

FUNCTIONAL AND ANTIOXIDANT PROPERTIES OF NEW BUCKWHEAT PRODUCTS*

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ABSTRACT: This study investigated wheat milling fractions (flours T-400, T-500, T-850, wholegrain flour and bran) and buckwheat (*Fagopyrum esculentum* Moench) milling fractions (hull, groat, dehulled grain, wholegrain flour and refined flour). Content of total polyphenols and total flavonoids, and antioxidant activity were determined in ethanolic extracts of wheat and buckwheat milling fractions. ESR spectroscopy was used for investigation of antiradical activity of wheat and buckwheat milling fraction extracts on reactive superoxide anion and hydroxyl radicals. HPLC analysis was used for quantitative and qualitative determination of polyphenols and tocopherols composition of wheat and buckwheat milling fractions. The correlation between phytochemicals content and antioxidant activity of wheat and buckwheat milling fractions has been analyzed.

After investigation of rheological properties of buckwheat dough, new cracker formulation has been developed and two types of gluten-free buckwheat crackers have been produced. Quality parameters of produced buckwheat crackers (refined and wholegrain) were analyzed and compared with control wheat crackers (refined and wholegrain). Content of total polyphenols and quantitative and qualitative composition of polyphenols and tocopherols were determined in crackers. Scavenging activity of crackers on DPPH radicals has been tested. Shelf-life of buckwheat and wheat crackers was determined applying gas chromatographic analysis of the formed aldehydes as secondary products of lipid oxidation. Sensory quality of the new buckwheat crackers has been established applying point-based method and instrumental analyses of color and texture.

Key words: buckwheat, phenolic compounds, tocopherols, antioxidant activity, crackers, functionality, gluten-free products

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INTRODUCTION

Consumers are increasingly interested in functional foods and this has led to greater supply of such products on the market. In the area of bakery products this trend is still relatively underdeveloped (Siro et al., 2008). Therefore, different alternative crops (amaranth, quinoa, buckwheat, etc.), as raw materials, are in focus for development of new bakery products.

Buckwheat (*Fagopyrum esculentum* Moench) is highly nutritious pseudocereal

known as a dietary source of protein with favorable amino acid composition, vitamins, starch, dietary fiber, essential minerals and trace elements (Bonafaccia et al., 2003). Phenolic compounds are also found in abundance in buckwheat, including rutin, orientin, vitexin, quercetin, iso-vitexin, kaempferol-3-rutinoside, isoorientin, and catechins (Kreft et al., 2006).

In comparison to most frequently used cereals, buckwheat has been reported to

posses higher antioxidant activity, mainly due to high rutin content. Another functionality of buckwheat stems from its gluten-free characteristics making buckwheat suitable for the diet for celiac disease patients.

MATERIAL AND METHODS

Commercially available buckwheat milling fractions (hull, groat, dehulled grain, wholegrain flour and refined flour) and wheat milling fractions (flours T-400, T-500, T-850, wholegrain flour and bran) were compared by: 1) quantification of main antioxidant components: phenolic compounds and tocopherols, and the total phenolics and flavonoids content, and 2) determination of antioxidant activity of milling fraction extracts by different direct and indirect methods (through measuring scavenging activity on 1,1-diphenyl-2-picrylhydrazyl (DPPH[•]), hydroxyl ([•]OH) and superoxide anion (O₂^{•-}) radicals, reducing

activity, and chelating activity on Fe²⁺. Rheological properties of two types of buckwheat and wheat flours (refined and wholegrain) were investigated in order to estimate the potential usage of flours as appropriate ingredients for formulation of bakery products.

New formulations for gluten-free buckwheat crackers (refined and wholegrain) were developed under the laboratory conditions and compared with wheat based crackers (refined and wholegrain). Proximate composition, content of main antioxidant compounds (polyphenols and tocopherols), antioxidant activity (scavenging activity on DPPH[•]) and sensory quality were analyzed and compared with those of wheat crackers made from refined and wholegrain wheat flours. Additionally, shelf-life of created crackers was compared by determination of five aldehydes selected as markers for lipid oxidation.

Table 1.

