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The antioxidant capacity and macroelement content of several onion cultivars

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Abstract: The aim of this study was to determine the phosphorus, magnesium, sodium, potassium, and calcium contents, as well as the total phenolic content and antioxidant activity in white, yellow, and red onion varieties. It is evident from the results that the highest content of all of these macroelements except phosphorus was found in the cultivar Fireball. In this cultivar, the phosphorus content was the lowest of all cultivars. The total phenolic content ranged from 1.17 to 2.10 g of gallic acid equivalents kg^{-1} and the antioxidant capacity ranged from 1.26 and 1.86 g of ascorbic acid equivalents kg^{-1} of fresh weight and was slightly higher in red onion cultivars than in white and yellow cultivars. The significant influence of color was determined by total phenolic content, antioxidant capacity, and macroelements except phosphorus ($P < 0.05$). While the season had influence on phosphorus and potassium content and on antioxidant capacity, the growing season significantly influenced the total phenolic content of the onions.

Key words: Onion, polyphenols, antioxidant capacity, macroelements

1. Introduction

Onion is a natural part of the daily diet for most of the world´s population and it is also considered a part of a group of functional foods that offer a particular health benefit due to the traditional nutrients they contain (Fidan and Koç, 2001). The broad spectrum of onion activity is based on chemical composition. Onion contains vitamins, a broad spectrum of antibiotics, sugar complexes, sulfurous compounds, enzymes, glycosides, flavonoids, saponins, and minerals (Golubev et al., 2003). Reports of health benefits from onion include anticarcinogenic properties, antiplatelet activity, antiallergenic as well as antithrombotic activities, and antiasthmatic and antibiotic effects (Mogren et al., 2006). These pharmacological effects can be ascribed both to organosulfur compounds, which are responsible for the onion's typical odor and flavor, and flavonoids, in particular quercetin, which is well known for its anticarcinogenic properties (Marotti and Piccaglia, 2002).

Onion is one of the richest sources of flavonoids in the human diet. The highest concentrations of flavonoids in onion are found in the outer dry peel, so the greatest loss of flavonoids happens when the onions are peeled (Santas et al., 2008). Flavonols and anthocyanins are the dominant subclasses of flavonoids present in onions. The main flavonoids are represented by quercetin and its conjugates. Anthocyanins are only minor components of the flavonoid spectrum in the edible portion of red varieties (Lanzotti, 2006; Siddiq et al., 2013).

The high level of antioxidant activity of onion is attributed to the flavonoids quercetin, kaempferol, myricetin, and catechin as well as to anthocyanins, according to Karadeniz et al. (2005). Quercetin especially has shown an anti-HIV property and the ability to protect low-density lipoprotein cholesterol from oxidation, reducing the risk of cardiovascular diseases. The epidemiological data of flavonoids and cancer are still limited and further research is needed. However, a protective association against lung

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cancer has been observed for people consuming onion (Yang et al., 2004; Lu et al., 2011).

The most important minerals of onion are potassium, calcium, and selenium (Mota et al., 2010). According to the current understanding, the health of a population is determined in many respects by the level of nutritional consumption of micronutrients. Mineral elements play a critical role in building body tissue and regulating numerous physiological processes (Golubev et al., 2003). Many factors influence the composition of these micronutrients in onion, such as soil characteristics, environmental and agronomic conditions, cultivar, and ripening stage. The mineral contents of onion and other vegetables across different parts of the globe have been determined for the purposes of health risk assessment, nutrient content analysis for consumers, determination of geographic origin of food products, etc. (Kitata and Chandravanshi, 2012). Therefore, the first aim of this work was to characterize the antioxidant activity and total phenolic content of selected onion cultivars, and the second aim was to examine the content of important macroelements in these cultivars.

2. Materials and methods

2.1. Plant material and growth conditions

The field experiment was done on moderately heavy fluvisol-type soil in the area of the Botanical Garden of Slovak University of Agriculture in Nitra in 2011 and 2012, the characteristics of which are mentioned in Table 1. This location belongs to a very hot agroclimatic macroarea, a very dry subarea, and a district of mostly mild winter in terms of territorial classification of atmospheric processes and weather conditions within the period 1991–2000. The average annual air temperature reaches 9.0 to 10.2 °C and the average annual rainfall is 595 mm (Špánik et al., 2002).

