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T. I. Balanchuk*, A. V. Mazulin**, T. V. Oproshanska***, A. O. Ostapenko****

**Vinnytsya National Pirogov Memorial State Medical University*
***Zaporozhzhia State Medical University*
****National University of Pharmacy*
*****Zaporozhzhia State Medical Academy of postgraduate education*

THE STUDY OF NITRATES AND INORGANIC ELEMENTS COMPOSITIONS CONTENTS IN TYPES OF GENUS *CARDUUS* L. HERBS AND EXTRACTS

By ionometric and atomic emission spectroscopy methods has been used for research. The contents of nitrates and 15 inorganic elements has been determined in groves of genus Carduus L. herbs and extracts. The herbs of Carduus nutans L. genus: Carduus nutans L., Carduus acanthoides L. species are perspective for use as hepatoactive, hepatoprotective and antioxidant drugs. The content of nitrates in flowers (leaves) of Carduus L. genus: Carduus nutans L. (mg/1000 g), up to 180.90 ± 15.33 (220.14±18.33); Carduus acanthoides L. (mg/1000 g), up to 188.86 ± 15.67 (228.30 ± 20.72) has been determined. The herbs of Carduus nutans L., Carduus acanthoides L. are contented of macro- and micro-inorganic elements (K, Ca, Mg, Fe) in sufficiently high concentrations; the inorganic element (Sr) in chronic values; the inorganic elements (Pb, Co, Cd, As, Hg) in significant concentrations. The contents of nitrates in lyophilized water extracts of herbs of Carduus nutans L., Carduus acanthoides L. up to 27.0-31.5 %; inorganic elements up to 10.5-11.0 % has been determined.

Key words: ionometric; atomic emission spectroscopy methods; herbs; flowers; *Carduus nutans* L.; *Carduus acanthoides* L.; nitrates; inorganic elements; lyophilized water extracts; hepatoprotective; antioxidant actions

INTRODUCTION

The *Carduus* L. genus of *Asteraceae* family counts to 120 species in native flora of Europe, Asia, North Africa, North America and Canada, China, Argentina, Australia, New Zealand and other countries [5, 8, 9, 15, 16].

Up to 30 species of *Carduus* L. genus are grows in Ukraine. The most widespread species it is been *Carduus nutans* L. and *Carduus acanthoides* L. They sprout as ruderal plants in steppes of east and western Ukraine up to left-bank of Polesya (Palsy), in Crimea, South and central regions. They mainly grows on open muddy places, pastures, sides of roads, steppe hills, lime stones, black earth soils [8].

For the first time a chemical composition of flowers and leaves of *Carduus nutans* L. genus species had been studies: flavonoids, hydroxycinnamic acids, organic acids, amino acids, coumarins, mineral elements, essential oils, sesquiterpenoids lactones have been quantified [5, 13, 14].

There is infusion (1:10) of species of *Carduus* L. genus in modern medicine of many countries of the world is applied. Infusion is appointed for treatment of diseases of gastrointestinal tract, hepatoprotective and antioxidant medicinal means. Also a water extract with roots shows scolative, antioxidant and anti epilepsy actions. The normalizing operating is set on functioning of liver, especially at viral, chemical and mechanical damages [5, 11, 13].

For treatment and prophylaxis of diseases of liver apply a phylogenetic near type *Carduus marianus* L. of *Carduoideae Kitam*. subfamily and drugs from the herbal raw materials.

They shows the expressed antioxidant, detoxical, immune modulating, membrano – proliferative activities, stimulated the biosynthesis of proteins and phosphotides [6].

Pharmacological studies undertaken, that lyophilized water extracts from the herbs *Carduus nutans* L., *Carduus acanthoides* L. species on the laboratory setting "Chris Alpha 1-2 LD plus (Germany)" expose an hepatoactive, hepatoprotective and antioxidant actions.

The biological activity did not yield to basic drugs from the herb of *Carduus marianus* L. specie. They are less toxic and well carried by laboratory animals at the protracted application.

The most widespread species *Carduus nutans* L. and *Carduus acanthoides* L. are perspective for a purveyance and receipt of modern medicinal means.

The species of genus *Carduus* L. sprout in unfavorable terms and accumulate toxic pollutants from an environment.

