NUTRITIONAL PROPERTIES OF SUGAR-FREE WHEAT-FLOUR COOKIES

Barbara Borczak **●** [⊠], Elżbieta Sikora **●**, Marek Sikora **●**, Edyta M. Kutyła-Kupidura, Joanna Kapusta-Duch **●** University of Agriculture in Krakow, Faculty of Food Technology

Summary. This study aims at evaluating the impact of selected sweeteners on the nutritional properties of sugar-free wheat-flour cookies. The following parameters were measured: slowly digestible starch (SDS), rapidly digestible starch (RDS), resistant starch (RS), the starch digestibility index (SDI), total reducing activity and the antioxidant activity by ABTS method. Sorbitol and maltitol cookies had significantly lower amount of RDS, while SDS fraction was significantly higher only in maltitol cookies (p < 0.05). The amount of RS was significantly higher and the calculated starch digestibility indices decreased in all sugar-free cookies (p < 0.05). The total reducing activity was increased in all biscuits with polyols, while the antioxidant activity was decreased (p < 0.05). The replacement of the selected sugar alcohols such as xylitol, maltitol and sorbitol led to obtain a bakery product characterized by reduced starch digestibility and starch digestibility index, as well as enhanced total reducing activity.

Key words: wheat cookies, polyols, antioxidants, starch digestibility

INTRODUCTION

Crusty biscuits are popular snack starchy products. However, most of the starch products, including wheat biscuits, regardless of milling of flour used for baking, have a high glycemic index (above 70%), due to the high content of saccharose and rapidly digestible starch (i.e. RDS) [Brouns et al. 2005]. In the prevention of chronic non-communicable diseases, such as type 2 diabetes, obesity, heart disease and cancer, it is recommended the

Barbara Borczak https://orcid.org/0000-0001-6380-7344; Elżbieta Sikora https://orcid. org/0000-0002-0301-0306; Marek Sikora https://orcid.org/0000-0002-8437-889X; Joanna Kapusta-Duch https://orcid.org/0000-0003-3882-2483

[™] barbara.borczak@urk.edu.pl

[©] Copyright by Wydawnictwo SGGW

consumption of products with a low glycemic index and energy-reduced, and at the same time rich in dietary fibre [De Angelis et al. 2003]. According to forecasts of the World Health Organization, in 2030, the type 2 diabetes, will be the seventh disorder responsible for the occurrence of death worldwide, and the number of people affected will double [Mathers and Loncar 2006]. The increasing consumers' nutritional consciousness forces an enhanced production of foods for particular nutritional purposes, including energy--reduced. The application of sweeteners which replace the sucrose, is currently common on the market. Commercially available alternatives of sucrose permitted for use are classified into two categories [O'Brien Nabors 2001, Yebra-Biuurun 2005]. One of them are polyols, also called alditols or polyhydric alcohols, e.g. xylitol, sorbitol, maltitol or erythritol. Energy value is lower than that of sucrose, and the intensity of sweetness somewhat smaller, but they are digested more slowly and thus do not contribute to the high postprandial glycaemia [O'Brien Nabors 2001]. Another group of compounds are intensively sweetening agents, such as acesulfame K, alitame, aspartame, sucralose or saccharin [O'Brien Nabors 2001]. These compounds are characterized by several hundred (acesulfame K) to several thousands (alitame) times the sweetness intensity of sucrose [O'Brien Nabors 2001]. As a rule, they are not digested to energy delivering products, but due to their extreme sweetness, their content in food products is very small, and thus the energy value - not significant [Chattopadhyay et al. 2014]. Use of sweeteners (polyols and intensive sweeteners) in the manufacture of sugar-free cookies previously have been described by Górecka et al. [2007], or Lin et al. [2010], Kutyła-Kupidura et al. [2015]. However, those researches have focused on quality parameters such as texture, rheology of dough or organoleptic assessment.

There is a lack of information on the effect of the sucrose substitutes on the nutritional value and the starch digestibility, as well as on the antioxidative properties.

The purpose of the study was to investigate the effect of saccharose replacements, such as sorbitol, maltitol and xylitol, on the nutritional starch fractions and the starch digestibility index, the total reducing and the antioxidant activity.