In the experiments, the onion varieties Diamant, Arenal, Birdie, Hamlet, Mundial, Rolex, Starito, Tioga, Fireball, and Kamal (analyzed in spring varieties and late varieties) were used. In terms of color, Diamant was white; Arenal, Birdie, Hamlet, Mundial, Rolex, Starito, and Tioga were yellow; and Fireball and Kamal were red.

The seeds of the 10 onion varieties were sown on 5 April 2011 in 3 rows with a length of 4 m each, and the spaces between the rows were 0.30 m. Young onions of all varieties were collected from the first 2 m of all rows for bundling on 23 June 2011 and chemical analyses were conducted. The onions in the remaining 2 m of the rows were harvested in the fall at the time of full maturity. After further drying in a ventilated stock, the varieties were analyzed again for the same parameters as in the young onions.

2.2. Extraction of samples

The extraction method used here is based on that of Kim et al. (2003). For each cultivar, 10 g of fresh sample (6 bulbs) was homogenized for 10 s in 100 mL of methanol. The resulting paste was placed into Erlenmeyer flasks (120 mL) and kept in a water bath at ±25 °C for 24 h. The residues were re-extracted twice using methanol. The combined methanolic extracts were evaporated at 40 °C using a rotary evaporator R-215 (Buchi Ltd., Oldham, UK) to dryness and dissolved again in methanol at a concentration of 100 mg mL^{-1}. These samples were stored at 4 °C for subsequent analyses.

2.3. Mineral composition

A 1 g portion of dry matter sample was homogenized using a SJ500 laboratory grinder (Mezos, Hradec Kralove, Czech Republic) resulting in a particle size of up to 1 mm. The sample was thereafter mineralized in digestion tubes with a mixture of concentrated sulfuric acid and 30% hydrogen peroxide and was stored in a Bloc Digest M 24 heating block digester (JP/Selecta, Abrera, Spain). The mineralized samples were quantitatively transferred to a 250-mL volumetric flask and its volume was refilled with double distilled water. The resulting sample was measured in a Philips PU 9200X atomic absorption spectrometer (Philips, Eindhoven, Netherlands). The content of phosphorus in the sample was measured using a Libra S6 spectrophotometer (Biochrom Ltd., Cambridge, UK). Then 10 mL of the sample was pipetted into a 100-mL volumetric flask, 10 mL of ammonium-vanadomolybdate reagent was added, the flask was refilled to volume with redistilled water, and the sample was measured at a wavelength of 410 nm. A standard stock solution of the monopotassium phosphate (KH_2PO_4) was used. The amounts of selected macroelements (Ca, K, Mg, Na, and P) were expressed as mg kg^{-1} of fresh weight.

Table 1. Agrochemical characteristics of the soil before the start of the experiment.

pH/KCl	Nutrient content (mg kg^{-1}) of the soil							% mold
	$N–NH_4^+$	$N–NO_3^-$	P	K	S	Ca	Mg	
6.96	28.7	18.2	130	575	32.5	7300	662.5	3.79

2.4. Total phenolic content

The total phenolic content of each extract was determined in duplicate using the Folin–Ciocalteu procedures as follows. Briefly, 0.5 mL of onion extract was diluted with deionized water in a 50 mL volumetric flask, mixed with 2.5 mL of Folin–Ciocalteu reagent, and incubated for 10 min at room temperature (ca. 20 °C). Then 7.5 mL of 20% Na_2CO_3 solution (w/v) was added. The mixture was left to stand in the dark (ca. 20 °C) for 45 min before measuring the absorbance. It was measured at 765 nm using a Libra S6 spectrophotometer (Biochrom Ltd., Cambridge, UK) against a reference blank containing deionized water instead of sample extract. The results were expressed as g gallic acid equivalents kg^{-1} of fresh weight (g GAE kg^{-1} FW) (Kim et al., 2003).

