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Comparative evaluation of biochemical parameters and mineral composition of *Cucurbita ficifolia, C. maxima* and *C. moschata* fruit, grown in the northern hemisphere

Abstract

Fruit peel/pulp distribution of biologically active compounds is an important characteristic of plant physiology and the basis of zero waste production in agriculture. Among *C. ficifolia, C. maxima* and *C. moschata* the former showed the lowest dry matter content, especially in peel, similar peel and pulp values of antioxidant activity (AOA) and polyphenol content (TP), with the highest levels in fruit placenta. Peel carbohydrate profile of *C. ficifolia* fruit was characterized by lower levels of disaccharides compared to *C. maxima* and *C. moschata* peel and an opposite pattern of monosaccharides accumulation. The analysis of 25 elements content in *Cucurbita* peel and pulp, using ICP-MS, indicated that *C. ficifolia* fruit are characterized by significantly high concentrations of Sr, Si and I in pulp compared to the values of *C. maxima* and *C. moschata*. On the contrary, *C. maxima* and *C. moschata* were characterized by low concentration of pulp Mn. Highly significant positive correlations were recorded between Cr-Sr, Cr-Ca and Ca-Sr (r=0.906; 0.939 and 0.974 respectively) and P-Cu (r=0.968). Despite *C. ficifolia*, does not contain carotenoids, it is highly valuable due to the high levels of Si, I, Cr and Ca in peel and pulp, which reveals new areas of its application.

Keywords: ***Cucurbita ficifolia; Cucurbita maxima; Cucurbita moschata;*** **antioxidants; minerals**

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Сравнительная оценка биохимических показателей и минерального состава плодов *Cucurbita ficifolia, C. maxima* и *C. moschata*

Abstract

Распределение биологически активных соединений между кожурой и мякотью плодов является важной характеристикой особенности физиологии растения и может служить основой для безотходного производства в сельском хозяйстве.

Результаты. **Установлено, что среди трех видов тыквы: фиголистной (*C. ficifolia*), крупноплодной (*C. maxima*) и мускатной (*C. moschata*), – фиголистная тыква содержит наименьшее количество сухого вещества, особенно в кожуре плодов, сходные уровни общей антиоксидантной активности (АОА) и содержания полифенолов (ТР) в кожуре и мякоти при максимальных показателях антиоксидантного статуса в плаценте. Углеводный профиль кожуры фиголистной тыквы *C. ficifolia* характеризовался наименьшими уровнями дисахаридов по сравнению с кожурой крупноплодной *C. maxima* и мускатной тыквы *C. moschata* и наибольшими уровнями моносахаров. ИСП-МС анализ содержания 25 элементов в кожуре и мякоти исследованных видов тыквы показал, что фиголистная тыква отличается значительно более высокими уровнями накопления в мякоти Sr, Si, I по сравнению с аналогичными данными для тыквы крупноплодной *C. maxima* и мускатной *C. moschata*. Напротив, плоды крупноплодной и мускатной тыквы характеризовались низкими концентрациями Mn в мякоти. Установлены статистически достоверные положительные корреляции между Cr-Sr, Cr-Ca и Ca-Sr (r=0.906; 0.939 и 0.974 соответственно), а также P-Cu (r=0.968). Несмотря на то, что плоды фиголистной тыквы *C. ficifolia* не содержат каротиноиды, их пищевая ценность в значительной степени связана с высокими уровнями Si, I, Cr и Ca в кожуре плодов и мякоти, что открывает новые горизонты использования этого вида.**

Keywords: ***Cucurbita ficifolia; Cucurbita maxima; Cucurbita moschata;*** **антиоксиданты; минералы**

1. Introduction

Pumpkins have long been used in traditional medicine in many countries, such as China, Argentina, India, Mexico, Brazil, and Korea, particularly due to high levels of proteins, minerals, antioxidants, vitamins, carotenoids, and tocopherols [1,2], and low levels of fat and calories.

All representatives of *Cucurbita family* demonstrate anti-obesity, hepato- and nephroprotective, diuretic, antioxidant, anticancer, anti-inflammatory, antidiabetic and immuno-modulating activity [3, 4, 5, 6, 7, 8, 9]. *C. ficifolia* is known to possess a powerful antidiabetic potential [4, 10, 11], *C. maxima* and *C. moschata* fruit are good sources of carotenoids (beta-carotene, zeaxanthin, lutein and violaxanthin) highly valuable in ophthalmology, providing a protection of human retina against macular dystrophy [6]. The high adaptability of *C. ficifolia* promoted grafting technology of black-beauty watermelon onto *Cucurbita ficifolia* [12]. The high nutritional value of this plant became the basis of *Cucurbita Ficifolia*/maca vine production [13].

Despite the numerous works devoted to pharmacological significance of *Cucurbita* fruit utilization, little attention has been paid to the peculiarities of peel/pulp mineral and antioxidant distribution [14, 15, 16]. Indeed, detailed investigation of *Cucurbita maxima, C. pepo, C. moschata* and *C. ficifolia,* achieved by Kostecka-Gugala et al. [1], presents no data on peel/pulp nutrient distribution in fruit of eighteen *Cucurbita* cultivars. At the same time, literature data indicate the high nutritional value of fruit peel, with remarkable levels of minerals in citrus plants [17] and higher peel AOA in *Canarium odontophyllum* Miq. fruit compared to pulp tissues [18]. Several investigations indicate prospects of *Cucurbita* peel utilization in bread baking [15, 19].

