anti-inflammatory, [antioxidant](#), immunomodulatory [activities](#). These results suggest that *L. narynensis* is recommended as plant with pharmaceutical importance. However, further studies are needed to undertake its bioactivity and toxicity profile.

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LIGULARIA NARYNENSIS ӨСІМДІГІНІҢ ХИМИЯЛЫҚ ҚҰРАМДАРЫ

Аннотация. Бұл жұмыста Қазақстанда өсетін дәрілік өсімдіктің *Ligularia narynensis* фитохимиялық құрамының сандық және сапалық талдауы бірінші рет жүргізілді. Өсімдіктің ылғалдылығы (5.98 %), күлділігі (7.58 %) және экстрактивтілігі (25.1 %), сонымен бірге органикалық қышқыл (0.58 %), флавоноидтар (0.64 %) сияқты биологиялық активті компоненттер құрамы анықталды. Атомдық эмиссия спектральды талдау әдісін қолдана отырып, өсімдіктің күліндегі он бір макро- және микроэлементтері зерттелді және оның негізгі құрамы К (1308.25 мкг/мл), Са (1312.77 мкг/мл), Mg (231.18 мкг/мл). Бұдан басқа, *L. narynensis* жер үсті бөлігінің этилацетат сіріндісі сұйықты хроматография–масс-спектрометрияның (ЖХ-МС) әдісімен талданды.

Түйін сөздер: *Ligularia narynensis*, биоактивті құрамдастар, макро-, микроэлементтер, ЖХ-МС.

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ХИМИЧЕСКИЕ СОСТАВЛЯЮЩИЕ РАСТЕНИЯ LIGULARIA NARYNENSIS

Аннотация. В данной работе впервые был сделан количественный и качественный анализ фитохимических составляющих лекарственного растения Казахстана *Ligularia narynensis*. Определены биологически активные компоненты *L. narynensis*, такие как органические кислоты (0,58 %), флавоноиды (0,64 %) вместе с содержанием влаги (5,98 %), общей золы (7,58 %) и экстрактивных веществ (25,1 %). При использовании метода многоэлементного атомно-эмиссионного спектрального анализа в золе растения были идентифицированы одиннадцать макро-, микроэлементов, основными из которых являются К (1308.25 мкг/мл), Са (1312.77 мкг/мл), Mg (231.18 мкг/мл). Кроме того, этилацетатный экстракт надземной части *L. narynensis* был проанализирован методом жидкостной хроматографии–масс-спектрометрии (ЖХ-МС).

Ключевые слова: *Ligularia narynensis*, биоактивные компоненты, макро-, микроэлементы, ЖХ-МС.

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