2.5. DPPH radical scavenging activity

The antioxidant capacity of the onion extracts was measured using a DPPH method described by Brand-Williams et al. (1995) using free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) with some modifications (Thaipong et al., 2006). The stock solution was prepared from 24 mg of DPPH dissolved in 100 mL of methanol. The working solution was obtained by mixing 10 mL of the stock solution with 45 mL of methanol (i.e. an absorbance of 1.1 ± 0.02 units at 515 nm) using a Libra S6 spectrophotometer (Biochrom Ltd., Cambridge, UK). Onion extracts (150 µL) were mixed with 2850 µL of the DPPH solution, kept in the dark for 1 h, and absorbance was recorded. Antioxidant capacity was calculated as a decline in the absorbance value using the formula:

$$\%DPPHscavenging = [(A_0 - A_{1)}/A_0] \, 100\%$$

where A_0 is the absorbance of the control (without the sample) and A_1 is the absorbance of the mixture containing the sample.

The absorbance results were converted using a calibration curve of the standard and expressed as g ascorbic acid equivalents kg^{-1} of fresh weight (g AAE kg^{-1} FW) (Rupasinghe et al., 2006).

2.6. Statistical analysis

Each experiment was performed 3 times. The data were analyzed using Adstat v.1.25 (TriloByte) and expressed as means ± standard deviations. Any significant differences between samples were determined by one-way analysis of variance, considering differences significant at $P < 0.05$. This statistical analysis was performed with Statistica v.1.25 (StatSoft).

3. Results and discussion

3.1. Mineral composition

The results obtained for the concentration of macroelements (Ca, K, Mg, Na, and P) analyzed in all samples and their differentiation according to the cultivars considered are shown in Tables 2 and 3. The ranking of macroelements based on their established amount in the examined onion cultivars was K > Ca > P > Mg > Na. The highest concentrations of phosphorus were detected in red onion cultivar Kamal F1 and in the yellow onion cultivars Mundial and Arenal, while the lowest content of this element was found in the red onion cultivar Fireball. The data were similar to those reported by Gundersen et al. (2000) and Galdón et al. (2008), but the minimum found in the cultivar Fireball is much lower than they presented.

The K concentration was determined as the highest in cultivar Fireball and was about 2–3 times higher than data shown by Galdón et al. (2008); however, it was 2 times lower in comparison with results from Gundersen et al. (2000). In contrast, the lowest content of potassium was measured in the yellow varieties of Arenal and Hamlet. These values were much higher than those reported by the authors mentioned above, but were very similar to those found by Chope and Terry (2009). The sodium concentration of Fireball was higher than that of the other yellow varieties (Table 2). The lowest Na concentration was determined in the yellow variety Rolex F1 and the highest was again in the Fireball variety. Our results were similar to those presented in other studies. The maximum concentration of magnesium was determined in Fireball. This value was 2 times higher than in the yellow variety Arenal and higher than most of the results found in the literature. The highest concentration of calcium was detected in Fireball and in the yellow variety Hamlet. The lowest Ca concentration was established in the yellow variety Tioga. The data obtained in our research for Ca concentration were much higher than those presented by Gundersen et al. (2000), Galdón et al. (2008), and Chope and Terry (2009). According to Ariyama et al. (2006), calcium is an essential and often deficient element in human diets and therefore the cultivation of crops with high Ca content is desired.

From a statistical point of view, the color of the cultivar had a significant influence on the content of all of the macroelements examined in the onions except phosphorus ($P < 0.05$). The influences of season and crop year were statistically conclusive only for the contents of phosphorus and potassium. Ariyama et al. (2006) reported that these elements accumulate in soil during a whole crop year and this affects onions as well. Generally, onions of different cultivars growing on the same site (i.e. same soil and climatic conditions) still have significant differences in the mineral composition of the bulbs. It is therefore likely that the source of this variation is genotypic. It can be also deduced that environmental and agronomic practices may affect the genetic information of the seeds, resulting in changes in mineral and trace element composition (Galdón et al., 2008; Chope and Terry, 2009).