The aim of the present work was the comparative evaluation of fruit biochemical characteristics and macro- and trace elements profile of peel/pulp *Cucurbita* species *C. ficifolia* (Pamiaty Tarakanova cv), *C. maxima* (Spasitelnitsa cv) and *C. maschata* (Penguin cv) grown in the Northern emisphere.

2. Materials and Methods

2.1. General methods

Research was conducted on three pumpkin species, *C. ficifolia* ('Pamyati Tarakanova' cv), *C. maxima* ('Spasitelnitsa' cv) and *C. moschata* ('Pingvin' cv), cultivated at the experimental fields of the Russian State Agrarian University, Moscow region, Russia (55°.39'58'' N, 43°82'64'' E) (55° 47′ 28″ N; 37° 57′ 29″ E) in 2019 and 2020. The trial was carried out on a sod-podzolic loamy soil with pH 6.5, 2.5 organic matter, 153 mg·kg^{-1} mobile phosphorus; 114 mg·kg^{-1} exchangeable potassium; 2.9 mg-eq hydrolytic acidity.

The 3 pumpkin species were compared to assess the differences in quality and antioxidant characteristics. A randomized complete block design was used for the treatment distribution in the field, with three repetitions, and the experimental unit had a 294 m^2 (21 x 14 m).

Seeds were manually sown in multicell containers in greenhouse, on 3 and 5 May, in 2019 and 2020, respectively. The seedling planting was carried out on 6 and 8 June, in 2019 and 2020, respectively, according to the spacing of 210 x 140 cm, with the density of 0.34 plants m^{-2}.

The pumpkin crops received 30 g·m^{-2} NPK fertilizer (16 N, 16 P, 16 K) at planting, followed by 30-35 g m^{-2} Kemira GrowHow fertilizer (12 N, 8 P, 14 K), at the beginning of flowering and at fruit growth phase. Weeds were manually removed. Harvesting was achieved on 28 September for *C. ficifolia*, 18 September for *C. maxima* and 15 September for *C. moschata.*

The values of mean temperature and rainfall during the crop period are presented in Table 1.

Table 1. Values of mean temperature and rainfall from May to September, 2019 and 2020

Month	2019		2020	
	Temperature (°C)	Rainfall (mm)	Temperature (°C)	Rainfall (mm)
May	16.3	57	11.7	156
June	19.6	64	19.0	159
July	16.8	69	18.7	170
August	16.4	57	17.6	34
September	12.3	29	13.9	65

2.2. Sample preparation

After harvesting, pumpkin fruits were cleaned and weighted. Peel, placenta and pulp of one quarter of each of the 5 fruits sampled were separated, weighed and homogenized. Fresh homogenized material was used for nitrate and carotenoids determination. Aliquots of fresh samples were dried at 70°C to constant weight, homogenized to fine power and used for the determination of polyphenols and antioxidant activity.

2.3. Dry residue and soluble solids

Dry residue was assessed via drying of samples in an oven at 70 °C until constant weight. Soluble solids (°Brix) were determined at 20°C on the supernatant obtained by centrifuging the raw homogenate, using a digital refractometer by Bellingham and Stanley, model RFM 81.

2.4. Sugars

Monosaccharides were determined using ferricyanide colorimetric method, based on the reaction of monosaccharides with potassium ferricyanide [20]. Total sugars were analogically determined after acidic hydrolysis of water extracts with 20% hydrochloric acid. Fructose was used as an external standard.

2.5. Elemental composition

Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, I, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Si, Sn, Sr, V and Zn contents of dries pumpkin pulp and peel powder were assessed using an ICP-MS on quadruple mass-spectrometer Nexion 300D (Perkin Elmer Inc., Shelton, CT 06484, USA) equipped with the 7-port FAST valve and ESI SC DX4 autosampler (Elemental Scientific Inc., Omaha, NE 68122, USA) in the Biotic Medicine Center (Moscow, Russia). Rhodium 103 Rh was used as an internal standard to eliminate instability during measurements. Quantitation was performed using external standard (Merck IV, multi-element standard solution), potassium iodide for iodine calibration and Perkin-Elmer standard solutions for P, Si and V. All the standard curves were obtained at 5 different concentrations. For quality checking purposes, internal controls and reference materials were tested together with the samples on a daily basis. Microwave digestion of samples was achieved with sub-boiled HNO3 diluted 1:150 with distilled deionized water (Fluka No. 02650 Sigma-Aldrich, Co., Saint

