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CHEMICAL COMPOSITION OF CARDOON (*CYNARA CARDUNCULUS* L.) GROWN IN SOUTH BULGARIA

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ABSTRACT

Comparative research has been conducted to allow us to determine the content of macro- and microelements in the vegetative and reproductive organs of *Cynara cardunculus* L. and quality of *Cynara cardunculus* L. oil. The experiment was performed on an agricultural field near Plovdiv (South Bulgaria). The contents of macro- and microelements in plant materials (roots, stems, leaves, seeds) and oils were determined. The oils were extracted using a Soxhlet apparatus from seeds of *Cynara cardunculus* L. The quantitative measurements were carried out with inductively-coupled plasma (ICP). Oil fatty acids characterization for unsaturated and saturated acids was performed by gas chromatography. The cardoon shows adaptability to local conditions and can be grown in southern Bulgaria and used for oil production. All plant parts of the cardoon are a rich source of macro and microelements and exhibit high nutritional value. The distribution of macro and microelements in the cardoon organs is selective, specific for the individual elements. Cd, Cu and Fe are accumulated in the roots, K - in the stems, Pb and Ca - in the leaves, and Zn, Mn, Mg and P - in the seeds. Cardoon seeds were a rich source of macro- and microelements (K, P, Mg, Ca, Fe, and Zn). Cardoon oil was abundant in unsaturated fatty acids (linoleic (61.67%%) and oleic acids (22.82%)), followed by palmitic acid (10.50%) and stearic acid (3.29%). Cardoon oil has a P/S index higher than 1 (4.2), which indicates that oil can have a good effect on human health and are oils suitable for consumption. Cardoon oil is a rich source of polyunsaturated linoleic fatty acid with potentially beneficial therapeutic activity.

Keywords: *Cardoon, fatty acid composition, micro and macroelements, oil, Bulgaria.*

INTRODUCTION

Cynara is a genus of thistle-like perennial plants of the Asteraceae family. They are found in the Mediterranean region, the Middle East, Northwest Africa and the Canary Islands. Among the known species of this genus are artichoke (Cynara Cardunculus Var. Scolymus (L.) Fiori) and cardoon, which is divided into

cultivated cardoon (C. Cardunculus Var. Altilis DC) and wild cardoon (C. Cardunculus Var. Sylvestris (Lamk) Fiori) (Foti et al., 1999; Portis et al., 2005; Ierna and Mauromicale, 2010).

C. cardunculus is a crop with various applications. Cardoon is rich in sugars, carotene, mineral salts, vitamins C, B1, B3, B5, B6, folic acid, Mg, Fe, Mn, Zn, and phosphorus. The edible parts of the plant are its unripe capitula (flowering heads), and fragile stalks and celery-flavoured leaf stalks that are usually consumed roasted, boiled, fried, or in salads (Fernández et al., 2006; Christaki et al., 2012). The aboveground biomass (leaves and stems) can be used as animal feed, for energy production (Mancini et al., 2019) and in the food industry (Almeida and Simões, 2018; Llorente et al., 2014). Cardoon leaves can be used to flavour alcoholic beverages (Foti et al., 1999) and its flowers for production of juices and high quality goat and sheep's milk cheese suitable for vegetarian consumers (Fernandez et al., 2006; Pino et al., 2009; Borgognone et al., 2014). Cardoon roots are a good source of inulin, which is used for nutritional and non-nutritional purposes (Ritsema and Smeekens, 2003). Cardoon seeds can be used for the production of biofuels (Gominho et al., 2011). Moreover, cardoon oil is suitable for human consumption because of its high nutritional value (Curt et al., 2002; Fernández et al., 2006; Raccuia и Melilli, 2007). Although cardoon is a non-wood plant, its stems can be used as a source of fibre (17% lignin) for paper production. Cardoon leaves are used for medical purposes because of their polyphenols content (Curt et al., 2002). Usually these leaves have a diuretic and hepatoprotective effect, they improve the function of the gallbladder, stimulate the secretion of digestive juices, especially bile, and can inhibit the cholesterol synthesis (Fernandez et al., 2006; Grammelis et al., 2008). Root extracts have significant antioxidant and antimicrobial properties that can be used for therapeutic and pharmaceutical purposes (Falleh et al., 2008). These physiological properties are due to the phenylpropanoids (flavonoids, mono- and dicaffeoylquinic acids) and sesquiterpene lactones (Lattanzio et al., 2009; Menin et al., 2010; Pandino et al., 2015) contained in them.