Table 1

THE QUANTITATIVE CONTENCE OF NITRATES IN FLOWERS, LEAVES AND LYOPHILIZED WATER EXTRACTS FROM HERBAL RAW MATERIALS *CARDUUS NUTANS* L., *CARDUUS ACANTHOIDES* L. SPECIES ($x \pm \Delta\bar{x}$), mg/kg, μ = 6, (MAY-JULY) 2013-2015

The botanical name	Flowers	Leaves	Lyophilized water extracts
Carduus acanthoides L., Donetsk region, s. Druzhkovka	118.20 ± 10.72	140.19 ± 12.72	39.60 ± 3.55
Carduus acanthoides L., Zaporozhzhia region, s. Tokmak	150.30 ± 13.65	180.11 ± 16.30	46.98 ± 4.20
Carduus acanthoides L., Donetsk region, s. Kramatorsk	188.86 ± 15.67	228.20 ± 20.72	60.00 ± 5.09
Carduus acanthoides L., Zaporozhzhia region, s. Melitopol	110.10 ± 9.24	133.41 ± 12.00	27.06 ± 2.55
Carduus acanthoides L., Kherson region, s. Nova Kachovka	130.31 ± 11.81	153.10 ± 12.80	46.12 ± 4.20
Carduus nutans L. Dnipro region, s. Nicopol	120.20 ± 10.77	144.08 ± 13.00	42.34 ± 3.55
Carduus nutans L., Poltava region, s. Piriatin	180.90 ± 15.33	220.14 ± 18.33	54.11 ± 4.51
Carduus nutans L., s. Jalta, AR Krym	170.14 ± 14.13	198.18 ± 16.66	52.92 ± 4.80
Carduus nutans L., s. Khmelnytsk	80.13 ± 7.34	111.55 ± 9.34	29.70 ± 2.74
Carduus nutans L., Dnipro region., s. Solone	90.55 ± 7.60	122.18 ± 11.00	27.54 ± 2.50

Standartization of herbal raw materials and extracts must set contains of toxic nitrates, inorganic elements and general ash [1, 7, 10, 12].

MATERIALS AND METHODS

A research object were flowers and leaves procured in the different regions of Ukraine in the period of flowering (may-september) (DFU, Vol. 1, add. 1.2.) [4]. Drying was conducted in a drying chamber during 15 hours.

An analysis was conducted by physical and physical-chemical methods.

The nitrates identified on a reaction with a diphenylamine in the concentrated sulphuric acid.

The quantitave contain of nitrates was conducted by a ionometric method on a device EV-74 (Belarus) with nitrate-selective electrode of type EI-NO_3^- (an electrode of comparison is a chlorine-silver) [7].

Hinge-plate of the herbal raw materials (lyophilized water extracts) 10.0 g was dispergated, carried in a retort on 100 mls, added 50 ml solution 1 % of $KAl(SO_4)_2 \times 12H_2O$, mixed carefully 3 min, measured potential of electrode (mV).

The quantities contain of nitrates was expected on the gouge chart of standard solution of potassium of nitrate in a solution 1 % of $KAl(SO_4)_2 \times 12H_2O$.

Authentication and quantitative determination of element composition contain of the investigated herbal raw materials (lyophilized water extracts) was conducted by the method of atomic-emission analysis on the spectrometer of DFC-8 with the sprayer of IBC-28 at characteristic long waves [1, 2, 12].

Hinge-plate of the herbal raw materials (lyophilized water extracts) 0.3 g was dispergated, was entered in a quartz cups, added 10 ml solution of sulphuric acid 5 %, dried out (t = 105 °C) to permanent mass.

The quartz cups was entered in a muffle stove up to 5 hours (t = 500 °C), cooled, weighed. Was dissolved in the diluted sulphuric acid, entered in the electro termical analyzer of device.

The atomization of tests was conducted on the graphite electrodes of device in the digit of arc of altemating current (I = 16 A, U = 220 v, t = 60 sec).

The spectrums were registered on a spectrograph DFC-8 (diffraction grate 600 st./mm at the three-lens system of illumination of crack). Intensity of lines in spectrums was fixed by a micrometer MF-4 (λ = 196-706.5 nm). Measuring temperature (t = 23-25 °C).

In parallel was conducted measuring of solution of comparing to the analogical reagents. The results were treated by the method of mathematical statistics with the use of license program "Statistica 6.0 for Windows" (Stat. Soft. Inc., No. AXXR712D833214FANS).

Authenticity of differences sizes of concentrations was estimated on the t-criterion of Student (p > 95%) [2, 3].

The results of researches is driven to the Tab. 1, 2.

RESULTS AND DISCUSSION

The accumulation of nitrates in the leaves of *Carduus nutans* L., *Carduus acanthoides* L. species were higher than in flowers. It is not between with the species of *Carduus* L. genus differences.

The lyophilized water extracts from water extractions (1 : 5) were distinquished on the laboratory freez dryer "Christ Alpha 1-2 LDplus" (Німеччина) by the method of drying during at 6 hours.

The flowers, leaves and lyophilized water extracts from herbs of *Carduus nutans* L., *Carduus acanthoides* L. species were contented the nitrates level more than toxically concentrations (up to 300-370 мг/кг) [7, 10].

The concentrations of nitrates and inorganic elements in lyophilized water extracts from herbs of *Carduus nutans* L., *Carduus acanthoides* L. species up to 27.0-31.5 % and 10.5-11.0 % has been determined.