Louis, MO, USA) in the Berghof SW-4 DAP-40 microwave system (Berghof Products + Instruments GmbH, 72800 Eningen, Germany). The instrument conditions and acquisition parameters were: plasma power and argon flow, 1500 and 18 L min^{-1} respectively; aux argon flow, 1.6 L min^{-1}; nebulizer argon flow, 0.98 L min^{-1}; sample introduction system, ESI ST PFA concentric nebulizer and ESI PFA cyclonic spray chamber (Elemental Scientific Inc., Omaha, NE 68122, USA); sampler and slimmer cone material, platinum; injector, ESI Quartz 2.0 mm I.D/; sample flow, 637 L min^{-1}; internal standard flow, 84 L min^{-1}; dwell time and acquisition mode, 10–100 ms and peak hopping for all analytes; sweeps per reading, 1; reading per replicate, 10; replicate number, 3; DRC mode, 0.55 L min^{-1} ammonia (294993-Aldrich Sigma-Aldrich, Co., St. Louis, MO 63103, USA) for Ca, K, Na, Fe, Cr, V, optimized individually for RPa and RPq; STD mode, for the rest of analytes at RPa = 0 and RPq = 0.25.

2.6. Nitrates

They were assessed using ion selective electrode by ionomer Expert-001 (Econix, Russia). Five grams of fresh homogenates were homogenized with 50 ml of distilled water. Forty-five ml of the resulting extract were mixed with 5 ml of 0.5 M potassium sulfate background solution (necessary for regulating the ionic strength) and analyzed through the ionomer for nitrate determination.

2.7. Total dissolved solids (TDS)

TDS were determined in water extracts using portable TDS-3 conductometer (HM Digital, Inc., Seoul, Korea).

2.8. Antioxidants

2.8.1. Polyphenols (TP)

They were determined in 70% ethanol extract, using Folin-Ciocalteu colorimetric method as previously described [21]. Half gram of dry pumpkin samples powder was extracted with 20 ml of 70% ethanol at 80°C in 1 h. The mixture was cooled, quantitatively transferred to a volumetric flask and the volume was adjusted to 25 ml. The mixture was filtered through filter paper and 1 ml of the resulting solution was transferred to 25 ml volumetric flask, to which 2.5 ml of saturated Na_2CO_3 solution and 0.25 ml of diluted (1:1) Folin-Ciocalteu reagent were added and the volume was brought to 25 ml with distilled water. One hour later the solutions were analyzed through a spectrophotometer (Unico 2804 UV, USA) and the concentration of polyphenols was calculated according to the absorption of reaction mixture at 730 nm. As an external standard, 0.02% gallic acid was used.

2.8.2. Antioxidant activity (AOA)

The antioxidant activity of pumpkin samples was assessed using redox titration method [21], via titration of 0.01 N KMnO4 solution with ethanolic extracts produced from pumpkin samples as described in 2.8.3. The reduction of $KMnO_4$ to colorless Mn^{+2} in this process reflects the amount of antioxidants dissolvable in 70 % ethanol. The values were expressed in mg gallic acid equivalents (GAE)·100 g^{-1} d.w.

2.8.3. Carotenoids

Carotenoid content was analyzed using quantitative TLC [21]. About 0.7 g of fresh homogenized pulp/peel samples were grinded in a mortar with acetone (3x2 mL). The resulting extract was mixed with 9 mL of hexane and washed with distilled water until disappearance of acetone odor.

The extract was quantitatively transferred to volumetric flask and the volume was adjusted with hexane to 10 mL. The solution was filtered through a small pad of anhydrous sodium sulfate. Quantitative separation of carotenoids was achieved on chromatographic paper Whatman 3A in a hexane-acetone (10:0.5) system using 0.5 mL of the extract per one chromatographic plate. Areas of individual carotenoids were cut with scissors and extracted with 3.5 ml of hexane : acetone mixture (3:0.5). The resulting solutions were subjected to spectrophotometer and the amount of individual carotenoids was determined using λmax and E1%1cm values for β-carotene, lutein, zeaxanthin and violaxanthin [22].

2.9. Statistical analysis

Data were processed by one-way analysis of variance and mean separations were performed through the Duncan multiple range test, with reference to 0.05 probability level, using SPSS software version 21. Data expressed as percentage were subjected to angular transformation before processing.

3. Results and discussion

3.1. Yield and Biometrical parameters

The yield parameters of *Cucurbita* species investigated indicate that *C. ficifolia* is a late-ripening species with higher yield, fruit number and mean weight compared to *C. maxima* and *C. moschata* (Table 2), as also reported previously [23, 24].

Table 2. Yield and Biometric parameters of Cucurbita plants

	C. ficifolia	*C. maxima*	*C. moschata*
Number of fruits per plant	4.5±0.2a	2.5±0.5b	3.5±0.5ab
Yield (t ha^{-1})	91±4a	62.5±1.5b	57.5±1.5c
Fruit weight (kg per plant)	16±8a	11±3b	7±1c
Mean fruit weight (kg)	3.8±0.3b	4.9±0.4a	2.5±0.3c

Along each line, values with the same letter do not differ statistically according to Duncan test at $p<0.05$.

Indeed, at the end of vegetation period *C. ficifolia* main shoot length varied from 335 to 1000 cm, the leaves number and plant leaves area reached 135-354 and 12.3-17.8 m^2 respectively, while the total length of all shoots per plant varied from 19.4 to 183.1 m and the number of side shoots per plant ranged from 10 to 37.