Table 2. The concentrations of selected macroelements (mg kg^{-1} FW) in several onion cultivars.

Cultivar	Factor/ season	P		K		Ca		Mg	
		2011	2012	2011	2012	2011	2012	2011	2012
Diamant	Spring	292.48 ± 1.61	239.38 ± 1.81	2564.69 ± 2.64	2779.67 ± 126.01	823.01 ± 0.38	712.09 ± 1.87	183.24 ± 1.89	194.88 ± 2.51
	Autumn	269.35 ± 3.13	310.38 ± 1.26	2580.67 ± 25.55	2752.92 ± 1.50	763.62 ± 3.01	719.83 ± 4.52	209.82 ± 5.78	204.83 ± 2.24
Arenal	Spring	263.07 ± 3.04	294.84 ± 1.49	2058.29 ± 0.47	2081.61 ± 12.23^{C}	504.86 ± 2.04^{C}	504.60 ± 0.53^{C}	115.63 ± 1.57^{C}	124.31 ± 2.22^{C}
	Autumn	268.85 ± 0.84	316.38 ± 2.21^{B}	1856.47 ± 4.34^{D}	2156.43 ± 0.77^{D}	433.25 ± 1.86	706.58 ± 4.36	118.51 ± 0.77^{D}	129.53 ± 0.91^{D}
Birdie	Spring	273.76 ± 1.32	267.51 ± 1.50	2440.10 ± 1.16	2523.62 ± 8.72	694.31 ± 2.18	654.77 ± 0.51	148.36 ± 0.97	143.51 ± 4.02
	Autumn	266.89 ± 1.24	279.99 ± 1.39	2312.29 ± 2.07	2646.10 ± 3.91	612.37 ± 2.52	616.24 ± 3.71	157.13 ± 1.28	146.42 ± 0.83
Hamlet	Spring	256.90 ± 1.23	152.48 ± 1.13	1983.18 ± 2.26^{C}	2274.55 ± 48.32	902.13 ± 2.20	911.48 ± 1.15^{A}	215.07 ± 2.41	223.69 ± 0.49
	Autumn	290.78 ± 4.41	222.61 ± 2.34	1971.88 ± 3.81	2313.99 ± 1.94	855.48 ± 1.35	883.72 ± 1.62^{B}	232.58 ± 2.16^{B}	233.31 ± 0.75
Mundial	Spring	303.86 ± 1.48	292.07 ± 1.55	2112.95 ± 2.63	2260.01 ± 5.23	686.33 ± 1.48	743.54 ± 1.01	191.32 ± 1.47	213.05 ± 3.66
	Autumn	539.89 ± 1.24^{B}	314.01 ± 2.64	2091.27 ± 6.91	2270.43 ± 0.44	603.89 ± 3.65	737.18 ± 4.07	198.00 ± 2.07	241.72 ± 0.70
Rolex	Spring	195.81 ± 1.54	187.83 ± 1.31	2052.57 ± 0.99	2126.06 ± 2.11	713.75 ± 2.39	766.01 ± 1.43	164.33 ± 2.05	159.14 ± 2.36
	Autumn	231.86 ± 1.19	203.90 ± 2.68	1988.00 ± 1.66	2188.73 ± 0.36	488.69 ± 3.73	715.12 ± 2.01	160.95 ± 0.64	163.87 ± 0.80
Starito	Spring	205.20 ± 0.80	144.20 ± 0.24	2655.47 ± 1.76	2617.42 ± 1.21	601.87 ± 2.17	588.06 ± 1.07	150.04 ± 0.94	172.18 ± 9.23
	Autumn	243.17 ± 1.56	214.61 ± 1.67	2632.89 ± 14.40	2686.20 ± 3.20	545.04 ± 3.13	603.31 ± 1.26^{D}	150.41 ± 0.47	177.71 ± 1.41
Tioga	Spring	151.74 ± 0.71	152.98 ± 0.65	2112.29 ± 2.35	2217.75 ± 3.85	782.78 ± 1.29	753.66 ± 1.17	163.56 ± 2.28	157.60 ± 1.04
	Autumn	201.13 ± 1.59	157.12 ± 1.64	2114.91 ± 3.42	2359.51 ± 3.16	304.04 ±1.14^{D}	792.16 ± 2.06	148.01 ± 1.32	159.84 ± 2.13
Fireball	Spring	98.25 ± 0.68^{C}	104.20 ± 1.32^{C}	2953.18 ± 1.32^{A}	2866.27 ± 12.46^{A}	923.05 ±0.82^{A}	830.43 ± 1.92	262.72 ± 1.29^{A}	256.88 ± 2.62^{A}
	Autumn	130.63 ± 1.10^{D}	115.79 ± 1.60^{D}	3007.29 ± 6.56^{B}	2911.11 ± 0.83^{B}	898.49 ± 2.44^{B}	766.50 ± 1.46	231.66 ± 1.26	261.46 ± 1.22^{B}
Kamal	Spring	314.62 ± 8.59^{A}	307.42 ± 1.25^{A}	2386.53 ± 1.94	2514.32 ± 2.75	845.78 ± 0.85	833.65 ± 1.19	137.08 ± 1.25	146.86 ± 2.64
	Autumn	351.77 ± 1.62	314.43 ± 3.96	2315.27 ± 3.60	2600.53 ± 1.13	817.90 ± 0.67	861.79 ± 1.82	129.27 ± 6.06	161.65 ± 1.47