MATERIALS AND METHODS

Materials

Research material consisted of four kinds of wheat cookies with (i) saccharose (control) and instead of saccharose, with an addition of polyols: (ii) xylitol; (iii) sorbitol; (iv) maltitol. The dough components were as follows: wheat-flour, type 450 (500 g) ("Złote Pola", Polish Plants Grains S.A., Kraków, Poland), margarine (250 g) ("Kasia" Unilever, Warszawa, Poland), saccharose (200 g) ("Królewski" Südzuker Polska S.A., Wrocław, Poland), eggs (150 g) ("Ale jaja" Poultry ferm Woźniak Sp. z o.o., Rawicz, Poland), baking powder (6 g) (Dr. Oetker Poland Sp. z o.o., Gdańsk, Poland).

In the recipe of the cookies, the saccharose was replaced with: (i) xylitol (200 g) (ii) sorbitol (300 g) (iii) maltitol (350 g) (Smart Cafe, Józefów, Poland). The weight of the added sweetener was calculated taking into account its sweet taste sensation (STS) in relation to the STS of saccharose, which equals [Kutyła-Kupidura et al. 2015].

After mixing, the ingredients were kneaded into the dough and left in a refrigerator (4°C, 30 min). After this, the dough was rolled into 7 mm thickness and cut out into the same size (3.5 cm), round cookies. Such cookies were then baked (200°C, 8 min) and cooled down.

Methods

Starch digestibility index determination. The content of total starch (TS) was measured by commerical kit (K-TSTA 07/11, Megazyme International Ireland, Bray Business Park, Bray, Co. Wicklow, Ireland). In short, freshly ground sample (100 mg) was incubated with the mixture of thermostable α -amylase (3,000 U·ml⁻¹) and amyloglucosidase (3,300 U·ml⁻¹) for 30 min at 50°C. The hydrolyzed glucose was designated by using GOPOD reagent having glucose oxidase and peroxidase. The absorbance of the obtained colored products was measured at 510 nm in a spectrophotometer (Spectro 2000RS, Labomed, Inc.) and the amount of the TS was calculated.

The content of slowly digestible (SDS) and rapidly digestible (RDS) starches, as well as the free glucose (FG) were measured by the procedure described by Englyst et al. [1992], and modified by Chung et al. [2010]. The following enzyme blend was freshly prepared and added: porcine pancreatic α -amylase (P-7545, 8 × USP specifications, Sigma, St. Louis, MO), amyloglucosidase (3300 U·ml⁻¹, Megazyme International Ireland Ltd., Bray, Ireland) and invertase (I-4504, \geq 300 units·mg⁻¹ solid, Sigma, St. Louis, MO, USA). The cookies were weighed in the quantity containing 100 mg of TS and 4 ml of 0.5 M sodium acetate buffer (pH 5.2). The enzyme mixture and glass balls were introduced into the tube and incubated in a shaking water bath (37°C, 200 shakes·min⁻¹). The released glucose was determined after 20 min [RDS = (G₂₀ – FG) · 0.9] and after 120 min [SDS = (G₁₂₀ – G₂₀) · 0.9] with the use of GOPOD reagent at 510 nm (K-GLOX, Megazyme International Ireland, Bray Business Park, Bray, Co. Wicklow, Ireland) in a spectrophotometer (Spectro 2000RS, Labomed, Inc.). Finally, the starch digestion index was obtained by following calculation: SDI = (RDS · TS⁻¹) · 100. The analyses were made in three repetitions.

Total reducing activity. This parameter was measured by the procedure described by Swain and Hillis [1959] with the use of Folin–Ciocalteau reagent (Sigma-Aldrich, St. Louis, MO, USA). The sample (5 g) was extracted with 40 ml of 80% acidified methanol (20 ml of 0.08 M HCl and 20 ml of 80% methanol) for 2 h in 25°C and centrifuged (1,500 g, 15 min). The residues were extracted with 40 ml of 70% acetone for the subsequent 2 h and then centrifuged (1,500 g, 15 min). The supernatants were mixed together, diluted and incubated with Folin–Ciocalteau reagent for 20 min and the absorbance was measured at 760 nm in a spectrophotometer (Spectro 2000RS, Labomed company, Inc.). The total reducing activity was calculated in mg of gallic acid per 100 g of dry matter. The analyses were made in three repetitions.

Determination of ABTS activity. The antioxidant potential of the tested cookies was measured by the procedure presented by Re et al. [1999] with the application of ABTS [2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt] (Sigma-Al-drich, St. Louis, MO, USA). Amount of 0.5 ml of methanol-acetone extracts were moved into the tubes and added to the mark with methanol to the volume of 1 ml. Afterwards,

2 ml of ABTS solution was added. The mixture was incubated at 30°C for 6 min. The absorbance of the solution was measured in a spectrophotometer (Spectro 2000RS, Labomed, Inc.) at 734 nm. The analyses were made in three repetitions.

Statistical methods. To assess the impact of the selected polyols on starch nutritional fractions and antioxidant activity of wheat cookies, the one-way analysis of variance was used. The significance of differences was examined using the Duncan test at p < 0.05 with Statistica 10 software (Statsoft, Inc., Tulsa, OK, USA).

RESULTS AND DISCUSSION

Starch digestibility of the tested biscuits

In the current work, the nutritional quality of cookies in terms of starch digestibility was performed using well-established *in vitro* assays, which allowed the determination of nutritionally important starch fractions [Englyst et al. 1992, Chung et al. 2010] – Table 1.

 Table 1.
 Nutritional starch fractions and starch digestibility index of the tested biscuits

 Tabela 1.
 Frakcje żywieniowe skrobi and indeks strawności skrobi badanych herbatników

Sweetener Słodzik	RDS	SDS	RS	SDI
		g·100 g ⁻¹ d.m.		
Saccharose Sacharoza	32.9 ^b ±2.6	3.7 ^a ±1.5	7.4 ^b ±2.6	82.3°±6.2
Xylitol Ksylitol	$30.3^{ab}\pm0.0$	3.4 ^a ±0.8	$11.8^{a}\pm1.4$	$70.3^{a}\pm1.0$
Sorbitol	27.7 ^a ±1.4	$3.2^{a}\pm0.0$	12.3 ^a ±1.0	67.3 ^a ±0.3
Maltitol	11.3°±1.8	8.2 ^b ±1.5	$20.5^{\circ}\pm1.0$	29.6 ^b ±5.2

Different characters in columns indicate statistically essential differences at p < 0.05.

Różne litery w kolumnach oznaczają statystycznie istotne różnice przy p < 0.05.

Starch fractions were influenced by the application of polyols: the RS level increased (p < 0.05) from 7.4 to 11.8, 12.3 and 20.5 g⁻¹ d.m., whereas RDS level decreased from 32.9 to 30.3, 27.7 and 11.3 g⁻¹00 g⁻¹ d.m. for saccharose, xylitol, sorbitol and maltitol biscuits, respectively (Table 1). The SDS level remained unchanged (p > 0.05) from 3.2, 3.4 and 3.7 g⁻¹00 g⁻¹ d.m. for saccharose, sorbitol and xylitol cookies, respectively, while for maltitol cookies increased significantly (p < 0.05) up to 8.2 g⁻¹00 g⁻¹ d.m. (Table 1).

In the literature, there is no information on the content of starch fractions in the cookies in which the saccharose was replaced by the polyols. This study has been made for the first time.

Generally, the rapidly digestible starch is present in the cereals in high amounts. The hydrolyzed glucose is absorbed quickly in the upper part of the small intestine, what creates the potential to produce high glycemic response [Taylor et al. 2015]. Sorbitol and maltitol cookies had significantly lower amount of RDS compared with xylitol and saccharose biscuits, while the fraction of SDS was significantly higher only in the case

of maltitol cookies (p < 0.05) – Table 1. Maltitol is a polyol basing on the disaccharide. Both sorbitol and xylitol base on the monosaccharides. The disaccharides have more hydroxyl groups than monosaccharides [Sun et al. 2014]. In comparison to xylitol and sorbitol, maltitol has more hydroxyl groups and hence the larger molecular weight. More linkages between starch and polyols may be developed which limit the swelling of the starch [Sun et al. 2014]. It has been evidenced that polyols significantly decreased the breakdown and setback of wheat starch pasting at the ratio of sugar alcohol to starch of 2 : 1.

The application of sugar alcohols resulted in significant amount of RS in the tested cookies (p < 0.05), with maltitol being the greatest (Table 1). This phenomenon might be explained by the fact that sugar alcohols have the ability to facilitate retrogradation, because of the hydroxyl groups, as well as by their internal structure, since the sugar hydration depends on the balance between equatorial and axial hydroxyl groups [Sun et al. 2014]. It has been also evidenced that xylitol retards starch gelatinization and enhances gelatinization temperature, because it generates a decline in the system's water activity [Torres et al. 2013]. The relatively high content of RS in the tested biscuits might be also a result of amylose-lipid complexes that reduced the starch digestibility, as well as of limited gelatinization due to the low moisture of the biscuit dough and short baking time [Taylor et al. 2015].

Finally, the SDI decreased (p < 0.05) from 82.3 to 70.3, 67.3 and 29.6% d.m. for saccharose, xylitol, sorbitol and maltitol, respectively. The indices presented in the literature for wheat biscuits were between 50–81.4% [Englyst et al. 1992, Giuberti et al. 2016]. The maltitol biscuits were below this range. The replacement of the saccharose with polyols significantly reduced the SDI, which is beneficial from the nutritional point of view.

TOTAL REDUCING AND ANTIOXIDANT ACTIVITY

Basing on the mechanism of the reaction, it was stated that there are many compounds, including proteins or metal ions, as well as the polyphenols compounds with which Folin–Ciocalteau reagent may interact, which have reducing properties. With respect to this, in the literature it was suggested [Kowalski and Łukasiewicz 2014] to use rather the term "total reducing activity" instead of "total polyphenols". Taking into account the above mentioned, the total reducing activity increased from 7.3, 29.7 and 32.0 to 38.6 mg·100 g⁻¹ d.m. for saccharose, sorbitol, maltitol and xylitol biscuits, respectively (Table 2). Inversely, the antioxidant activity measured as an ability to quench free ABTS radical decreased from 1.2 to 1.0 and 0.9 µmol Trolox·g⁻¹ d.m. for saccharose, xylitol, maltitol and sorbitol cookies, respectively (Table 2).

This is the first study, which describes the antioxidant properties of wheat biscuits with polyols. The data of the total polyphenols presented in the literature (given in mg of gallic acid per 100 g of dry matter) of the wheat flour was reported to be between 13.4–344 [Pérez-Jiménez and Fulgencio 2005, Luthria et al. 2015, Mesías et al. 2016]. Most of phenolic compounds in cereals constitute of phenolic acids (salicylic, vanillin, gallic acid, protocatechic, p-hydroxybenzoic, and ellagic acid) and phenylpropanoic acids

Sweetener Słodzik	Total reducing activity Całkowita aktywność redukcyjna [mg·100 g ⁻¹ d.m.]	ABTS [µmol Trolox [.] g ⁻¹ d.m.]
Saccharose – Sacharoza	7.3 ^b ±0.4	1.2 ^b ±0.1
Xylitol – Ksylitol	38.6° ±1.1	1.0 ^a ±0.0
Sorbitol	29.7 ^a ±2.7	$0.9^{a} \pm 0.0$
Maltitol	32.0 ^a ±1.0	$1.0^{a} \pm 0.1$

Table 2. The total reducing activity and the antioxidant activity of wheat cookies

Table 2. Całkowita aktywność redukcyjna i aktywność antyoksydacyjna herbatników pszennych

Different characters in columns indicate statistically essential differences at p < 0.05.

Różne litery w kolumnach oznaczają statystycznie istotne różnice przy p < 0.05.