Significantly lower concentrations of dry matter were also recorded in *C. ficifolia* fruit pulp and peel compared to the same parameters of *C. maxima* and *C. moschata* (Fig. 1).

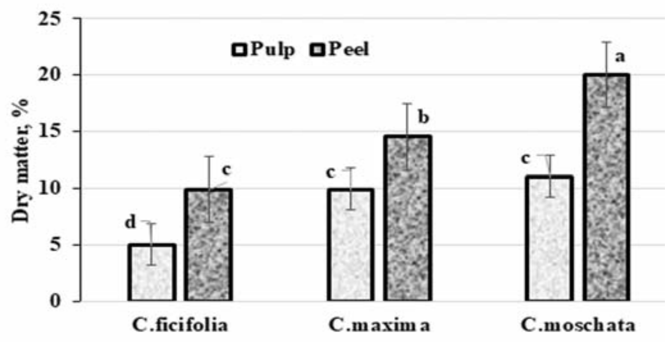

Fig. 1. Dry matter content in C. ficifolia, C. maxima and C. moschata fruit

Among other peculiarities of *C. ficifolia*, there is the unusual high level of monosaccharides in fruit peel, not statistically different from the values detected in fruit pulp (Table 3). Table 3 data indicate that the amount of peel monosaccharides decreases according to: *C. ficifolia* > *C. maxima* > *C. moschata.* On the contrary, peel disaccharides content was the highest in *C. moschata* fruit and the lowest in *C. ficifolia.* Consequently, monosaccharide peel/pulp ratio increased according to: *C. ficifolia* < *C. maxima* < *C. moschata* and decreased for disaccharide ratio: *C. ficifolia* > *C. maxima* > *C. moschata,* while pulp total soluble sugar content was rather stable between the species investigated, consistently with the literature reports [1]. The higher levels of disaccharides in *C. moschata* fruit compared to *C. maxima* is in agreement with previous findings [25]. The high monosaccharide accumulation in *C. ficifolia* peel may reflect a protection effect of these compounds as natural osmolytes.

The present results indicate that the revealed differences in mono- and di-saccharide peel/pulp distribution is of great significance, suggesting the peculiarities of pumpkin carbohydrate metabolism and high nutritional value of *C. ficifolia* peel.

3.2. Antioxidants

3.2.1. Carotenoids

The main antioxidants of *Cucurbita* fruit include carotenoids and polyphenols [1]. The orange or red colored pumpkin fruits of *Cucurbita maxima* L. and *C. moschata* L. are valuable sources of powerful antioxidants, and particularly carotenoids of vegetables pulps or vegetable juices [26]. The importance of antioxidant consumption relates to their health preservation by preventing oxidative damages leading to cancer, premature aging, cataracts, age-related macular degeneration, atherosclerosis, and a series of other degenerative diseases [27]. Depending on the pumpkin species, carotenoids may be either represented by a rather complex mixture, including beta-carotene, lutein, zeaxanthin and violaxanthin, unevenly distributed between pulp, peel, and placenta (Fig. 3a), or contained only in pulp and placenta (Fig, 3b), or absolutely absent in the fruit, as can be recorded in *C. ficifolia*. Notably, *C. maxima* cv Konfetka, a Russian selection, reportedly contains exclusively lutein in pulp [28].

Table 3. Peel/pulp distribution of sugars in C. ficifolia, C. maxima and C. moschata fruit

Cucurbita species	Fruit part	Monosaccharides (%)	Disaccharides (%)	Total sugars (%)
C. ficifolia	Pulp	23.7±2.1ab	22.5±2.0b	45.2±4.1b
	Peel	20.0±1.7b	3.3±0.9d	23.3±2.1d
	Pulp/peel ratio	1.185	6.818	1.940
C. maxima	Pulp	26.6±2.2a	22.4±2.0b	49.0±4.2ab
	Peel	17.0±1.1c	8.9±0.8c	25.9±2.1d
	Pulp/peel ratio	1.565	2.517	1.892
C. moschata	Pulp	19.9±1.6bc	38.0±3.1a	57.9±5.2a
	Peel	7.6±0.6d	26.4±2.2b	34.0±3.0c
	Pulp/peel ratio	2.618	1.439	1.70

Within each column, values with the same letters do not differ statistically according to Duncan test at $p<0.05$

Pectin accumulation is a valuable characteristic of Cucurbuta fruit. Among the three *Cucurbita* species investigated, *C. maxima* demonstrated the highest content of pectin, whereas rather similar values of pulp pectin content were recorded in *C. ficifolia* and *C. moschata* fruit (Fig. 2).

