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Effects of baking conditions and dough formulations on phenolic compound stability, antioxidant capacity and color of cookies made from anthocyanin-rich corn flour

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ABSTRACT

In this study, the effect of baking conditions and dough formulations on phenolic compounds, antioxidant capacity and color of cookies made from anthocyanin-rich corn flour were investigated. The control cookies were prepared from dark-red popping corn, blue popping corn and blue-standard corn flour according AACC method 10–54 and baked at 200 °C for 7 and 10 min. In control corn cookies, the content of total flavonoids and anthocyanins, as free water-soluble phenolic compounds, was reduced by applied baking conditions. Our results show that citric acid significantly increased the total flavonoids and anthocyanins content in the cookies prepared from blue popping corn and blue-standard corn. Compared with the control cookies baked at 200 °C for 7 min, the cookies prepared with 0.5 g/100 g added citric acid and baked at 150 °C for 12 min had higher contents of total flavonoids and anthocyanins by 60 and 70%, respectively. However, as a result of Maillard reaction inhibition at low pH, antioxidant capacity of anthocyanins-rich blue popping corn and blue standard corn cookies with 0.5 and 1 g/100 g citric acid was lower by 56 and 39%, respectively, compared to antioxidant capacity of their control cookies baked at 200 °C for 10 min.

1. Introduction

From the market standpoint, attractive and stable color is the important sensory property of foods. In recent years, the food industry has been increasingly using various natural colorants of plant origin that have both coloring and antioxidant properties. Contrary to the artificial additives, natural colorants have attracted considerable interest due to their presumed safety, as well as potential health effects. However, the incorporation of natural colorants to food systems is a certain challenge due to their low stability regarding the factors such as light, oxygen, temperature and pH (Bąkowska-Barczak, 2005).

In addition to the carotenoids and betalains, flavonoids/anthocyanins are the main class of plant pigments (Tanaka, Sasaki, & Ohmiya, 2008) that have found usage in functional food systems due to their antioxidant properties and potential health benefits. Summing up the results of many studies, He and Giusti (2010) reported that anthocyanins possess anti-inflammatory and anti-carcinogenic activity, cardiovascular disease prevention, obesity control and diabetes alleviation properties. As a class of flavonoids, anthocyanins are water-soluble glycosides with a flavylium nucleus that provide a wide spectrum of colors ranging from red to purple/blue. Anthocyanin pigments are labile compounds. Their structures, stability and specific color of anthocyanins depend on co-pigments, sugars, metal ions, oxygen, temperature and pH (Stintzing, Stintzing, Carle, Frei, & Wrolstad, 2002). Generally, increasing hydroxylation of the B-ring shifts anthocyanins to bluer shades, while the presence of many methoxyl groups shifts the color towards red (Grotewold, 2006). At the same time, instability has the direct relation with the number of hydroxyl groups and the indirect with the number of methoxyl groups (Brouillard, 1982). The glycosylation level also affects stability. Diglucosides are more stable than monoglucosides. Nevertheless, due to the presence of additional sugar molecules, browning is more pronounced in the diglucosides (Delgado-Vargas, Jiménez, & Paredes-López, 2000). In addition, color of foods rich in pelargonidin, cyanidin or delphinidin is less

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stable than that of food containing petunidin or malvidin aglycones (von Elbe & Shwartz, 1996). Indeed, a major problem for the food industry is the thermal degradation of anthocyanins whose extent during heating depends on both the specific composition of anthocyanins and the characteristics of the food matrix. The presence of the sucrose (Nikkhan, Khaymay, Heidari, & Jamee, 2007), reducing sugars and Maillard reaction products (Debicki-Pospi, Lovri, Trinajsti, & Sablji, 1983), as well as ascorbic acid (De Rosso & Mercadante, 2007), and phenolic compounds (Galli & Clemente, 2013), may alter degradation kinetics. According to Li, Walker, and Faubion (2011) acylation of anthocyanins with organic acids improves color and pigment stability.

As a gluten-free, corn is one of the grains suitable for celiac consumption and, together with rice, the most cultivated cereal in the world (de la Hera, Talegón, Caballero, & Gómez, 2014). Among cereals, pigmented corn is the most important sources of anthocyanins. Simple or acylated, anthocyanins are mainly located in the aleurone layer or pericarp of the corn endosperm, greatly affecting the color and antioxidant capacity of the kernels (Betran, Bocholt, & Rooney, 2000). According to our previous research (Žilić, Serpen, Akıllıoğlu, Gökmen, & Vančetović, 2012), the corn kernels having red and blue colors were found to contain a wide concentration range of total anthocyanins with cyanidin 3-glucoside (Cy-3-Glu) as the most dominant form. However, given that corn-based foods have to be thermally processed prior to consumption, the thermal degradation of anthocyanins and other phenolic compounds is a major problem in the use of pigmented corn as raw materials in the baking and confectionery industry. Among bakery products, cookies could easily be fortified with polyphenols to promote health and reduce disease risk. Recently, refined wheat flour is being partially replaced by ingredients such as anthocyanins-rich fruits or tea extract (Mildner-Szkudlarz, Zawirska-Woitasiak, Obuchowski, & Gośliński, 2009; Pasqualone et al., 2014). In this study, red and blue corn flours were used for functional cookie preparation. The objective was to determine the effect of baking conditions, such as baking time and temperature, as well as dough formulations on the content of phenolic compounds, antioxidant capacity and color of cookies made from anthocyanin-rich corn flour. The primary goal was to establish the effect of citric acid on the anthocyanins stability in corn cookies in order to assess the organic acid usefulness as an ingredient of bakery foods.