Table 2

THE QUANTITATIVE CONTENCE OF INORGANIC ELEMENTS IN HERBS AND LYOPHILIZED WATER EXTRACTS *CARDUUS NUTANS* L., *CARDUUS ACANTHOIDES* L. SPECIES, ZAPORIZHZHIA REGION, S. TOKMAK (MAY-JULY 2015 p.) (mg/100 g ($x \pm \Delta\bar{x}$, $\mu = 6$)

The name of elements	(λ, нм)	*Carduus nutans* L.	*Carduus acanthoides* L.
Zinc (Zn)	213.9	5.18 ± 0.47 (0.47 ± 0.05)	4.50 ± 0.41 (0.45 ± 0.05)
Nickel (Ni)	232.0	0.14 ± 0.01 (0.01 ± 0.001)	0.12 ± 0.01 (0.01 ± 0.001)
Iron (Fe)	248.3	43.20 ± 3.93 (3.93 ± 0.42)	30.19 ± 2.73 (3.03 ± 0.31)
Silicon (Si)	251.6	140.14 ± 12.74 (12.73 ± 1.29)	60.14 ± 5.00 (5.47 ± 0.55)
Manganese (Mn)	279.5	0.48 ± 0.05 (0.04 ± 0.003)	0.33 ± 0.03 (0.03 ± 0.002)
Magnesium (Mg)	285.2	238.40 ± 21.64 (2.17 ± 0.22)	180.40 ± 13.59 (18.02 ± 1.90)
Aluminum (Al)	309.3	2.65 ± 0.23 (0.24 ± 0.02)	1.99 ± 0.18 (0.20 ± 0.02)
Molybdenum (Mo)	313.3	0.09 ± 0.01 (0.01 ± 0.001)	0.07 ± 0.01 (0.01 ± 0.001)
Copper (Cu)	324.7	1.70 ± 0.21 (0.15 ± 0.02)	0.90 ± 0.08 (0.08 ± 0.001)
Phosphorus (P)	357.9	78.18 ± 7.05 (7.82 ± 0.76)	56.20 ± 5.10 (5.62 ± 0.55)
Calcium (Ca)	422.6	840.44 ± 75.19 (77.36 ± 7.80)	500.00 ± 48.18 (45.46 ± 4.66)
Strontium (Sr)	460.0	2.80 ± 0.26 (0.25 ± 0.03)	1.65 ± 0.15 (0.15 ± 0.02)
Natrium (Na)	589.0	56.14 ± 4.20 (5.61 ± 0.52)	35.55 ± 3.22 (3.23 ± 0.34)
Potassium (K)	706.5	290.20 ± 25.42 (26.38 ± 2.77)	165.13 ± 15.10 (16.51 ± 1.79)
Mass of general ash (%)		7.88 ± 0.72 (0.82 ± 0.09)	6.25 ± 0.59 (0.73 ± 0.08)

The herbs of *Carduus nutans* L., *Carduus acanthoides* L. species were contented 15 inorganic elements, from that essential macro- and micro- inorganic elements (Ca, Cu, Fe, K, Mg, Mn, Zn, Co, P, Mo) in sufficiently high concentrations. The herb of *Carduus nutans* L. specie in high concentrations was contented macro- inorganic elements (mg/100 g): Ca (840.44 ± 75.19), K (290.20 ± 25.42), Mg (238.40 ± 21.64), Si (140.14 ± 12.74), P (78.18 ± 7.05), Na (56.14 ± 4.20); micro- inorganic elements (mg/100 g): Fe (43.20 ± 3.93), Zn (5.18 ± 0.47), Al (2.65 ± 0.23). The herb of *Carduus acanthoides L.* specie in high concentrations was contented macro- inorganic elements (mg/100 g): Ca (500.00 ± 48.18), K (165.13 ± 15.10), Mg (180.40 ± 13.59), Si (60.14 ± 5.00), P (56.20 ± 5.10), Na (35.55 ± 3.22); micro- inorganic elements (mg/100 g): Fe (30.19 ± 2.73), Zn (4.50 ± 0.41), Al (1.99 ± 0.18).

The accumulation of toxically inorganic elements (Pb, Cd, Co, Hg, As,) were contented (< 0.01-0.03 mg/100 g), the inorganic element (Sr) in chronic values (0.95 ± 0.09-2.21 ± 0.02) [1].

Formation of general ask is insignificant higher in a herb of *Carduus nutans* L. (mg/100 g) (up to 7.88 ± 0.72), than in a herb of *Carduus acanthoides* L. (mg/100 g) (up to 7.88 ± 0.72), that is may be related to the different level of accumulation of inorganic elements.

