Chapter 11

Functional Properties and Maillard Reaction Product Formation in Rye-Buckwheat Ginger Cakes Enhanced with Rutin

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Additional information is available at the end of the chapter

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Abstract

A study of functional properties and Maillard reaction progress in rye-buckwheat ginger cakes supplemented with low and high rutin amount was conducted. The cakes were formulated on rye flour substituted by flour from husked buckwheat or flour from roasted buckwheat groats at 30 % level. The dough was either spontaneously fermented for 72 h at 21 °C, or the fermentation step was omitted. The cakes were baked at 180 °C for 18 min. Fortification of rye-buckwheat ginger cakes by low and high level of rutin was associated with the beneficial progress of the Maillard reaction towards the formation of melanoidins, while furosine formation at the early stage of Maillard reaction was decreased. However, loss of the nutritional value due to the formation of high amount of fluorescent (carboxymethyllysine (CML)) and fluorescent-intermediate compounds was observed. It has also been proved that rye-buckwheat ginger cakes fortified with low and high rutin doses are a rich source of biologically active compounds. Therefore, the cakes showed a high ability to inhibit the formation of advanced glycation end products (AGEs) in vitro and revealed high antioxidant potential. These findings may be important factors in complete evaluation of functional properties of ginger cakes. Stronger influence of rutin enrichment was observed in cakes baked from fermented-like dough than without this process.

Keywords: maillard reaction products, antioxidant potential, AGE inhibition, bioactive compounds analysis, buckwheat-based product, ginger cakes

1. Introduction

Ginger cakes are traditional pastries from Central and Eastern Europe. The very important feature of ginger cakes is their ability to remain fresh and savoury for a long time. Currently, ginger cakes are baked on the basis of wheat and rye flour. However, a traditional recipe for ginger cakes was based on the use of rye flour. In Poland, rye (*Secale cereale* L.) is an important grain for bread making and cookies production; therefore, in 2012 18 % of cereal products were made of rye [1]. Rye grain is considered to be a good source of biologically active compounds like antioxidants [2]. Referring to the up-to-date literature, it is highlighted that there is a lack of wider use of buckwheat in pastry.

The buckwheat is a rich source vitamin B1 and B2, lysine, protein with balanced amino acid composition [3], flavonoids [4], phytosterols [5], soluble carbohydrates, D-chiro-inositol and other fagopyritols [6] and thiamin-binding proteins [7]. Buckwheat is also rich in antioxidant compounds such as flavonoids, phenolic acids, tocopherols, reduced glutathione, inositol phosphates and melatonin [8]. Furthermore, buckwheat contains a high amount of rutin (quercetin-3-rutinoside) and has antioxidant, anti-inflammatory and anticarcinogenic properties [9]. According to various chemical compositions, buckwheat-based products were found to display several biological activities, including the increasing number of lactic acid bacteria in rat intestine, treatment of allergic inflammation, reducing the serum glucose level, suppressing cholesterol level, inhibiting protease and scavenging free radicals [10, 11]. These healthy and dietary benefits of buckwheat are main aspects in determining the usage of buckwheat to produce functional products.

The wide spectrum of buckwheat-based bakery and pastry products, e.g. bread, biscuits, crackers, cookies or muffins, was designed by researchers [12]. Mancebo et al. [13] observed that consumers' rating of cookies prepared from buckwheat did not reach high quality score which was mainly related to unpleasant and pungent taste of buckwheat. Therefore, Filipčev et al. [14] noted that 30 % of buckwheat flour is appropriate to create buckwheat-based product with high sensorial acceptability. Chlopicka et al. [15] also showed that 30 % addition of buckwheat flour is highly acceptable, and moreover buckwheat bread has a high antioxidant potential. Moreover, while analysing gluten-free products' sensory profiles, Loredana et al. [16] suggested that the optimum buckwheat flour addition is different for cake, cookies and muffins. The optimum amount in cake was established on the level of 30 % and 10 % for cookies, while for muffins 20 %. Not only the optimisation of the recipes but also technological process parameters for buckwheat-based product preparation have acquired an increasing interest. Lee [17] achieved high overall acceptance for steam bread (wheat with 3 % of buckwheat flour). However, the addition of buckwheat flour was not as high as in the previous studies yet, during the steaming process, not as high amount of an undesirable Maillard reaction products may be formed. Moreover, it is said that dough fermentation step can lead to nutritive and antinutritive compound formation, but some studies also suggested that fermentation process negatively influenced sensory properties of Turkish bread yufka supplemented with 10 % of buckwheat flour [18, 19].