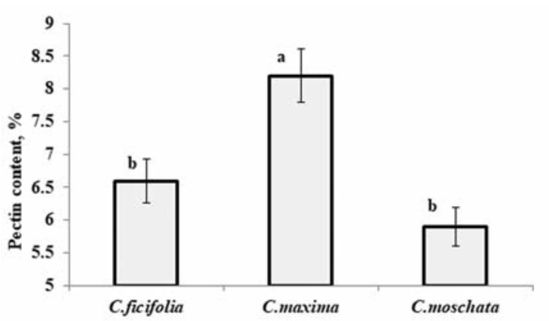

Fig. 2. Differences in pectin content in C. ficifolia, C. maxima and C. maschata fruit pulp

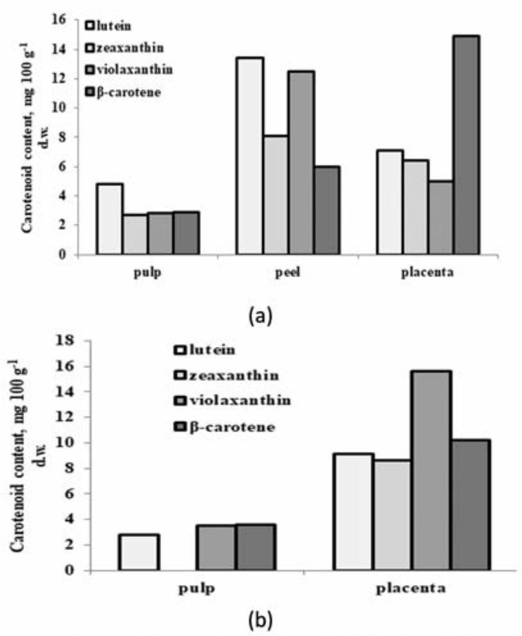

Fig. 3. Carotenoid composition of Cucurbita maxima fruit (cv Spasitelnitsa) (a) and Cucurbita moschata (cv Pingvin) (b)

Despite the great variability of carotenoid content in *Cucurbita* fruit and the report that *C. maxima* accumulates predominantly β-carotene and *C. moschata* – lutein [29], the results of the present research suggest that placenta is a richer source of carotenoids compared to pulp and peel.

The importance of these compounds in plant antioxidant defense may be illustrated by the highest levels of carotenoids in pumpkin fruit placenta (Fig. 3).

3.2.2. Polyphenols (TP) and total antioxidant activity (AOA)

Phenolic compounds can strengthen the activity of other reducing agents, especially lipid soluble vitamins, and often function as a group of reducing agents. They act via different patterns, for example, enhance the dissimilation of free radicals to compounds of a virtually lower reactivity, by inhibiting or enhancing the activity of enzymes, chelating metals, and 'scavenging' free radicals [30].

In this respect, *C. ficifolia* is more dependent on phenolic content for the maintenance of antioxidant defense, because it lacks carotenoids in fruits. Nevertheless, the total antioxidant activity (AOA) and polyphenol concentration was either not significantly different or lower in fruit of *C. ficifolia* compared to *C. moschata* and *C. maxima* (Table 4). On the other hand, taking into account the higher yield and fruit number per plant, the values detected in *C. ficifolia* fruit are valuable. Contrary to *C. maxima and C. moschata, C. ficifolia* showed its peel AOA exclusively due to TP accumulation, whereas in the other two species polyphenols reached only 61.5-63.0% of peel total antioxidant activity (AOA) (Table 4). The opposite situation was recorded in placenta: while *C. ficifolia* fruits were characterized by relatively small participation of TP in placenta AOA (about 59%), in *C. maxima* and *C. moschata* fruits about 94-96% of placenta AOA relates to polyphenols accumulation (Table 4). In general, lower levels of phenolics were recorded in placenta of *C. ficifolia* compared to those of *C. moschata* and *C. maxima.* Notably, *C. ficifolia* and *C. maxima* demonstrated similar levels of AOA in peel and pulp.

3.3. Elemental composition

Taking into account the results of the above-described comparison between *C. ficifolia*, *C. moschata* and *C. maxima*, differing in the amount of carotenoids, an important role of macro- and micro- elements in maintaining Cucurbita health may be supposed. Though total dissolved compounds (TDS) in Cucurbita fruit prevailed in pulp compared to peel, the differences between TDS peel and pulp values are much smaller in *C. ficifolia* fruit than in that of *C. maxima* and *C. moschata* (Fig. 4).

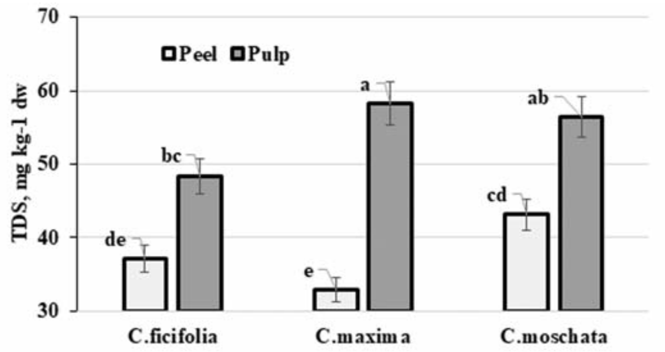

Fig. 4. Total dissolved compounds content in Cucurbita fruit

The elemental composition of pumpkin fruit presented in Table 5 and Fig. 5-6 indicates even more interesting peculiarities. Indeed, all the three species accumulated predominantly P, Mg, Al, Cu, V, Fe, Mn and Mo in peel, K, Li, Si and Se in pulp, while Cd was equally distributed between peel and pulp. On the contrary, *C. ficifolia* fruit showed equal peel/pulp content of Ca, Cr, Sr, Ni and Zn, contrary to *C. maxima* and *C. moschata* characterized by significantly higher concentrations of these elements in peel. Furthermore, *C. ficifolia* demonstrated predominant pulp accumulation of B; the distribution of the latter element in peel and pulp of *C. maxima* and *C. moschata* fruit was rather similar. The highest concentrations of I, Si, Sr