CONCLUSIONS

1. By ionometric method in a herbal raw materials of *Carduus nutans* L., *Carduus acanthoides* L. species in the period of flowering were contented the nitrates, considerably higher in leaves (111.55 ± 9.34-228.20 ± 20.72 (mg/kg)), than in flowers (80.13 ± 7.34-188.86 ± 15.67(mg/kg)). The passing of nitrates in lyophilized water extracts up to 27.0-31.5 %.
2. By atomic emission spectroscopy method in flowers and leaves of *Carduus nutans* L., *Carduus acanthoides* L. species in the period of flowering were contented the 15 inorganic elements, from that 10 essential macro- and micro- inorganic elements in sufficiently high concentrations, 6 toxically inorganic elements (Pb, Cd, Co, Hg, As,) were contented (< 0.01-0.03 mg/100 g),the inorganic element (Sr) in chronic values (0.95 ± 0.09-2.21 ± 0.02 mg/100 g).
3. Herbal raw materials, related to ruderal, it is necessary to store in according to the ratified requirements for prevention of contamination toxic nitrates and inorganic elements.
4. High content level of nitrates and inorganic elements in the investigated herbal raw materials and water lyophilized extracts testifies to the necessity of determination of these substances.

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Т. И. Баланчук, О. В. Мазулин, Т. В. Опрошанская, А. О. Остапенко

ИЗУЧЕНИЕ СОДЕРЖАНИЯ НИТРАТОВ И НЕОРГАНИЧЕСКИХ ЭЛЕМЕНТОВ В РАСТИТЕЛЬНОМ СЫРЬЕ И ЭКСТРАКТАХ ИЗ ВИДОВ РОДА *CARDUUS* L.

Методами ионометрии и атомно-эмиссионной спектроскопии установлено содержание нитратов и 15 неорганических элементов в растительном сырье и экстрактах из видов рода *Carduus* L.: *Carduus nutans* L., *Carduus acanthoides* L., перспективных для применения в качестве гепатозащитных и антиоксидантных средств. Содержание нитратов в соцветиях *Carduus nutans* L. (мг/1000 г) составляло до 180,90 ± 15,33, *Carduus acanthoides* L. до – 188,86 ± 15,67; для листьев *Carduus nutans* L. – до 220,14 ± 18,33, *Carduus acanthoides* L. – до 228,30 ± 20,72. Переход нитратов в лиофилизированные водные экстракты составлял в пределах 27,0-31,5 %, неорганических элементов – 10,5-11,0 %. При заготовке растительного сырья для предотвращения побочного действия необходимо контролировать содержание токсичных нитратов и неорганических элементов (Sr, Ni, Pb, Co, Cd, As, Hg) по показателям предельно-допустимой концентрации.

Ключевые слова: ионометрия; атомно-эмиссионная спектроскопия; трава; соцветия; чертополох поникший; чертополох акантовидный; нитраты; лиофилизованные водные экстракты; гепатопротекторная и антиоксидантная активность

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Т. І. Баланчук, О. В. Мазулін, Т. В. Опрошанська, А. О. Остапенко

ВИЗНАЧЕННЯ ВМІСТУ НІТРАТІВ ТА НЕОРГАНІЧНИХ ЕЛЕМЕНТІВ У РОСЛИННІЙ СИРОВИНІ ТА ЕКСТРАКТАХ З ВИДІВ РОДУ *CARDUUS* L.

Методами іонометрії та атомно-емісійної спектроскопії встановлено вміст нітратів та 15 неорганічних елементів у рослинній сировині та екстрактах з видів роду *Carduus* L.: *Carduus nutans* L., *Carduus acanthoides* L., перспективних для застосування в якості гепатозахисних та антиоксидантних засобів. Вміст нітратів у суцвіттях *Carduus nutans* L. (мг/1000 г) складав до 180,90 ± 15,33, *Carduus acanthoides* L. – до 188,86 ± 15,67; для листя *Carduus nutans* L. – до 220,14 ± 18,33, *Carduus acanthoides* L. – до 228,30 ± 20,72. Перехід нітратів у ліофілізовані водні екстракти був у межах 27,0-31,5 %, неорганічних елементів– 10,5-11,0 %. При заготівлі рослинної сировини для запобігання побічній дії необхідно контролювати вміст токсичних нітратів та неорганічних елементів (Sr, Ni, Pb, Co, Cd, As, Hg) за показниками гранично-припустимої концентрації.

Ключові слова: іонометрія; атомно-емісійна спектроскопія; трава; суцвіття; будяк пониклий; будяк акантоподібний; нітрати; ліофілізовані водні екстракти; гепатопротекторна та антиоксидантна дія

Адреса для листування:
69095, м. Запоріжжя, пр. Соборний, 144, к. 153.
Тел. роб. (0612) 34-23-31.
E-mail: mazulalev@rambler.ru.
Мазулін О. В.

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