The white cultivar is Diamant; the yellow cultivars are Arenal, Birdie, Hamlet, Mundial, Rolex, Starito, and Tioga; and the red cultivars are Fireball and Kamal. A = highest value in spring, B = highest value in autumn, C = lowest value in spring, and D = lowest value in autumn.

Table 3. The concentrations of selected macroelements (mg kg^{-1} FW), total phenolic content (TPC) in g GAE kg^{-1} FW, and antioxidant capacity (TAC) in g AAE kg^{-1} FW in several onion cultivars.

Cultivar	Factor/ season	Na		TPC		TAC	
		2011	2012	2011	2012	2011	2012
Diamant	Spring	102.78 ± 1.14	94.72 ± 3.51	1.44 ± 0.00	1.64 ± 0.02	1.56 ± 0.00	1.54 ± 0.01
	Autumn	98.17 ± 1.61	106.54 ± 2.41	1.17 ± 0.02^{D}	1.79 ± 0.01	1.46 ± 0.01	1.66 ± 0.01
Arenal	Spring	74.62 ± 0.70	66.96 ± 1.01^{C}	1.51 ± 0.01	1.75 ± 0.03	1.63 ± 0.02	1.64 ± 0.01
	Autumn	76.11 ± 1.64	74.30 ± 2.33	1.36 ± 0.01	1.93 ± 0.02	1.66 ± 0.02	1.83 ± 0.01
Birdie	Spring	76.00 ± 1.25	75.40 ± 1.30	1.44 ± 0.02	1.68 ± 0.01	1.52 ± 0.03	1.54 ± 0.01
	Autumn	78.96 ± 0.91	81.52 ± 0.78	1.38 ± 0.01	1.98 ± 0.04	1.65 ± 0.04	1.72 ± 0.03
Hamlet	Spring	56.65 ± 1.05	66.47 ± 0.60	1.62 ± 0.00	1.81 ± 0.03	1.80 ± 0.02	1.67 ± 0.02
	Autumn	69.58 ± 0.94	72.64 ± 2.37^{D}	1.17 ± 0.01^{D}	1.92 ± 0.01	1.26 ± 0.05^{D}	1.71 ± 0.01
Mundial	Spring	96.17 ± 1.25	78.04 ± 0.10	1.48 ± 0.01	1.67 ± 0.02	1.58 ± 0.01	1.53 ± 0.02
	Autumn	96.18 ± 0.43	87.44 ± 2.32	1.47 ± 0.02	1.71 ± 0.02^{D}	1.62 ± 0.02	1.60 ± 0.01^{D}
Rolex	Spring	51.21 ± 2.00^{C}	83.17 ± 0.88	1.53 ± 0.01	1.73 ± 0.04	1.63 ± 0.01	1.63 ± 0.02
	Autumn	63.30 ± 0.64^{D}	92.04 ± 0.87	1.27 ± 0.00	2.03 ± 0.03	1.57 ± 0.01	1.86 ± 0.02^{B}
Starito	Spring	61.97 ± 1.54	68.37 ± 1.58	1.41 ± 0.01^{C}	1.62 ± 0.03^{C}	1.50 ± 0.01^{C}	1.52 ± 0.01^{C}
	Autumn	59.68 ± 0.72	78.11 ± 0.95	1.33 ± 0.02	1.95 ± 0.03	1.57 ± 0.05	1.75 ± 0.03
Tioga	Spring	94.20 ± 0.79	91.99 ± 0.66	1.47 ± 0.01	1.71 ± 0.02	1.57 ± 0.03	1.57 ± 0.01
	Autumn	95.41 ± 1.09	96.06 ± 1.05	1.31 ± 0.02	1.84 ± 0.03	1.62 ± 0.00	1.65 ± 0.03
Fireball	Spring	110.22 ± 0.68^{A}	104.96 ± 0.33^{A}	1.63 ± 0.02^{A}	1.90 ± 0.01^{A}	1.82 ± 0.02^{A}	1.76 ± 0.01^{A}
	Autumn	102.00 ± 1.24^{B}	119.78 ± 3.60^{B}	1.59 ± 0.03	2.01 ± 0.01	1.74 ± 0.08	1.83 ± 0.01
Kamal	Spring	101.39 ± 1.17	90.07 ± 0.86	1.53 ± 0.02	1.70 ± 0.01	1.62 ± 0.02	1.61 ± 0.01
	Autumn	91.81 ± 1.51	90.44 ± 1.43	1.63 ± 0.03^{B}	2.10 ± 0.04^{B}	1.81 ± 0.02^{B}	1.80 ± 0.01