Table 4. Total antioxidant activity and phenolics content in pulp, peel, and placenta of C. ficifolia, C. maxima and C. moschata fruit

Cucurbita species	Fruit part	AOA (mg GAE g^{-1} DW)	TP (mg GAE g^{-1} DW)	TP (% in the total AOA)
C. ficifolia	Pulp	17.3±1.2c	11.3±0.9f	65.3
	Peel	16.5±1.1c	15.6±1.0e	94.5
	Placenta	34.1±3.0a	20.0±1.7bc	58.7
C. maxima	Pulp	23.0±2.1b	18.5±1.3cd	80.4
	Peel	26.2±2.1b	16.5±1.1d	63.0
	Placenta	36.2±3.1a	34.8±3.0a	96.1
C. moschata	Pulp	17.5±1.2c	15.7±1.2e	89.7
	Peel	27.5±2.2b	16.9±1.1de	61.5
	Placenta	25.5±2.1b	23.9±2.0b	93.7

Within each column, values with the same letters do not differ statistically according to Duncan test at $p<0.05$

and Mn were recorded in *C. ficifolia* pulp. Taking into account the protective role of Si in plants against biotic and abiotic stresses [31, 32], this element may be supposed to play a significant role in *C. ficifoliar* integrity.

Furthermore, the mentioned phenomena may become of practical significance for more targeted applications of *C. ficifolia* pulp and peel as sources of Ca, Sr, Cr, Si and I. In this respect, Ca, Si and Sr are valuable for bone health, I contributes to improve human immunity, whereas Cr is closely connected with the protection of human organism against diabetes [33, 34]. Indeed, the results of high Cr accumulation in C ficifolia is in accordance with the protective effect of *C. ficifolia* fruit against diabetes [35].

Taking into account the high moisture content of *C. ficifolia*, it may be hypothesized the use of the whole fruit of this plant for production of beverages with high nutritional value, which is consistent with the Chinese patent describing *C. ficifolia*/maca wine receipt (CN201510433999.3A).

Table 5. Pulp and peel elemental composition of C. ficifolia, C. maxima and C. moschata

Element	*C. ficifolia*		C. maxima		C. moschata	
	pulp	peel	pulp	peel	pulp	peel
Macroelements (g kg^{-1} dw)						
Ca	5.030b	4.746b	1.801d	6.430a	1.344e	3.369c
K	27.241a	14.888c	28.444a	21.019b	31.387a	17.527bc
Mg	2.473c	4.533b	1.386d	6.247a	1.425d	4.437b
Na	23.25d	59.39ab	63.61a	49.59b	17.9e	38.62c
P	3.305d	5.970b	3.599d	10.257a	4.584c	10.471a
Al, As and heavy metals (mg kg^{-1} dw)						
Al	3.27d	4.74c	5.49c	11.18ab	9.4b	12.45a
As	0.008ab	0.006bc	0.01a	0.01a	0.005c	0.01a
Cd	0.04ab	0.03b	0.04ab	0.05a	0.006c	0.008c
Cr	1.49b	1.47b	0.97c	2.38a	0.76c	1.37b
Cu	2.24d	5.49b	3.73c	8.62a	3.85c	7.55a
Ni	0.74b	0.85b	0.66b	1.41a	0.41c	0.79b
Pb	0.23a	0.22a	0.20a	0.15b	0.10c	0.16b
Sr	12.02b	14.06ab	5.35d	16.68a	3.70e	7.26c
V	0.03b	0.01d	0.02c	0.05a	0.03b	0.04ab
Microelements (mg kg^{-1} dw)						
B	27.57a	21.49b	22.7ab	25.49a	15.69c	19.39bc
Co	0.07b	0.09ab	0.09ab	0.11a	0.04c	0.07b
Fe	52.39d	70.75bc	63.66cd	95.61a	36.78e	81.84ab
I	0.39a	0.17b	0.17b	0.09c	0.12c	0.1c
Li	0.04d	0.02e	0.23a	0.08bc	0.10b	0.07c
Mn	17.9b	30.29a	4.55c	28.38a	4.03c	34.62a
Mo	0.47e	1.04c	0.83cd	2.67a	0.73d	1.45b
Se	0.03c	0.02d	0.27a	0.02d	0.02d	0.007b
Si	78.1a	12.34e	40.0bc	33.46cd	44.48b	30.52d
Zn	23,64dc	30.6d	58.25b	77.6a	25.24cd	47.91b

Along each line, values with the same letters do not differ statistically according to Duncan test at $P<0.05$