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The baking process is inherent in Maillard reaction product formation. The Maillard reaction is a reaction which might have nutritional and toxicological effects on processed food. The Maillard reaction is initiated by the reaction between the carbonyl group of a reduced sugar and a free amino group of proteins, and then subsequent and parallel reactions go. The progress of the reaction can be considered in the context of early, advanced and final Maillard reaction product formation such as furosine (ε-N-2-furoylmethyl-L-lysine) [20], fluorescent intermediary compounds (FIC) formed at the advanced stage [21], carboxymethyllysine (CML) [22] and melanoidins [23]. The latter are responsible for product's colour formation, nevertheless possessing the ability to scavenge free radicals. The degradation of proteins is usually expressed as FAST index [24], based on the measurement of the fluorescence of tryptophan and formation of intermediatory compounds. Moreover, in thermally treated food *via* Maillard reaction, dietary advanced glycation end products (dAGEs) can be formed [25]. dAGEs are an important contributor to the total pool of AGEs formed in the living organism and can induce oxidant stress and inflammation resulting in increasing risk of diabetes and cardiovascular diseases [26]. The AGE accumulation in the body can be regulated by low dAGE diet or by consuming food with natural AGE inhibitors such as plant extracts and plant products, which are good source of antioxidant polyphenols [27, 28]. Thereby, the high antiglycation potential of wheat-buckwheat bread extract has been recently reported [29].

Gathering all the above-mentioned information led to enriching the traditional ginger cakes recipe with 30 % of light buckwheat flour or flour obtained from roasted buckwheat groats. The new recipe for buckwheat ginger cakes has been created, which fits well with contemporary trends in the bakery. Furthermore, characterisation of the changes occurring during fermentation and baking processing and effect of rutin supplementation should be valuable for the understanding of quality and safety of buckwheat ginger cakes. To achieve the aim, the evaluation of the total phenolics; rutin; products of early, advanced and final Maillard reaction stages; and antioxidative capacity of rye-buckwheat ginger cakes enriched with rutin was addressed in this study.

2. Research methods

2.1. The rye-buckwheat ginger cake preparation

The ginger cakes were prepared using a mix of rye flour (70 %) and light buckwheat flour/flour from roasted buckwheat groats (30 %). Then the rye-buckwheat ginger cake recipe was modified by the addition of low (50 mg/of rutin/100 g of flour mix) and high rutin (100 mg/of rutin/100 g of flour mix) dosage. The rutin dosage added to buckwheat ginger cakes was adjusted to rutin content in one tablet of OTC drugs. The control cake was prepared from rye flour. The ingredient list used for rye-buckwheat ginger cake preparation is included in **Table 1**. All the ingredients were well mixed, and then half of dough was set aside, and the other half was cut into regular discs and baked at 180 °C for 18 min. The first half of dough was spontaneously fermented for 72 h at 21 °C in fermented chamber. Then, the fermented dough was prepared as the previous one. The cakes were freeze-dried and powdered after baking and cooling. The powdered samples were stored at −20 °C until analysis of functional properties and Maillard reaction product formation.

Ingredients	RGC	BERGC-1	BERGC -1L	BERGC -1H	BERGC -2	BERGC -2L	BERGC -2H
Rye flour [g]	100	70	70	70	70	70	70
Light buckwheat flour [g]	–	30	30	30	–	–	–
Flour from roasted buckwheat groats [g]	–	–	–	–	30	30	30
Buckwheat honey [g]	50	50	50	50	50	50	50
Sugar [g]	20	20	20	20	20	20	20
Baking soda [g]	3	3	3	3	3	3	3
Butter [g]	25	25	25	25	25	25	25
Spice mix for ginger cakes [g]	2	2	2	2	2	2	2
Rutin [mg]	0	0	50	100	0	50	100

Table 1. The list of ingredients used for rye-buckwheat ginger cake formulation.

Sample description: RGC (control), rye ginger cake; BERGC-1, buckwheat-enhanced rye ginger cake formulated on (1) light buckwheat flour; BERGC-1L, buckwheat-enhanced rye ginger cake with low rutin dose; BERGC-1H, buckwheat-enhanced rye ginger cake with high rutin dose; BERGC-2, buckwheat-enhanced rye ginger cake formulated on (2) flour from roasted buckwheat groats; BERGC-2L, buckwheat-enhanced rye ginger cake with low rutin dose; and BERGC-2H, buckwheat-enhanced rye ginger cake with high rutin dose.

2.2. The determination of total phenolic, rutin contents and antioxidant capacity in ginger cakes

The initial step included preparation of ginger cake extracts. Therefore, 100 mg of powdered samples was extracted with 1 ml of 80 % (v/v) methanol solution. Then, the mixture was treated by ultrasounds (30 s) and vortexed (30 s) three times. After centrifugation (6860 rpm at controlled temperature 4 °C, 5 min) the supernatant was collected into 5-ml flask. That step was repeated five times to achieve the final extract concentration 20 mg/ml.

The total phenolic content (TPC) was measured using Folin-Ciocalteu reagent according to Przygodzka et al. [30], whereas the rutin content was determined with HPLC with UV detector (330 nm), reported by Zielińska [31]. The antioxidant properties were determined by measurement of scavenging ability against ABTS radical cation, DPPH radical and superoxide anion radical ($O_2^{\bullet-}$) [30]. The measurements were carried out using spectrophotometer UV-160 1PC (Shimadzu, Japan) and Photochem® apparatus (Analytical Jena, Germany). The Trolox was used as a standard.

2.3. The Maillard reaction product determination: furosine, fluorescent intermediary compounds (FIC), carboxymethyllysine (CML) and melanoidins

In these buckwheat ginger cakes, markers of early (furosine), advanced (carboxymethyllysine (CML), total fluorescent intermediate compounds) and final (melanoidins) Maillard reaction compounds were identified and quantified.

The furosine content was determined as described by Delgado-Andrade et al. [32], using HPLC (Shimadzu, Japan) with PDA detector setup at 280 nm. To determine the furosine quantity, the external standard of furosine at concentration range 0.2–9 μg/ml was applied. In the next step, the fluorescent intermediary compounds (FIC) was measured. The total sum of intermediatory compounds in buckwheat ginger cake extracts was determined according to procedure described by Delgado-Andrade et al. [21]. The analysis was followed by enzymatic hydrolysis step using pronase E to break the bindings between intermediatory compounds and proteins. The fluorescent readings were registered at extinction wavelength 347 nm and emission, 415 nm, using a luminescent spectrofluorometer (LS-50B, PerkinElmer, USA). The results are expressed as fluorescence intensity (FI) per milligram of dry matter.

The degradation of proteins (nutritional value) was expressed as FAST index according to Damjanovic Desic and Birlouez-Aragon's procedure [24]. The FAST index was calculated as a ratio of the fluorescence of intermediatory compounds, measured at extinction wavelength 347 nm and emission, 415 nm, using a luminescent spectrofluorometer (LS-50B, PerkinElmer, USA), to fluorescence of tryptophan (extinction ,290 nm, and emission, 340 nm) and described as a percentage.

The carboxymethyllysine (CML), one of the intermediatory compounds, was quantified and determined by HPLC method. The CML extraction was followed by a detailed description of Peng et al. [9]. The OPA reagent solution, which is a mixture of 10 mg of *o*-phthaldialdehyde (OPA) in 2 ml of methanol and the CML determination, was evaluated by HPLC (Dionex, USA) with fluorescent detector (SFLD-3400RS, Dionex, USA). The detector settings were established as the excitation wavelength 455 nm and emission, 340 nm, whereas the oven temperature was adjusted at 35 °C and flow rate 0.2 ml/min. The CML was separated on Luna® 3 μm C18 column (Phenomenex, USA) and eluted in isocratic gradient by water with 0.05 % of *o*-phosphoric acid and acetonitrile with 0.05 % of *o*-phosphoric acid. For quantitative analysis, calibration curve of CML standard was prepared in the range from 2.5 to 20 μM. The results were expressed in μg per gram of dry matter.

The formation of final Maillard reaction products was estimated as reported previously by Zieliński et al. [33]. The absorbance of buckwheat ginger cake methanolic extracts was measured at 410 nm using UV-Vis spectrophotometer (Shimadzu, Japan). Final results were expressed as the absorbance units (AU).

2.4. The evaluation of buckwheat ginger cake inhibitory activity against advanced glycation end-product formation

The inhibitory effect on formation of advanced glycation end products (AGEs) in ginger cakes was studied according to the procedure described by Szawara-Nowak et al. [29] in two in vitro model systems: bovine serum albumin-glucose (BSA-glu) and bovine serum albumin-methylglyoxal (BSA-MGO). The fluorescence intensity was measured at the excitation wavelength 330 nm and emission 410 nm using a luminescent spectrofluorometer (LS-50B, PerkinElmer, USA). The results are expressed in percentage inhibition of AGE formation. Aminoguanidine solution (1 mmol/l) was used as a positive control in this experiment.

3. Results and discussion

3.1. The results of total phenolic and rutin contents and antioxidant capacity in buckwheat ginger cakes

Table 2 shows total phenolic content (TPC) in rye-buckwheat ginger cakes prepared with and without dough fermentation-like step, respectively. The substitution of rye flour by buckwheat flours at level of 30 % w/w on total flour basis resulted in higher TPC values in rye-buckwheat ginger cake BERGC-1 and BERGC-2 obtained without dough fermentation-like step than RGC, 52 and 85 %. In contrast, this effect was not seen in BERGC-1 and BERGC-2 cakes after dough fermentation-like preparation. