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Effect of roasting time of buckwheat groats on the formation of Maillard reaction products and antioxidant capacity

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ABSTRACT

Changes in the formation of Maillard reaction products and antioxidant capacity of buckwheat, induced by roasting at 160 °C for 30, 40 and 50 min, were evaluated in the study. Furozine, was detected after roasting, in all buckwheat samples. Increase of FIC, the presence of significant amounts of CML and enhanced browning were observed, along with increasing times of roasting. The formation of acrylamide in the obtained buckwheat products was also significantly connected with the time of roasting. A significant degradation was observed in natural antioxidants, as affected by heat treatment time. The colour parameter changed significantly with the increasing of roasting time. Overall, 30 min of roasting was beneficial from a nutritional point of view for the obtained buckwheat product.

1. Introduction

Buckwheat is usually processed into flour, but in the central and eastern Europe the roasting process is commonly used for buckwheat groats. In order to obtain good quality roasted groats, the dehulling process is preceded by raising the moisture content of the raw whole seeds, followed by simultaneous steaming and heating. All of these serial steps form a unique technological process and the resulting roasted groats (roasted kasha) are ready for cooking. Investigations of the effects of thermal processing on buckwheat-derived food mainly concern the contents of total phenolics and flavonoids and also the antioxidant capacity due to its role in human health and disease management (Zieliński et al., 2012). Heat treatment of buckwheat was found to evoke changes in its chemical composition and, above all, to affect the functional properties of selected bioactive compounds. Zieliński, Michalska, Amigo-Benavent, del Castillo, and Piskuła (2009) related the antioxidant capacity of buckwheat products to the concentration of flavonoids after hydrothermal treatment. Also, proteins contribute in the development of the antioxidant capacity of buckwheat products. Zieliński et al. (2009) reported that roasting caused a decrease in the antioxidant capacity, along with a decrease in the quality and content of protein, in groats. Furthermore, during heat treatment, Maillard compounds are formed, due to a chemical reaction between free amino groups of lysine and carbonyl groups of reducing sugars (Delgado-Andrade, 2014). Zieliński et al. (2009) observed the formation of Maillard products induced by the heat treatment of both whole seeds and groats. It should be noted that, as well as the formation of colour, aroma and flavour precursors in foods, Maillard reaction products also take part in the formation of beneficial compounds having antioxidant, antiallergenic, antimicrobial or cytotoxic properties (Silván, van de Lagemaat, Olano, & del Castillo, 2006). Still, more studies are needed to recognize the effect of thermal processing on functional compounds of buckwheat products.

The aim of this study was to evaluate how the roasting time of buckwheat may affect the formation of Maillard reaction products and antioxidant capacity.

2. Materials and methods

2.1. Material

The roasted common buckwheat groats (*Fagopyrum esculentum* Moench) were provided by a local company located in the north-east of Poland. Roasting was done according to the procedure

Abbreviations: FIC, free fluorescence of intermediary Maillard reaction products compounds; FAST index, fluorescence of advanced Maillard reaction products and soluble tryptophan; TPC, total phenolic content; CML, Nε-(carboxymethyl)-L-lysine; OPA, *o*-phthaldialdehyde; $ORAC_{FL}$, oxygen radical absorbance capacity.

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described by Zakrzewski, Zieliński, Piskuła, and Zielińska (2010), which included initial raising of the moisture content of whole seeds to 22% of dry matter by simultaneous steaming (overheated water vapour at 588 kPa) and heating at 160 °C). The heating was performed for 30, 40 and 50 min. Afterwards, the buckwheat samples were freeze-dried, ground and stored at −20 °C prior to analysis.

2.2. Methods

Protein content in all samples was measured, following AOAC method 979.09, using a nitrogen-to-protein conversion factor of 6.25 (AOAC, 2002).

Assays of available lysine, furosine, FIC (free fluorescent intermediate compounds), FAST index (fluorescence of advanced Maillard reaction products and soluble tryptophan), browning, TPC (total phenolic content), and CML (Nε-(carboxymethyl)-L-lysine) were conducted according to methods described in detail by Michalska, Amigo-Benavent, Zielinski, and del Castillo (2008).

Material for the analysis of available lysine, FIC, FAST index and browning was prepared as follows: dry samples were mixed with 6% of aqueous SDS (sodium dodecyl sulphate), incubated for 30 min with stirring every 10 min for 30 s and filtered, and then the filtrates were used for the analysis.

Available lysine was determined by OPA assay (*o*-phthaldialdehyde) to estimate its level of blockage during processing. Fluorescence was measured at λ_{Ex} = 340 and λ_{Em} = 455 nm. The external standard method was used for quantitative lysine analysis. Data are presented as mean values expressed as mg/100 g of dry matter (d.m.).

Furosine (2-furoylmethyl-lysine) content was evaluated by the chromatographic method. The samples (with protein contents from 40 to 50 mg) were hydrolysed with 8 ml of 8 M HCl at 110 °C for 23 h under anaerobic conditions, and then the hydrolysates were filtered and used for further analysis. Quantitative analysis of furosine was performed by the external standard method, using a commercial standard of pure furosine. Data are presented as mean values expressed as milligrammes per 100 g of protein.