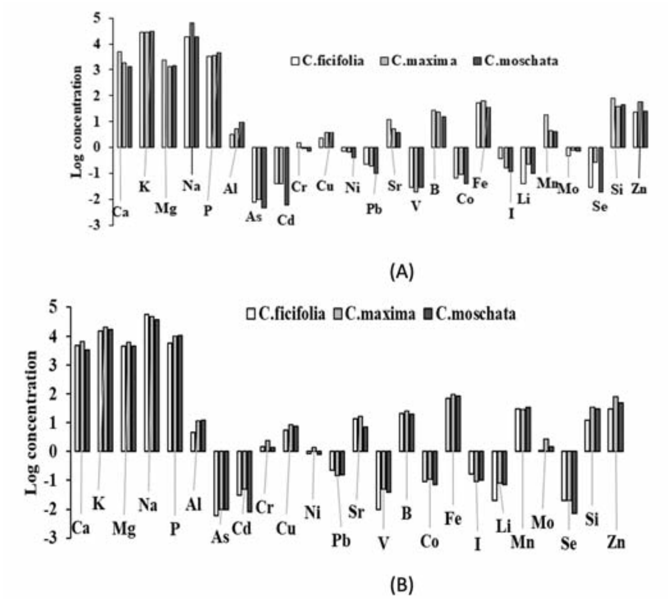

Fig. 5. Elemental profile of Cucurbita fruit: A – pulp; B – peel

The data reported in Table 5 also indicate that *C. maxima* peel is a good source of Ca, K, Mg along with Cr, Cu, Sr, Fe, Mo and Zn. Furthermore, the highest concentrations of Zn were recorded both in peel and pulp of *C. maxima*.

Peel/pulp element distribution in Cucurbita fruit is a valuable characteristic of genetic peculiarities (Fig. 6). Indeed, unusually high Mn peel/pulp ratios are recorded in *C. maxima* and *C. moschata*, Mo, Sr, Mg, Ca high peel/pulp ratios in *C. maxima*, while Cu peel/pulp ratio is the highest in *C. ficifolia*. Furthermore, the data shown in Fig. 6 indicate that in *C. ficifolia* the peel/pulp element distribution ratio is higher even compared to *C. maxima* and *C. moschata*, which is presumably connected with the significantly lower dry matter content in peel of *C. ficifolia*.

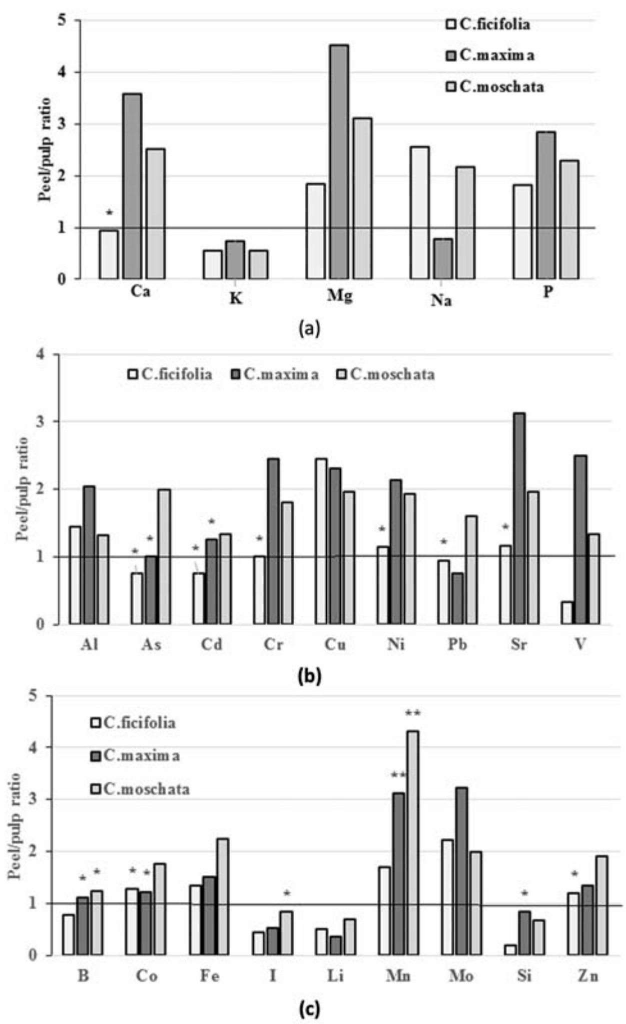

Fig. 6. Peel/pulp distribution of elements in Cucurbita fruit: (a) macro-elements; (b) As, Al and heavy metals; (c) micro-elements. * no differences between peel and pulp values; ** values are decreased twice

Table 6. Relationship between elements in C. ficifolia, C. maxima and C. moschata fruit