(ferulic, caffeic, synaptic, p-coumaric). Matilla et al. [2005] reported also the presence of the alkylresorcinols in considerable quantities in wheat grain. The total reducing activity of the tested biscuits was influenced by the content of polyphenols naturally presented in wheat flour, by the proteins as well as polyols. The lowest total reducing activity of sugar cookies was caused by the fact that saccharose does not possess reducing properties and does not react with Folin–Ciocalteau reagent used in this study.

The antioxidant activity of polyols added biscuits was significantly lower compared with control (saccharose biscuits) – Table 2. These results were surprising because in the case of total reducing activity, the polyols sweetened cookies exerted higher values than saccharose ones (Table 2). This phenomenon might be explained by the fact that an application of polyols in sugar-free cookies resulted in lighter color of the products as polyols do not take part in Maillard reaction, because they lack a reactive aldehyde group [Ronda et al. 2005]. The products of Maillard reaction have proven antioxidant activity, together with some chemo-preventive effects [Grajek 2007, Kowalski and Łukasiewicz 2014].

CONCLUSIONS

The substitution of the selected polyols such as xylitol, maltitol and sorbitol resulted in a bakery product characterized by reduced starch digestibility and starch digestibility index, as well as enhanced total reducing activity. However, further studies are needed – with the participation of human volunteers, to understand the real impact of the polyols containing cookies on the glycemic index and the bioavailability of polyols and bioactive compounds.

Acknowledgements

This study has been carried out with financial support from Agricultural University in Krakow (grant BM-4706/KZCz/2016-2017).

REFERENCES

- Brouns F., Bjorck I., Frayn K.N., Gibbs A.L., Lang V., Slama G., Wolever T.M.S., 2005. Glycaemic index methodology. Nutr. Res. Rev. 18, 145–171.
- Chattopadhyay S., Raychaudhuri U., Chakraborty R., 2014. Artificial Sweeteners a review. J. Food Sci. Technol. 51, 611–621.
- Chung H.J., Liu Q., Hoover R., 2010. Effect of single and dual hydrothermal treatments on the crystalline structure, thermal properties, and nutritional fractions of pea, lentil, and navy bean starches. Food Res. Int. 43, 501–508.
- De Angelis M., Gallo G., Corbo M.R., McSweeney P.L.H., Faccia M., Giovine M., Gobbetti M., 2003. Phytase activity in sourdough lactic acid bacteria: purification and characterization of phytase from *Lactobacillus sanfranciensis* CB1. Int. J. Food Microbiol. 87, 259–270.
- Englyst H.N., Kingman S.M., Cummings J.H., 1992. Classification and measurement of nutritionally important starch fractions. Eur. J. Clin. Nutr. 46 (suppl.), 33–50.
- Giuberti G., Gallo A., Fortunati P., Rossi F., 2016. Influence of high-amylose maize starch on in vitro starch digestibility and sensory characteristics of cookies. Starch/Stärke 68, 469– -475.
- Górecka D., Korczak J., Borowska-Parus A., 2007. Zastosowanie substancji słodzących w wyrobach ciastkarskich. ŻNTJ 6, 210–218.
- Grajek W., 2007. Przeciwutleniacze w żywności. Aspekty zdrowotne technologiczne molekularne i analityczne. WNT, Warszawa.
- Kowalski S., Łukasiewicz M., 2014. Wpływ warunków wypieku kruchych ciastek na powstawanie wybranych pochodnych furanowych oraz zmianę potencjału antyoksydacyjnego. ŻNTJ 1 (92), 187–199.
- Kutyła-Kupidura E.M., Sikora M., Krystyjan M., Dobosz A., Kowalski S., Pysz M., Tomasik P., 2015. Properties of sugar-free cookies with xylitol, sucralose, acesuflame K and their blends. J. Food Process Eng. 39 (4), 321–329.
- Lin S.H., Lee C.C., Mau J.L., Lin L.Y., Chiou S.Y., 2010. Effects of erythritol on quality characteristic of reduced-calorie Danish cookies. J. Food Qual. 33, 14–26.
- Luthria D.L., Lu Y., John K.M.M., 2015. Bioactive phytochemicals in wheat: Extraction, analysis, processing, and functional properties. J. Funct. Foods. 18, 910–925.
- Mathers C.D., Loncar D., 2006. Projections of global mortality and burden of disease from 2002 to 2030. PLos Med. 3 (11), E442.
- Matilla P., Pihlava J.M., Hellstrom J., 2005. Contents of phenolic acids, alkyl- and alkenylresorcinols, and avenanthramides in commercial grain products. J. Agric. Food Chem. 53, 8290–8295.
- Mesías M., Holgado F., Márques-Ruiz G., Morales F.J., 2016. Risk/benefit considerations of a new formulation of wheat-based biscuit supplemented with different amounts of chia flour. LWT – Food Sci. Tech. 73, 528–535.
- O'Brien Nabors L. (ed.), 2001. Alternative Sweeteners. CRC Press, New York.
- Pérez-Jiménez J., Fulgencio S.C., 2005. Literature underestimate the actual antioxidant capacity of cereals. J. Agric. Food Chem. 53, 5036–5040.
- Re R., Pellegrini N., Proteggente A., Pannala A., Yang M., Rice-Evans C., 1999. Antioxidant activity applying an improved ABTS radical cation decolorization assay. Free Radical Biol. Med. 9/10, 26, 1231–1237.
- Ronda F., Gomez M., Blanco C.A., Caballero P.A., 2005. Effects of polyols and nondigestible oligosaccharides on the quality of sugar-free sponge cake. Food Chem. 90, 549–555.
- Sun Q., Nan Ch., Ji N., Xiong L., 2014. Effect of sugar alcohol on physicochemical properties of wheat starch. Starch/Stärke 66, 788–794.