2. Materials and methods

2.1. Chemicals and consumables

The chemicals of analytical grade such as Folin-Ciocalteau reagent (2 N), gallic acid, 6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), 2,2′-azino-bis/3-ethyl-benzothiazoline-6-sulfonic acid (ABTS), ferulic acid, p-coumaric acid, as well as methanol and acetonitrile for HPLC gradient grade were purchased from Sigma–Aldrich (Steinheim, Germany). Formic acid (reagent grade) was purchased from JT Baker (Deventer, Holland). Sodium hydroxide, sodium carbonate, hydrochloric acid (12 mol/L), pure ethyl acetate and pure diethyl ether were purchased from Merck (Darmstadt, Germany). Potassium peroxydisulfate was purchased from Fluka Chemie AG (Buchs, Switzerland). Syringe filters (nylon, 0.45 μm) were supplied by Thermo Scientific (Waltham, MA, USA).

2.2. Flour samples and cookie ingredients

Blue popping corn (*Zea mays* L. spp. Everta), dark-red popping corn (*Z. mays* L. spp. Everta) and blue standard corn (*Z. mays* L.) genotypes were developed in the Maize Research Institute (MRIZP) in Belgrade, Serbia. Whole grain flours were produced at the laboratory by Perten 120 lab miller (Perten Ins., Sweden) (particle size < 500 μm). Sodium chloride, ammonium bicarbonate, sodium bicarbonate, sucrose, nonfat dry milk and high fructose corn syrup used in the formulation of cookies were obtained from local producers.

2.3. Preparation of cookies

The cookies were prepared in four recipes according to the AACC Method 10–54 (2000) with modifications as given in Table 1. All ingredients were mixed thoroughly in accordance with the AACC Method 10–54 procedure using the Kitchen Aid 5KSM150 dough mixer. Dough was rolled out to disks with a diameter of 5 cm and a height of 3 mm, and baked in the oven (Memmert, UNE 400) at 200 °C for 7 and 10 min. The cookies prepared by the modified recipes were baked at 150 °C for 12 min. All baking experiments were performed in duplicate. Dough and cookies are shown in Fig. 1. During the research, several recipes have been developed and various baking conditions were used. In order to keep the number of recipes/samples affordable, analyzes were performed on samples of cookies which, to visual assessments, had a satisfactory color and textural properties.

2.4. Extraction of total phenolic compounds from cookies

Phenolic compounds in the corn cookies samples were extracted according to the procedure described by Antoine, Peyron, Lullien-Pellerin, Abecassis, and Rouau (2004). Total phenolics in 500 mg of samples were released by alkaline hydrolysis for 4 h at room temperature using 10 mL of 4 mol/L NaOH. After the pH was adjusted to 2.0 by 6 mol/L HCl, 5 mL of all the hydrolyzates were extracted with 5 mL of ethyl acetate and diethyl ether (1:1, mL:mL) for four times. Five mL of combined extracts were evaporated under N_2 stream at 30 °C to dryness. Final residues were redissolved in 1.5 mL of methanol. Such prepared methanolic solutions were used for the analyses of total phenolic compounds, flavonoids and phenolic acids. The extracts were kept at −70 °C prior to analyses. All extractions were performed in duplicate per each replications of baking experiment.

2.5. Analysis of total phenolic compounds in cookies

The total phenolic content was determined by the Folin-Ciocalteu assay as described by Singleton, Orthofer, and Lamuela-Raventos (1999) and expressed as mg of gallic acid equivalent (GAE) per kg of dry matter (d.m.). One hundred μL of the extract was transferred into test tubes and their volume made up to 500 μL with distilled water. After addition of Folin-Ciocalteu reagent

Table 1
The composition of recipes used to prepare cookies.

Ingredients	Amount in the dough (g)			
	Recipe 1	Recipe 2	Recipe 3	Recipe 4
Corn flour	40.0	40.0	40.0	40.0
Shortening (refined palm oil)	16.0	16.0	16.0	16.0
Sucrose powder	16.8	16.8	16.8	16.8
Nonfat dry milk	0.4	0.4	0.4	0.4
High-fructose corn syrup	0.6	–	–	–
Sodium chloride	0.5	–	–	–
Sodium bicarbonate	0.4	0.4	0.4	0.4
Ammonium bicarbonate	0.2	–	–	0.5
Citric acid	–	0.2	0.4	–
Water	8.8	8.8	8.8	8.8