Cardoon, unlike artichoke, is a crop little known in Bulgaria. Cardoon is not grown in our country. Cardoon is a crop that is not demanding in terms of soil and can be grown without irrigation because it withstands drought. The climatic conditions in southern Bulgaria are suitable for its cultivation.

Most publications have focused on the evaluation of the use of cardoon seeds for biodiesel production, and there is insufficient information on the chemical composition of the cardoon.

The purpose of this research is to conduct a comparative study that will allow us to determine the quantities of macro and microelements in the vegetative and reproductive organs of the cardoon, the composition and quality of the oil, as well as to identify the possibilities for its cultivation in southern Bulgaria.

MATERIAL AND METHODS

The research has been carried out during the period 2017-2019. The study was conducted at the experimental field of Agricultural University-Plovdiv. The characteristics of soils are shown in Table 1. The soils are characterized by slightly alkaline reaction (pH 7.5) and average content of organic carbon (1.54%) and nutrients (N, P, K).

Table 1. Soil characteristics

pH	Organic carbon, %	Macroelements					Microelements and trace metals, mg/kg					
		N , %	K, %	Ca, %	Mg, %	P, mg/kg	Pb	Cd	Zn	Cu	Fe	Mn
7,5	1,54	0,13	0,68	1,6	1,0	354,9	24,6	2,7	33,9	16	27113	884,2

The test plant was cardoon (*Cynara cardunculus* L). Cardoon seeds were sown to a depth of 3-4 cm; between row and within row distances were 70 and 30 cm, respectively. The analyses were made in the second year of the growing of the plants. On reaching commercial ripeness the plants of cardoon were gathered. The oil from cardoon was derived under laboratory conditions through an extraction method with Socksle's apparatus, allowing the extraction of the oil from the ground seeds of cardoon by using petroleum ether and the subsequent liberation of the latter through distillation. Oil fatty acids characterization for unsaturated and saturated acids was performed by gas chromatography. The contents of trace metals, micro and macroelemens in different parts of cardoon (roots, stems, leaves, seeds), and oils were determined by the method of the microwave mineralization. Total content of trace metals in soils was determined in accordance with ISO 11466. The quantitative measurements were carried out with inductively coupled plasma emission spectrometry (ICP) (Jobin Yvon Emission - JY 38 S, France).

RESULTS AND DISCUSSION

Accumulation of trace metals, micro and macroelements in vegetative ad reproductive organs of cardoon

Table 2 shows the results obtained for the content of macro and microelements in the vegetative and reproductive organs of the cardoon. All plant parts of the cardoon are a rich source of macro and microelements and exhibit high nutritional value, as differences in the content of the studied elements are observed in the vegetative and reproductive organs of the plant. The distribution of trace metals, macro and microelements in the cardoon organs is selective, specific for the individual elements. Cd, Cu and Fe are accumulated in the roots, K - in the stems, Pb and Ca - in the leaves, and Zn, Mn, Mg and P - in the seeds (Fig. 1).

Table 2. Content of trace metals, micro and macroelements (mg/kg) in cardoon

	Roots	Stems	Leaves	Seeds	Oil
Pb	1,8	0,85	5,7	0,84	0,02
Cd	0,15	0,004	0,09	nd	nd
Zn	17,8	11,0	28,9	35,2	0,63
Cu	27,1	1,9	4,8	11,4	0,64
Fe	250,6	23,0	117,9	51,1	4.0
Mn	11,5	1,9	7,5	18,0	0,15
K	5127,8	14724,7	11596,9	6670,4	71,1
Ca	4118,2	3045,7	11676,3	2826,1	29,6
Mg	1765,2	255,7	3146,7	3572,3	10,9
P	847,3	1100,1	888,3	5398,2	12,7

nd-not detected

The content of Pb in cardoon stems and leaves varies from 0.85 to 5.6 mg/kg, Zn from 11.0 to 28.9 mg/kg, Cd from 0.003 to 0.09 mg/kg, Cu from 1.9 mg/kg to 4.8 mg/kg, Fe - 23.0 to 117.9 mg/kg, Mn - 1.9 to 7.5 mg/kg, K - 14724.7 to 11596.9 mg/kg, P - 1100 mg/kg to 888.3 mg/kg, Mg - 255.7 to 3146.7 mg/kg and Ca - from 3045.7 mg/kg 3146.7 mg/kg.