Total phenolic content, phenolic compounds of crackers and scavenging activity on DPPH[•]

| | Refined wheat cracker | Refined buckwheat cracker | Wholegrain wheat cracker | Wholegrain buckwheat cracker |
|---|--------------------------|---------------------------|--------------------------|------------------------------|
| Total phenolic content (mg GAE/100g) | 84 ± 1 ^a | 231 ± 1 ^c | 143 ± 3 ^b | 292 ± 0 ^d |
| Phenolic compounds (mg/100g) | | | | |
| Protocatechuic acid | 0.29 ± 0.01 ^a | 1.59 ± 0.03 ^c | 0.55 ± 0.01 ^b | 2.42 ± 0.05 ^d |
| Ferulic acid | 0.53 ± 0.00 ^a | 0.69 ± 0.01 ^b | 1.11 ± 0.01 ^d | 0.75 ± 0.00 ^c |
| Rutin | n.d. | 2.06 ± 0.05 ^a | n.d. | 5.02 ± 0.04 ^b |
| Quercetin | n.d. | 0.26 ± 0.01 ^a | n.d. | 0.91 ± 0.06 ^b |
| Scavenging activity on DPPH [•] (IC ₅₀ mg/mL) | 28.2 ± 1.17 ^c | 1.63 ± 0.07 ^a | 16.2 ± 1.85 ^b | 0.95 ± 0.17 ^a |

Values are means of three determinations ± SD. Values in each row with the same superscript are not significantly different ($P < 0.05$). n.d. - not detected

RESULTS

Considering all applied assays for determination of antioxidant activity (electron spin resonance (ESR) spectroscopy and spectrophotometry) it has been concluded that all investigated milling fractions showed remarkable antioxidant activity. Buckwheat milling fractions expressed higher antioxidant potential (Sedej et al., 2010a, 2010b).

These findings suggest the potential improvement of the antioxidant properties of wheat-based food products through addi-

tion of buckwheat flour (Filipčev et al., 2011) or even complete replacement of wheat flour.

Mixolab measurements confirmed that the absence of structure-forming gluten proteins influences the resistance of buckwheat dough (Sedej et al., 2011a). In contrast to bread, in crackers the gluten network needs to be only slightly developed for the dough to be cohesive without being too elastic, and therefore formulation of crackers with complete substitution of wheat buckwheat flour was accomplished. Buckwheat crackers were characterized

with higher content of dietary fiber in comparison to wheat crackers. Furthermore, crackers made from buckwheat flours have significantly higher ($P < 0.05$) total phenolic content than wheat crackers. Quantitative HPLC analysis (Mišan et al., 2011) revealed the presence of protocatechuic and ferulic acid in all tested crackers, whereas two flavonoids, rutin and quercetin were found in buckwheat crackers (Table 1). α -, γ -, δ -tocopherols in crackers were found in the following order: α - >> γ - > δ -tocopherol for all samples (Sedej et al., 2011b).

Content of γ -tocopherol and total tocopherols were significantly higher ($P < 0.05$) in both buckwheat crackers in comparison to wheat ones.

Consequently, buckwheat crackers were superior in scavenging activity on DPPH^{*} in comparison to wheat crackers as evi-

denced by their lower IC₅₀ value (Table 1). Sensory analyses of the crackers, which included evaluation of the representative properties of crackers done by the points-based method (Table 2), determination of surface color and texture analysis showed that buckwheat flours may be used in gluten-free cracker formulation without adversely affecting the sensory properties of crackers. Buckwheat and wheat crackers are presented in Figure 1.

Lipid oxidation in crackers, containing approximately 30% of vegetable fat, was monitored at the first day when they were baked, after 2 weeks, 1, 4, 6 and 12 months of storage at ambient temperature (22 ± 2 °C). According to the obtained results of static headspace gas chromatographic (SHS-GC) method, there was no significant change in content of propanal, pentanal, hexanal, heptanal and octanal in all cracker samples during four months.

Table 2.
Sensory scores of crackers

| Property | Refined wheat cracker | Refined buckwheat cracker | Wholegrain wheat cracker | Wholegrain buckwheat cracker |
|---|------------------------------|------------------------------|-------------------------------|-------------------------------|
| Appearance (shape, uniformity, surface) | 3,97 \pm 0,40 ^b | 4,57 \pm 0,40 ^a | 4,66 \pm 0,44 ^a | 4,37 \pm 0,39 ^{ab} |
| Texture | | | | |
| Structure, break, firmness | 4,49 \pm 0,79 ^a | 4,79 \pm 0,28 ^b | 4,25 \pm 0,52 ^{ab} | 4,14 \pm 0,65 ^{ab} |
| Chewiness and other textural properties | 3,57 \pm 0,69 ^a | 4,46 \pm 0,51 ^b | 3,97 \pm 0,37 ^{ab} | 3,83 \pm 0,66 ^{ab} |
| Aroma | | | | |
| Odour | 3,25 \pm 0,67 ^a | 3,18 \pm 0,67 ^a | 3,18 \pm 0,58 ^a | 3,27 \pm 0,68 ^a |
| Taste | 4,42 \pm 1,04 ^a | 4,83 \pm 1,41 ^a | 4,70 \pm 0,93 ^a | 4,39 \pm 1,47 ^a |
| Weighted mean value | 3,94 | 4,57 | 4,35 | 4,20 |

Scores are means of seven evaluations by seven panelists \pm SD. Values in each row with the same superscript are not significantly different ($P < 0.05$). Scores: 1 – unacceptable, 2 – acceptable, 3 – good, 4 – very good, 5 – excellent.

