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WHOLEGRAIN FLOURS OF DIFFERENTLY COLORED MAIZE KERNELS AS MACRO- AND MICRONUTRIENT-RICH FOOD INGREDIENTS

INTEGRALNO BRAŠNO OD KUKURUZA RAZLIČITE BOJE ZRNA KAO IZVOR MAKRO- I MIKRO- NUTRIJENATA

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ABSTRACT

Four commercial wholegrain flours made from differently colored kernels of maize genotypes produced in Maize Research Institute "Zemun Polje" were used as the subject of this study. Values of major chemical components as well as mineral nutrients, antioxidants and some vitamins of wholegrain flours obtained from white dent hybrid, yellow popping maize hybrid, red dent variety and blue popping maize landrace are presented. All flours had high fiber content (6.9-10.4%), while total protein ranged from 8.5% to 12.2%. A high level of anthocyanins was determined in blue popping maize wholegrain flour (910.0 mg CGE/kg), whereas yellow popping maize flour had a high content of total carotenoids (26.5 mg βCE/kg). Total antioxidant capacity was the lowest in white (15.50 mmol Trolox Eq/kg) and the highest in blue popping maize flour (37.6 mmol Trolox Eq/kg). All investigated wholegrain flours contained high levels of potassium and magnesium, as well as high content of trace elements, namely iron, zinc, copper and manganese. The maize flour is naturally gluten-free, which makes it highly suitable for persons susceptible to a gluten allergy and those with celiac disease. These results indicate that the wholegrain ZP maize flours can be used as functional food ingredients.
Keywords: *wholegrain maize flour, macro- and micro-nutrients, functional food.*

REZIME

Kao predmet ovog istraživanja korišćena su četiri komercijalna integralna brašna dobijena od genotipova kukuruza različite boje zrna proizvedenih u Institutu za kukuruz „Zemun Polje“. Prikazane su vrednosti glavnih nutritivnih parametara kao i mineralnih materija, antioksidanata i pojedinih vitamina integralnog brašna dobijenog od hibrida belog zubana, hibrida kukuruza žutog kokičara, sorte crvenog zubana i populacije kukuruza plavog kokičara. Sva brašna su imala visok sadržaj vlakana (6,9-10,4%), dok se sadržaj proteina kretao od 8,5% do 12,2%. Visok nivo antocijana utvrđen je u integralnom brašnu kukuruza plavog zrna (910,00 mg CGE/kg, pri čemu je u žutom kukuruznom brašnu utvrđen visok sadržaj karotenoida (26,5 mg βCE/kg). Ukupni antioksidativni kapacitet bio je najniži u belom (15,50 mmol Trolox Ek/kg), a najviši u plavom kukuruznom brašnu (37,60 mmol Trolox Eq/kg). Sva ispitivana integralna brašna sadržala su visok nivo kalijuma i magnezijuma, kao i visok sadržaj mikroelemenata, odnosno gvožđa, cinka, bakra i mangana. Ovi rezultati ukazuju da se integralna ZP kukuruzna brašna mogu koristiti kao funkcionalni sastojci hrane.
Ključne reči: *integralno kukuruzno brašno, makro- i mikro-nutrijenti, funkcionalna hrana.*

INTRODUCTION

Dietary preferences have changed tremendously worldwide in recent years because of the increasing consciousness about the strong relationship between nutrition and human health. The global functional flour market has lately been fast increasing and is expected to reach $91.23 billion by 2023 (*Statistics Market Research Consulting, 2017*). One of the factors urging the growth of the global functional flour market is gluten-free flour (*Rosell et al., 2014*).

Considering that a significant part of the population, primarily in the underdeveloped parts of the world, uses maize as the main bread grain, and bearing in mind that people in developed parts of the world live in an era of using functional "healthy" foods, the nutritive value of maize flour is very important. Apart from being of utmost importance for the nutritive value of the maize-based food and feed, the chemical composition of the maize grain dictates the direction in breeding new hybrids as well as upgrading the processing and utilization of this valuable cereal crop (*Radosavljević et al., 2015; Milašinović-Šeremešić et al., 2018; Radosavljević et al., 2020*). Dietary fiber, proteins, and bioactive phytochemicals present in these wholegrain flours, which could be either incorporated into the diet or be a part of the food itself, can be the source for gaining long-term health benefits (*Nikolić et al., 2020*). In the developing parts of the world, cereals represent the basis of an everyday diet and the main source of energy. However, cereals such as maize are usually low in micronutrient content, especially after processing by milling which removes the germ and bran - parts of the grain that abound in fiber and micronutrients (*Dunn et al., 2014*).