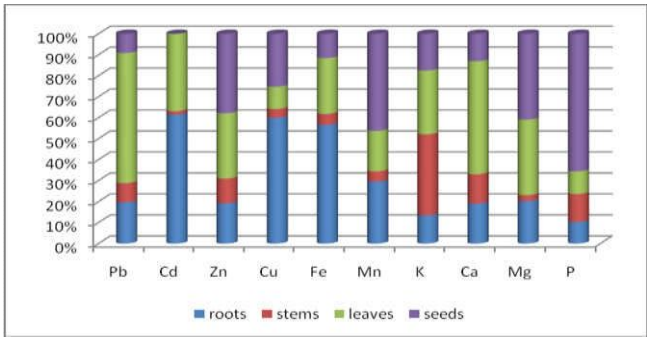

Fig. 1. Distribution of trace metals, micro and macroelements in cardoon

Significantly higher amounts of K (24000 mg/kg), Ca (26620 mg/kg), Mg (1910 mg/kg), Fe (230 mg/kg) and Mn (1910 mg/kg) were established by Petropoulos et al., 2018 in the cardoon leaves cultivated in southern Greece. Higher values for K (31700-34900 mg/kg), Mg (4500 mg/kg) and Ca (17000 mg/kg) in the leaves of hydroponically grown cardoon plants were also found by Rouphael et al. (2012) and Borgognone et al. (2014), while Colla et al (2013) report significant differences in the mineral composition of different genotypes sgrown under saline environment.

Variation between results may be due to cultivation conditions (hydroponic, greenhouse, and field trials), as well as with the differences in plant age, as the above studies refer to young plants and 5-year-old plants (Petropoulos et al., 2018).

Cardoon seeds can be a good source of minerals due to the high content of Ca, K, Mg and P in them. Macroelements (K, P, Mg, and Ca), followed by Fe and Zn, predominate in cardoon seeds. The content of Cu and Mn is significantly lower. The seeds also contain Pb, as its content in the seeds is significantly lower than that in the roots and the above-ground mass of the plants, while Cd is not accumulated in the seeds (below quantitative limits). Similar are the results of Petropoulos et al (2018), who found significant amounts of K, Ca, Mg and Fe in cardoon seeds, as Ca content reaches up to 11970 mg/kg, K up to 6630 mg/kg, Mg up to 4830 mg/kg, Fe up to 130 mg/kg, Zn up to 39.5 mg/kg, Na up to 180 mg/kg, and Mn up to 60 mg/kg. The values we obtained for K do not differ significantly from the results of Petropoulos et al. (2018). The content of Zn, Fe and Mg is slightly lower, while significantly higher values are obtained for Mn and Ca. The variation between the results may be due to growing conditions, genetic factors, varietal characteristics and other factors.

The content of P and Mg is highest in the cardoon seeds compared to other parts of the plant, while the content of K is lower than that in the stems and leaves. Similar results were established by Petropoulos et al., 2018, according to whom the content of K (6530 mg/kg) and Na (180 mg/kg) is lower than that in other parts of the plant, while higher levels of Mg (4830 mg/kg) were detected in the seeds.

Oil was obtained from the cardoon seeds in laboratory conditions by an extraction method with a Soxhlet apparatus, allowing the extraction of the fat from the pre-ground seeds with petroleum ether and subsequent distillation of the latter.

The content of Pb in cardoon oil reaches up to 0.02 mg/kg (Table 2). The maximum allowable concentration (MAC) for Pb in the vegetable oil is 0.1 mg/kg. The results obtained show that a very small amount of Pb contained in the cardoon seeds goes into the oil obtained, and its content in the oil is lower the MAC and it can be used for nutritional purposes.

The content of Cd is below the limits of the quantitative method used. According to the current standard, the content of Cd should not exceed 0.05 mg/kg.

The MAC for the content of Zn in vegetable fat is 10 mg/kg. The results obtained clearly show that the major part of Zn contained in the cardoon seeds does not do into the oil obtained, and its content in the oil is lower than the MAC.

The MAC for the content of Cu in refined oils is 0.1 mg/kg and in unrefined oil is 0.4 mg/kg. In our studies, the content of Cu in oil reaches 0.64 mg/kg and its quantity is above the MAC. It is noteworthy that although the content of Cu in the seeds is low, the oil contains Cu above the MAC. Probably the reason for this is the way the oil is extracted from the cardoon seeds. In terms of our experiment, the oil was obtained by extraction. However, there is evidence in the literature that shows that oils obtained by solvent extraction contain higher values of Cu and trace metals than cold-pressed oils. It is not desirable for the oil composition to contain significant amounts of microelements, in particular Cu. Cu ions are known to be effective pro-oxidants in the oxidation of lipids, so they are undesirable components in terms of oil resistance to oxidation. This is probably the reason for

the high criteria in terms of the content of Cu in oils, although Cu is not a toxic element to human health in a relatively wide range.

The content of Fe in cardoon oil reaches 4.0 mg/kg and is within the limit values for oils (for crude oils 5 mg/kg, for refined oils 1.5 mg/kg). The content of Fe in crude oils is due to the Fe contained in oilseeds (mainly related to proteins, phospholipids and other components).

Of the nutrients in the composition of cardoon oil, K (71.1 mg/kg) predominates followed by Ca (29.6 mg/kg), P (12.7 mg/kg) and Mg (10.9 mg/kg) (Table 4). There is no evidence of the negative impact of these elements on the stability of the oil. It is known that P and Ca form salts that are insoluble in oil and can be easily removed by refining the oil.

Fatty acid composition of cardoon oil

The fatty acid composition of the oil is the main factor that determines the use of the oil for nutritional purposes, for industrial purposes, as the variety, climate and production area have a significant impact (Velasco et al., 2005). Raccuia et al. (2011) found that cardoon oil is a rich source of unsaturated fatty acids such as linoleic and oleic acids (44.5 and 42.6%, respectively), while the content of saturated fatty acids such as palmitic and stearic acid is much lower (9.8 and 3.1%, respectively). Similar results were obtained by Petropoulos et al. (2018), according to whom linoleic and oleic acids (64.86 and 21.11%, respectively) predominate in cardoon oil, while palmitic and stearic acids are in smaller quantities (9.37 and 2.78%, respectively). Similar are the results of Maccarone et al. (1999) and Curt et al. (2002) according to whom linoleic and oleic acid are the main fatty acids, followed by palmitic and stearic acid. The composition of cardoon oil has been found to be similar to sunflower oil (Benjelloun-Mlayah et al., 1996; Curt et al., 2002; Fernández et al., 2006).

Table 3. Fatty acid composition of cardoon oil (expressed as % of total fatty acid composition)

Parameter	Measured	Reference				
		Greece(1)	Greece(2)	Italy(3)	Spain(4)	Portugal(5)
Saturated (S)	14.83	13.23				
Lauric acid (C12:0)	0.15	nd				
Myristic acid(C14:0)	0.05	0.094				
Palmitic acid (C16:0)	10.6	9.37	11.1	7.7-10.3	10.6	10.9
Magaric acid (C17:0)	0.08	0.072				
Stearic acd (C18:0)	3.3	2.72	3.2	2.8-3.6	3.56-3.7	3.3
Arachidic acid (C20:0)	0.15	0.277				
Lignoceric acid(C24:0)	0.5	0.121				
Monounsaturated(MUFA)	23.4	21.34				
Palmioletic acid(C16:1)	0.19	0.107				
Oleic acid (C18:1)	22.85	21.11	24.9	21.8-26.1	24.9-28.4	23.1
Gadoleic acid (C20:1)	0.36	0.11				
Polyunsaturated(PUFA)	61.77	65.43				
Linoleic acid(C 18:2)	61.69	64.86	59.1	61.2-	56.7 -	61.2

				62.7	59.7	
Linolenic acid (C 18:3)	0.08	0.108				
Total unsaturated (U)	85.17	86.77				
Saturated:unsaturated	14.83: 85.17	13.23: 86.77				
P/S index	4.2	4.94				

(1) Petropoulos et al. (2018); (2) Archontoulis et al. (2010); (3) Maccarone et al. (1999), Piscioneri et al. (2000), Raccuia and Melilli (2007); (4) Curt et al. (2002): (5) Carvalho et al. (2006)

Unsaturated fatty acids are predominant in the fatty acid composition of the oil we study, obtained during the extraction of cardoon seeds, with their amount reaching up to 85.06% respectively. The composition of the oil was dominated by linoleic acid (C18:2, 61.67%), followed by oleic acid (C18:1, 22.82%). The presence of linoleic (C18:3, 0.06%), palmitic (C16:1, 0.07%) and gadoleic (C20:1, 0.34%) acids was also found. Similar results are obtained by Petropoulos et al. (2018), according to whom the linolenic acid content is less than 1%. The low percentage of unsaturated acids with three double bonds, less than 1%, has a positive effect on the thermal and oxidative stability of the oil.

Of the saturated fatty acids, palmitic acid (C16:0) prevails in the amount of 10.5%, followed by stearic acid (C18:0, 3.29%). The oil also contains myristic (C14:0, 0.03%), margaric (C16:0, 0.06%), arachidonic (C20:0, 0.13%) and lignoceric (C24:0, 0.40%) acids. The content of saturated fatty acids in cardoon oil reaches 14.83% (Table 3).