The white cultivar is Diamant; the yellow cultivars are Arenal, Birdie, Hamlet, Mundial, Rolex, Starito, and Tioga; and the red cultivars are Fireball and Kamal. A = highest value in spring, B = highest value in autumn, C = lowest value in spring, and D = lowest value in autumn.

3.2. Antioxidant capacity and total phenolic content

The total phenolic content (TPC) of the 10 onion cultivars is shown in Table 3. The TPC of Fireball was the highest among all of the cultivars and the yellow variety Starito had the lowest. These same cultivars also showed the highest and the lowest antioxidant capacity. This conclusion relates to the results obtained for the spring onion varieties.

Of the late onion varieties, Kamal F1 and Rolex had the greatest total antioxidant capacity (TAC) whereas the lowest was found in Hamlet and Mundial. In connection with these results, Kamal F1 was found to have the highest phenolic content, while the lowest was determined in the white variety Diamant and the yellow variety Mundial. There were significant differences in TPC and TAC among all cultivars depending on the color of the onion varieties ($P < 0.05$). Our results correspond with those from Gökce et al. (2010) and support the findings that favor red onions, as we also recovered the highest antioxidant activities from the onion group with red peels.

The crop year also had a statistically significant influence on TPC and TAC. However, season was a significant factor only for antioxidant capacity, not for polyphenol content. The studies by the authors mentioned above showed that differences in the total phenolic and flavonoid contents among onion cultivars could be due to genetic differences and/or to growing location, climate, maturity, and harvest season variation. It is well known that genetic, agronomic, and environmental factors play important roles in the

phenolic composition and thus the nutritional quality of crops (Yang et al., 2004; Özgen et al., 2008; Lu et al., 2011).

In summary, the highest concentration of selected macroelements was predominantly observed in Fireball, except for phosphorus, which was at its lowest concentration in this cultivar. The values of TPC ranged from 1.17 to 2.10 g kg^{-1} and TAC was between 1.26 and 1.86 g kg^{-1}, and the results from the red onion varieties were higher than those from the white and yellow varieties. Our findings confirm that red onions in general have a higher antioxidant capacity in comparison with yellow and white onions, although some specific yellow onions might have high antioxidant capacity due to their high total phenolic content.

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