- Swain T., Hillis W.E., 1959. The phenolic constituents of *Prunus domestica*. The quantitative analysis of phenolic constituents. J. Sci. Food Agric. 10, 63–68.
- Taylor J.R.N., Emmambux M.N., Kruger J., 2015. Developments in modulating glycaemic response in starchy cereal foods. Starch/Stärke 67, 79–89.
- Torres M.D., Raymundo A., Sousa I., 2013. Effect of sucrose, stevia and xylitol on rheological properties of gels from blends of chestnut and rice flours. Carbohydr. Polym. 98, 249–256.
- Yebra-Biurrun M.C., 2005. Sweeteners. In: P. Worsfold, A. Townshend, C. Poole (eds.), Encyclopedia of analytical science. Elsevier Academic, San Diego, 562–572.

WŁAŚCIWOŚCI ŻYWIENIOWE PSZENNYCH HERBATNIKÓW BEZCUKROWYCH

Streszczenie. Celem pracy była ocena wpływu dodatku wybranych substancji słodzących na właściwości żywieniowe pszennych herbatników bezcukrowych. Badaniu poddano następujące parametry: skrobię wolno trawioną (ang. *slowly digestible starch* – SDS), skrobię szybko trawioną (ang. *rapidly digestible starch* – RDS), skrobię oporną (ang. *resistant starch* – RS), wskaźnik strawności skrobi (ang. *starch digestiblity index* – SDI), całkowitą aktywność redukcyjną oraz aktywność antyoksydacyjną mierzoną metodą ABTS. Herbatniki z dodatkiem sorbitolu i maltitolu charakteryzowały się istotnie statystycznie mniejszą ilością frakcji RDS, podczas gdy zawartość frakcji SDS była istotnie większa jedynie w przypadku herbatników z maltitolem (p < 0.05). Zawartość frakcji RS była istotnie więk-sza i wartość obliczonego SDI uległa zmniejszeniu we wszystkich herbatnikach bezcukrowych (p < 0.05). Całkowita aktywność redukcyjna uległa zwiększeniu, a aktywność antyoksydacyjna zmniejszeniu we wszystkich badanych herbatnikach bezcukrowych (p < 0.05). Zastąpienie sacharozy wybranymi poliolami pozwoliło na uzyskanie produktu piekarskiego charakteryzującego się zmniejszoną strawnością skrobi i mniejszą wartością wskaźnika strawności skrobi oraz zwiększoną całkowitą aktywnością redukcyjną.

Słowa kluczowe: herbatniki pszenne, poliole, antyoksydanty, strawność skrobi