The results obtained confirm that linoleic acid is predominant in cardoon oil (Maccarone et al.,1999, Piscioneri et al., 2000, Curt et al., 2002, Carvalho et al., 2006, Raccui and Melilli, 2007, Archontoulis et al., 2010, Petropoulos et al., 2018). According to the literature, the content of linoleic acid varies from 56.7% to 64.8%. Oils from Spain contain up to 59.7% linoleic acid (Curt et al., 2002), while oils from Italy, Portugal and Greece contain higher amounts of linoleic acid (61.2-64.8%) (Maccarone et al.,1999, Piscioneri et al., 2000, Carvalho et al., 2006, Raccui and Melilli, 2007, Archontoulis et al., 2010, Petropoulos et al., 2018)..

Oleic acid content was found to vary from 21.11% to 28.4% (Maccarone et al.,1999, Piscioneri et al., 2000, Curt et al., 2002, Carvalho et al., 2006, Raccui and Melilli, 2007, Archontoulis et al., 2010, Petropoulos et al., 2018). The content of palmitic acid in oil varies from 9.37% to 11.1%, while the content of stearic acid in oil varies from 2.78 to 3.7%.

The distribution of fatty acids is shown in Figure 2. The ratio of unsaturated to saturated fatty acids in cardoon oil is 85.17:14.83. Similar results were obtained by Petropoulos et al. (2018) for cardoon oils from southern Greece 86.77: 3.23.

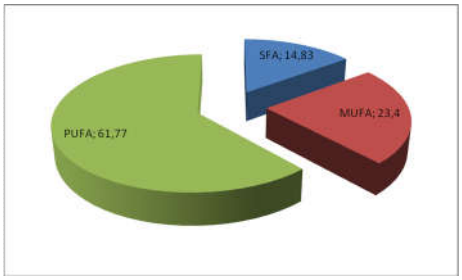

Fig.2. Distribution of fatty acids in cardoon oil

The total content of saturated fatty acids (SFA) in cardoon oil reaches 14.83% of the total amount of fatty acids and is comparable to the amounts of these acids in oils from Greece (Petropoulos et al., 2018). The content of monounsaturated fatty acids (MUFA) reaches up to 23.5% and the content of polyunsaturated fatty acids reaches up to 61.7%. The high PUFA content in cardoon oil makes it useful for therapeutic purposes in cardiovascular diseases. PUFAs are useful for reducing the risk of certain chronic conditions such as coronary heart disease, stroke and rheumatoid arthritis (Calder, 2008) and are used in the treatment of certain chronic conditions such as diabetes, cardiovascular diseases, inflammatory processes, atherosclerosis (Finley and Shahidi, 2001).

The relationship between the content of saturated and polyunsaturated acids is expressed as a P/S index. This value is an important parameter in determining the nutritional value of certain types of oils. Oils with a P/S index greater than 1 are considered valuable edible oils. The results obtained by Petropoulos et al. (2018) show that cardoon oil has a P/S index higher than 1 (4.94), which is in line with our results (4.2). These values indicate that cardoon oils can have a good effect on human health and are oils suitable for consumption.

CONCLUSIONS

Based on the obtained results the following conclusions can be made:

1. The cardoon shows adaptability to local conditions and can be grown in southern Bulgaria and used for oil production
2. All plant parts of the cardoon are a rich source of macro and microelements and exhibit high nutritional value, as differences in the content of the studied elements are observed in the vegetative and reproductive organs of the plant.
3. The distribution of macro and microelements in the cardoon organs is selective, specific for the individual elements. Cd, Cu and Fe are accumulated in the roots, K - in the stems, Pb and Ca - in the leaves, and Zn, Mn, Mg and P - in the seeds
4. Cardoon seeds can be a good source of minerals due to the high content of K(6670.4 mg/kg), P (5398.2 mg/kg), Mg (3572.3 mg/kg), Ca (2826.1 mg/kg), Fe (51.1 mg/kg), and Zn (35.2 mg/kg) in them.
5. Polyunsaturated fatty acids (PUFA-61.77%) are predominant in the fatty acid composition of the oil, followed by monounsaturated fatty acids (MUFA -23.4%) and saturated (SFA-14.83%).

6. Cardoon oil has a P/S index higher than 1 (4.2), which indicates that oil can have a good effect on human health and are oils suitable for consumption.
7. Cardoon oil is a rich source of polyunsaturated linoleic fatty acid with potentially beneficial therapeutic activity.

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