Studies have shown that the incorporation of whole grains, which include bran, germ, and endosperm, in the diet may provide many benefits for human health. The majority of vitamins, minerals, dietary fiber, as well as phytochemicals are mostly located in the outer layers of the grain (pericarp and aleurone) which are typically removed during grain milling and production of cereal flour (*Francavilla and Joye, 2020; Gani et al., 2012*). Wholegrain gluten-free flour produced from differently colored maize grains can be an excellent choice for improving nutrition by exhibiting some desirable health benefits and preventing nutrition-related diseases. The bioactive compounds present in the aleuronic and pericarp layer of the grain, provide the characteristic blue, red, purple, and black color to the maize genotypes and possess antioxidant properties (*Simić et al., 2021*). Up to now, out of all the colored cereals, maize and rice have mostly been utilized in the preparation of foods for human consumption. Specifically, blue and purple maize grains are used for blue and pink tortillas, while red rice is used in the production of commercial infant cereals (*Hirawan et al. 2011*).

The maize grain consists of the major chemical components, predominantly starch (71.3 %), followed by protein (9.91 %), oil (4.45 %), ash (1.42 %), and crude fiber (2.66 %) (*Eckhoff and Watson, 2009*). Because of the substantial and extensive application of maize grain in numerous food products, this cereal makes a significant source of these macronutrients (*Radosavljević et al., 2020)*. Furthermore, maize grain is also a rich source of bioactive components or micronutrients which have a role in the prevention of heart disease, cancer, and osteoporosis, as well as control of biological processes in the body and slowing down aging. Maize grain is a significant source of vitamin B1, B2, B5, B12, and vitamin E, β-carotene - a provitamin of vitamin A, also has high phenolic content compounds (among other anthocyanins), which have the role of antioxidants as well as minerals potassium (K) and magnesium (Mg) (*Farré Martinez, 2012*). Apart from the significant nutritional value the bioactive components of the maize grain can provide both health and economic benefits, which potentially could be utilized to add even more value to this grain (*Mladenović-Drinić et al., 2019*). This study aimed to examine the chemical composition of differently colored maize kernel wholegrain flours to asses and compare their nutritional potentials.

MATERIAL AND METHODS

Four commercial wholegrain flours made from differently colored kernel maize genotypes produced at the Maize Research Institute were used in this study. The maize hybrids developed at the Maize Research Institute, Zemun Polje, were sown at the location of Zemun Polje, Serbia (44°52´N, 20°19´E, 81m asl). The milling process was performed using a custom-made cereal stone mill, with a capacity of approximately 100 kg/h of maize grain (particle diameter ≤1.7 mm) in the production plant of the Maize Research Institute. The plant material used for the production of the wholegrain flour included: yellow popcorn hybrid ZP 611k, red dent variety ZP Rumenka, white dent hybrid ZP 552b, and a blue popping maize landrace. The basic chemical composition was determined according to the standard laboratory methods (*AOAC, 2000*), and the results were expressed as averages of at least three repetitions in % per dry matter (d.m.) ± standard deviation. The contents of different fatty acids were determined according to *ISO 12966-2* (*2011*). The energy value was calculated from the content of individual chemical components of the flour using an accredited *in-house* laboratory method HEM-03-059 of the Center for Food Examination (CIN) (*ATS, 2021*). The total anthocyanins content was determined spectrophotometrically according to the method by *Abdel-Aal & Hucl (1999)* modified as described by *Žilić et al (2012)* and expressed as mg of cyanidin 3-glucoside equivalent (CGE) per kg of dry matter. The total carotenoids were extracted and analyzed according to procedures described by *Žilić et al. (2012)* and expressed in mg of β-carotene equivalent (βCE) per kg of dry matter. The total antioxidant capacity was measured according to the direct or QUENCHER method as described by *Serpen et al. (2008)* and expressed as the Trolox equivalent antioxidant capacity (TEAC) and given as mmol of Trolox per kg of dry matter (mmol Trolox Eq /kg). The content of total tocopherols was determined by the HPLC method, by applying the extraction procedure with n-hexane, as described by *Žilić et al. (2015),* and niacin content according to a method described by *Žilić et al (2014)*. The contents of micronutrients were determined by atomic absorption spectrometry after microwave digestion after the methodology introduced by *Skoog et al., (2017)* and *Jorhem et al. (2000)*.