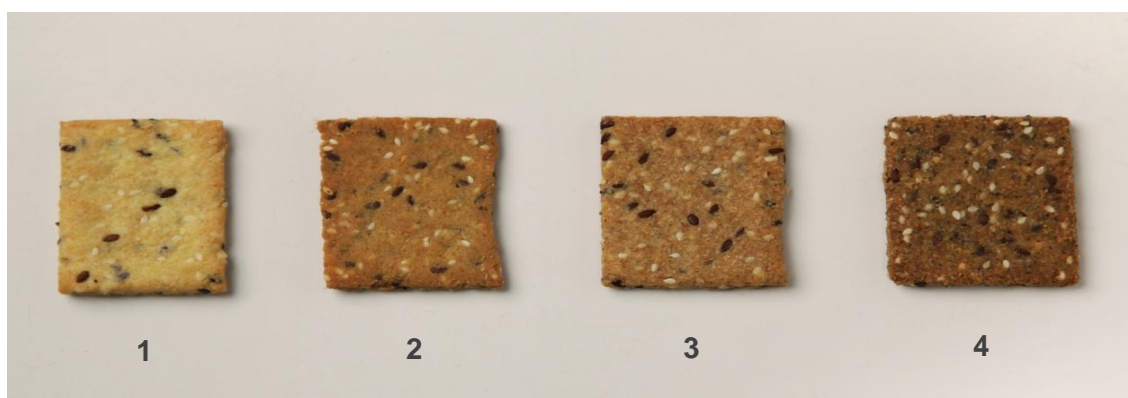


Figure 1. Appearance of crackers: 1 – refined wheat cracker, 2 – refined wholegrain cracker, 3 – wholegrain wheat cracker, 4 – wholegrain buckwheat cracker

After the sixth month of storage higher increase in aldehydes content was noticed in wheat than in buckwheat crackers, implying longer shelf-life of buckwheat crackers.

CONCLUSION

The results of this PhD thesis could be relevant for the production of gluten-free crackers based on buckwheat flours. Further research needs to be done in order to examine consumer acceptance of the new products and confirm biological activity of new products through *in vivo* experiments. The introduction of buckwheat crackers in the market would increase the diversity of functional bakery products and, even more importantly, of functional foods suitable for celiac disease patients.

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ФУНКЦИОНАЛНА И АНТИОКСИДАТИВНА СВОЈСТВА НОВИХ ПРОИЗВОДА ОД ХЕЉДЕ

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- Извод из докторске дисертације -

Сажетак: У раду су испитане фракције млевења пшенице (брашно Т-400, Т-500, Т-850, интегрално пшенично брашно и мекиње) и фракције млевења хељде (*Fagopyrum esculentum* Moench) (цело зрно хељде, љуска хељде, очишћено зрно, интегрално хељдино брашно и бело хељдино брашно). У етанолним екстрактима фракција млевења пшенице и хељде одређен је садржај укупних растворљивих полифенола, укупних флавоноида и антиоксидативна активност. ESR спектрометријом испитана је антирадикалска активност екстракта фракција млевења пшенице и хељде на реактивне супероксид анион и хидроксил радикале. HPLC анализом утврђен је квалитативни и квантитативни састав полифенолних једињења и токоферола испитиваних фракција млевења пшенице и хељде. Анализирана је корелација између садржаја фитохемикалија и антиоксидативне активности фракција млевења пшенице и хељде.

Након испитивања реолошких својстава теста од хељдиног брашна, развијена је нова формулација за крекере и произведени су безглутенски крекери од хељдиног брашна. Показатељи квалитета произведених крекера од хељдиног брашна (белог и интегралног) испитани су у поређењу са контролним крекерима од пшеничног брашна (Т-500 и интегралног). У крекерима је одређен садржај укупних растворљивих полифенола, утврђен је квалитативни и квантитативни састав полифенолних једињења и токоферола и испитана је антирадикалска активност на DPPH радикале. Испитивање одрживости крекера од хељдиног и пшеничног брашна обухватило је одређивање насталих алдехида, као секундарних производа оксидације липида, гасном хроматографијом. Сензорски квалитет новокреираних крекера од хељдиног брашна одређен је методом бодовања и инструменталним анализама боје и текстуре.

Кључне речи: хељда, полифенолна једињења, токофероли, антиоксидативна активност, крекери, функционалност, безглутенски производи

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