The free fluorescent intermediate compounds (FIC) were measured at λ_{Ex} = 353 and λ_{Em} = 438 nm. FIC data were expressed as the mean values in arbitrary fluorescence units (FU).

Measurement of fluorescent advanced Maillard reaction products (MRPs) and calculation of the FAST index were done according to Birlouez-Aragon, Leclere, Quedraogo, Birlouez, and Grongnet (2001), based on the analysis of fluorescence due to advanced MRPs measured at λ_{Ex} = 353 and λ_{Em} = 438 nm and tryptophan fluorescence at λ_{Ex} = 290 and λ_{Em} = 340 nm. Samples were analysed in triplicate, and FAST index data were expressed in per cent (w/w).

The formation of brown pigments in the examined buckwheat samples was estimated as absorbance at 420 nm (del Castillo, Ames, & Gordon, 2002). The assay was performed in a CoulterDU800 spectrophotometer (Beckman Instruments Inc., Fullerton, CA). All measurements were done in triplicate. Results were expressed as arbitrary absorbance units.

For carboxymethyllysine (CML) analysis, the buckwheat samples containing 22 mg of protein and 2,6-diaminopimelic acid (320 mg) (Sigma–Aldrich, Germany), as an internal standard, were digested by 4 ml of 6 N HCl in Pyrex glass bottles at 110 °C for 24 h. The hydrolysates were filtered and then aliquots of the hydrolysed sample were evaporated to dryness. A gas chromatograph (Hewlett–Packard 6890, Waldbronn, Germany) system equipped with a flame ionization detector was used for CML determination. All analyses were carried out in duplicate and data were expressed as mg/100 g of protein.

According to the methodology proposed by Ciesarová, Kukurová, Bednáriková, and Morales (2009), the acrylamide content was measured in the examined buckwheat samples. The homogenized samples were used for water extraction by pre-extraction into ethyl acetate, using RVC 2-33 IR (Christ, Osterode am Harz, Germany) for concentration of ethyl acetate extracts. Acrylamide analysis was conducted using a gas chromatograph 7890A coupled with a mass spectrometer MSD 5975 Inert (Agilent Technologies, Santa Clara, California, USA). Results were expressed as ng per g of the sample dry matter.

The oxygen radical absorbance capacity ($ORAC_{FL}$) assay was carried out according to del Castillo, Gordon, and Ames (2005). 175 mg samples were extracted with 6.25 ml of 75 mM phosphate buffer (pH 7.4), incubated for 60 min with stirring every 10 min for 30 s and filtered; then the filtrates were used for the analysis. Fluorescence readings were recorded at λ_{Ex} = 493 and λ_{Em} = 515 nm in a Perkin-Elmer LS 50 B Luminescence Spectrometer (Massachusetts, USA). Results were expressed as mmol of trolox equivalents (trolox Eq) per g of the sample dry matter.

The instrumental measurement of the buckwheat groats' colour was carried out with a ColorFlex (HunterLab, USA), and the results were expressed in accordance with the CIELab system with reference to illuminant D65 and a visual angle of 10°. The parameters determined were: L^* (L^* = 0 [black] and L^* = 100 [white]), a^* ($-a^*$ = greenness and $+a^*$ = redness) and b^* ($-b^*$ = blueness and $+b^*$ = yellowness).

2.3. Statistical analysis

The reported data are the mean results with the standard deviations. The obtained results were analysed by one-way ANOVA. The Fisher LSD Test, at a significance level of $p < 0.05$, was performed for *post hoc* comparison.

3. Results and discussion

Data on protein, lysine and furosine found in the buckwheat roasted at 160 °C at different times (30, 40 and 50 min) are shown in Table 1. Roasting time affected the total protein content. A statistically significant decrease of this component was observed with increasing of roasting time. The formation of early stage MRP, which are generally Amadori rearrangement products, was indirectly measured by the available lysine and furosine analysis (Resmini, Pellegrino, & Battelli, 1990). Decrease of lysine content was significantly correlated with the process time elongation. The decrease of lysine in the roasted buckwheat was accompanied by the formation of furosine (Table 1). In raw groats, furosine was not detectable, while in the roasted buckwheat its content increased with increasing roasting time. Van Boekel (1998) showed that furosine content was strongly dependent on the time and temperature of the process. Induction of furosine formation was noted by Zieliński et al. (2012) during long-time storage of rye ginger cake. In turn, Žilić et al. (2014) found a significant increase of furosine content during extrusion, infrared and microwave heating of soybean. A similar observation was made by Yüksel (2014) for milk samples during heat treatment. Ramírez-Jiménez, Garcia-Villanova, and Guerra-Hernandez (2001) found high correlations between furosine or available lysine content and time of prolonged toasting of wheat bread. Toasting of sliced bread for 7 min caused an increase of furosine level, and further prolongation of time resulted in a decrease of its level. In the case of lysine, there was a decrease of its content.

Advanced MRPs are represented by a heterogeneous group of compounds with characteristic pigmentation and fluorescence. Free fluorescent intermediate compounds (FIC) are characteristics of free and total intermediate products of the Maillard reaction. The formation of intermediate products of the Maillard reaction has been associated with tryptophan content, which confirms the