Fig. 1. Maize grain and the wholegrain maize flours: white dent, yellow popping, red dent and blue popping maize, respectively

RESULTS AND DISCUSSION

The nutritive value of the food product is best described by its basic chemical composition, i.e. the content of macronutrients. The results of the chemical composition of the investigated maize flours are shown in Table 1. Carbohydrates, predominantly starch, are the prevailing macronutrients of the maize grain (*Milašinović-Šeremešić et al., 2021*). The carbohydrate content ranged from 61.3±0.3% in blue popping maize flour to 69.1±0.3% in red dent maize flour. The blue popping maize flour showed the highest content of protein (12.2±0.4%), fiber (10.4±0.5%), oil (4.5±0.5%), and monounsaturated fatty acids (1.3±0.03%). The energy value did not differ significantly among the maize flours, as seen in Table 1. Beneficial health effects of dietary fiber, for example, the reduction of cholesterol, modification of the glycemic and insulinemic responses, changes in intestinal function, and antioxidant activity have made them an important ingredient in modern day-to-day nutrition (*Reyes-Caudillo et al., 2008*). Moreover, dietary fiber comprises different plant carbohydrate polymers including cellulose, hemicellulose, pectins, and gums that can be linked with lignin and other non-carbohydrate constituents (*Nikolić et al., 2020*). The results shown in Table 1 are in accordance with previously reported findings (*Radosavljević et al., 2015; Milašinović-Šeremešić et al., 2018; Radosavljević et al., 2020*).

Table 1. Chemical composition and energy value of the investigated maize flours

	Wholegrain flour			
Nutrient	White dent maize	Yellow popping maize	Red dent maize	Blue popping maize
Protein (%)	9.1±0.3	11.0±0.3	8.5±0.4	12.2±0.4
Total carbohydrates (%)	68.9±0.4	67.1±0.5	69.1±0.3	61.3±0.3
Total sugar (%)	1.7±0.1	1.2±0.1	1.7±0.1	2.2±0.1
Fiber (%)	6.9±0.3	7.1±0.3	7.3±0.4	10.4±0.5
Oil (%)	4.0±0.1	3.5±0.2	3.8±0.2	4.5±0.5
Saturated fatty acids (%)	0.6±0.02	0.5±0.02	0.5±0.03	0.8±0.04
Monounsaturated fatty acids (%)	0.9±0.03	1.2±0.01	1.2±0.02	1.3±0.03
Polyunsaturated fatty acids (%)	2.5±0.1	1.8±0.1	2.0±0.2	2.4±0.2
Energy value, KJ/100g	1514±3.1	1514±2.5	1517±1.7	1499±2.2

Maize oil is accounted as one of the high–quality plant-based oils that can show some health benefits such as lowering blood cholesterol levels and preventing the hardening of the arteries, as well as reducing the risk of heart disease. Numerous studies have shown that the grain of modern maize hybrids on average contains 4 - 5% oil (*Eckhoff and Watson, 2009; Laurie et al., 2004)*. The predominant are triglycerides (99%), of which 59% are present in the form of polyunsaturated fatty acids, 24% as monounsaturated, and 13% as saturated fatty acids. The carbon chains of these fatty acids range from 12 to 24, namely palmitic (16:0), stearic (18:0), oleic (18:1) and linoleic acid (18:2). The presence of unsaturated fatty acids in maize oil increases its quality by large, which influences the trends in novel maize breeding programs (*Orhun and Korkut, 2011*).

Table 2. Content of bioactive components and antioxidant capacity determined in maize flours

	Wholegrain flour			
Nutrient	White dent maize	Yellow popping maize	Red dent maize	Blue popping maize
Total anthocyanins (mg CGE/kg)	/	/	22.5±2.7	910.0±10.6
Total carotenoids (mg βCE/kg)	/	26.5±1.2	/	/
Tocopherols (mg/kg)	36.0±0.4	41.0±0.4	/	/
Niacin (vitamin B3) (mg/100g)	12.5±0.02	10.1±0.08	/	/
Potassium (K) (mg/100g)	356.0±7.2	294.0±6.3	299.0±6.1	346.0±7.4
Magnesium (Mg) (mg/100g)	138.0±4.3	119.0±2.1	110.0±1.7	109.0±3.2
Sodium (Na) (g/100g)	<10	<10	<10	42.2±0.4
Iron (Fe) (mg/kg)	28.4±0.2	19.4±0.2	15.4±0.1	22.1±0.3
Zinc (Zn) (mg/kg)	22.9±0.4	17.3±0.2	15.2±0.2	16.0±0.0
Copper (Cu) (mg/kg)	1.3±0.01	1.3±0.01	1.6±0.02	1.2±0.01
Manganese (Mn) (mg/kg)	5.9±0.07	7.6±0.06	3.6±0.05	8.1±0.03
CGE – cyanidin-3-glucoside equivalent; βCE – β-carotene equivalent				