	Ca	K	Mg	Na	P	Al	As	Cd	Cr	Cu	Ni	Pb	Sr	V	B	Co	Fe	I	Li	Mn	Mo	Se	Si
K	-0.565	1																					
Mg	**0.817**	**-0.805**	1																				
Na	0.166	-0.487	0.321	1																			
P	0.445	-0.657	**0.844**	0.162	1																		
Al	-0.024	-0.207	0.451	-0.132	**0.835**	1																	
As	0.267	-0.182	0.337	0.425	0.460	0.305	1																
Cd	0.630	-0.035	0.292	0.487	-0.095	-0.414	0.439	1															
Cr	**0.939**	-0.526	**0.888**	0.250	0.631	0.239	0.451	0.633	1														
Cu	0.449	-0.669	0.867	0.344	**0.968**	0.786	0.440	0.023	0.660	1													
Ni	**0.861**	-0.538	0.888	0.418	0.667	0.294	0.536	0.658	0.976	0.735	1												
Pb	0.381	-0.307	0.022	0.423	-0.352	-0.775	0.188	0.545	0.154	-0.342	0.116	1											
Sr	**0.974**	-0.589	**0.802**	0.296	0.371	-0.114	0.165	0.676	0.906	0.426	**0.851**	0.412	1										
V	0.353	0.029	0.467	-0.335	0.675	0.746	0.508	0.062	0.561	0.582	0.533	-0.517	0.195	1									
B	0.732	-0.101	0.300	0.223	-0.068	-0.446	0.486	**0.883**	0.646	-0.064	0.589	0.692	0.692	0.156	1								
Co	0.668	-0.513	0.656	0.798	0.376	-0.040	0.604	**0.811**	0.756	0.514	**0.849**	0.434	0.728	0.118	0.646	1							
Fe	0.654	-0.728	**0.881**	0.590	**0.823**	0.456	0.701	0.415	**0.807**	**0.869**	**0.883**	0.119	0.631	0.459	0.373	**0.823**	1						
I	0.194	0.285	-0.371	-0.314	-0.656	-0.797	-0.123	0.331	-0.079	-0.749	-0.227	0.687	0.146	-0.292	0.608	-0.139	-0.431	1					
Li	-0.613	0.544	-0.526	0.357	-0.287	0.005	0.399	0.133	-0.409	-0.190	-0.243	-0.142	-0.578	-0.076	-0.121	0.0789	-0.114	-0.2258					
Mn	0.706	**-0.928**	**0.881**	0.226	0.771	0.337	0.286	0.044	0.674	0.713	0.634	0.223	0.655	0.279	0.226	0.446	0.760	-0.183	-0.669	1			
Mo	0.588	-0.461	**0.850**	0.329	**0.851**	0.673	0.502	0.335	**0.818**	**0.917**	**0.887**	-0.313	0.570	0.692	0.190	0.656	**0.859**	-0.616	-0.097	0.551	1		
Se	-0.472	0.406	-0.527	0.543	-0.467	-0.348	0.379	0.336	-0.375	-0.349	-0.223	0.261	-0.403	-0.363	0.115	0.239	-0.106	0.040	0.912	-0.595	-0.252	1	
Si	-0.016	0.682	-0.486	-0.645	-0.505	-0.359	0.041	0.1767	-0.123	-0.643	-0.258	0.153	-0.145	0.213	0.432	-0.36	-0.493	0.771	0.041	-0.434	-0.435	0.049	1
Zn	0.314	-0.206	0.532	0.571	0.602	0.501	0.782	0.500	0.599	0.705	0.742	-0.162	0.307	0.552	0.283	0.751	0.797	-0.545	0.421	0.226	**0.836**	0.3048	-0.320

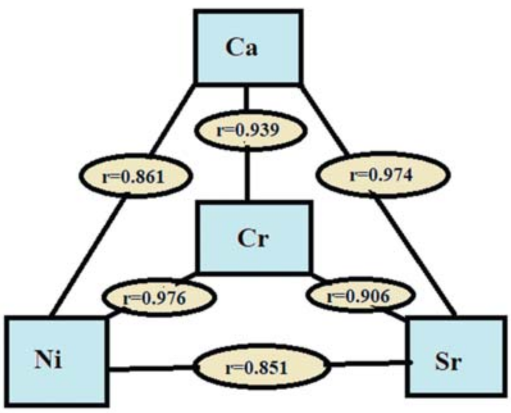

Fig. 7. The most significant relationships between elements in C. ficifolia, C. maxima and C. moschata fruits

The analysis of the relationship between elements in peel and pulp of Cucurbita fruit (Table 6) revealed significant correlations between Ca, Cr, Ni, Sr and Cu, P, Mo and Fe (Fig. 7). Participation of Fe and Cu in Mo metabolism of eukaryotes [36] reflected in Fe-Mo and Cu-Mo positive correlations.

4. Conclusion

The results of the present research demonstrate significant correlations between Cr, Ca, Sr and Ni in Cucurbita fruit, uneven element distribution between peel and pulp, reflecting genetic peculiarities of the examined species, and special distribution of polyphenols and carbohydrates between peel, pulp, and placenta with unique genetically determines parameters for each species. Further investigations on other Cucurbita representatives are needed to complete the biochemical and elemental frame of these highly valuable plants. Appropriate studies may be especially valuable with the aim to select new varieties with targeted biochemical and mineral composition and suitable for functional food production.

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