In contrast to carotenoids that contribute to the standard yellow-amber color of the grains, the anthocyanins, present in the aleuronic or pericarp layer of the kernel, are in control of the color of pigmented grains, which can vary from blue to purple, and red (*Ficco et al., 2014*). The total anthocyanins determined in the blue popping maize wholegrain flour amounted to 910.0 mg CGE/kg (Table 2). This anthocyanin content is comparable to that of some red fruits and berries. For example, the highest average content of anthocyanins (2,000 - 10,000 µg CGE/g d.m) is present in chokeberries, black and red currants from (800 - 4,000 µg CGE/g d.m), blueberries (250 - 5,000 µg CGE/g d.m), blackberries from (800 - 3,000 µg CGE/g d.m) and raspberries (100 - 600 µg CGE/g d.m) (*Žilić et al., 2019*). Previous findings by *Žilić et al. (2012)* reported that the red and blue-colored maize kernels contained a wide range of total anthocyanins (2.50 to 696.07mg CGE/kg d.m), while cyanidin 3-glucoside was the prevailing form of anthocyanins in these maize kernels.

The carotenoids were determined only in wholegrain flour produced from yellow kernel popping maize (26.5±1.2 mg βCE/kg), while tocopherols were detected in the red dent and blue popping maize wholegrain flours (Table 2). A study conducted by *Mladenović-Drinić et al. (2019)* also reported that carotenoids were not present in the investigated white maize inbred lines which was explained by the presence of a recessive gene that controls the first step in the carotenoid synthesis pathway. Similarly, these researchers found that standard yellow/orange kernel dent and popcorn genotypes had a higher content of carotenoids, predominantly β-carotene, lutein, and zeaxanthin. Furthermore, *Mladenović-Drinić et al. (2021)* found high contents of carotenoids and tocopherols in sweet maize hybrids, which were by large genotype-dependent.

Niacin, also known as vitamin B3, an important nutrient that helps in lowering cholesterol levels, easing arthritis, and boosting brain function, was determined only in white (12.5 ±0.02 mg/100g) and yellow (10.1±0.08 mg/100g) wholegrain flour. Furthermore, *Dunn et al. (2014)* reported comparable values of this vitamin determined in field maize, as well as values of iron, magnesium, potassium, sodium, and zinc, which are in accordance with our findings presented in Table 2. Apart from these macro- and micronutrients, cereal grains such as maize also contain significant amounts of phytate (4–9 g/kg), a compound that inhibits the absorption of minerals, especially iron, calcium, and zinc (*Boyer and Shannon, 2003*).

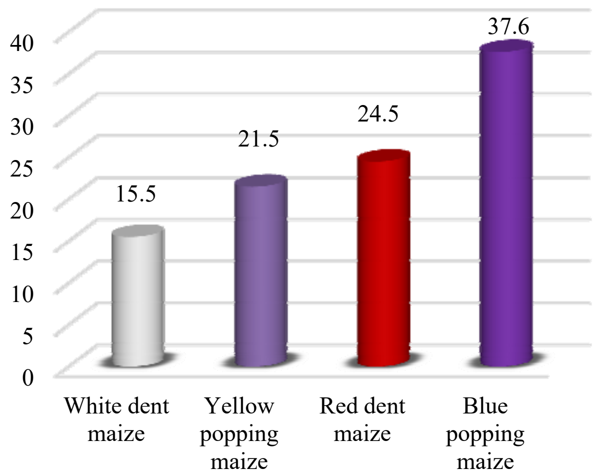

Fig. 2. Total antioxidant capacity (mmol Trolox Eq/kg)

The total antioxidant capacity determined in the investigated wholegrain maize flours ranged from 15.5±0.3 mmol Trolox Eq/kg in white to 37.6±0.2 mmol Trolox Eq/kg in flour obtained from blue popping maize grain (Figure 2). According to the obtained results, a higher content of bioactive compounds such as anthocyanins, tocopherols, and carotenoids in the maize grain has influenced their respective antioxidant capacity.

CONCLUSION

The results of this study have shown that wholegrain flours of differently colored maize kernels can be used as valuable ingredients for the preparation of various traditional and functional food products. Blue popping maize showed exceptionally high antioxidant capacity. The anthocyanins were detected in red and blue wholegrain maize flour, while white and yellow flours had a significant content of tocopherols. According to the literature, the abundant content of dietary fiber, as well as bioactive compounds determined in these gluten-free wholegrain flours, may provide several health benefits to consumers. The differences in the macro- and micro-nutrient composition of the differently colored wholegrain maize flours open up different possibilities for their utilization.

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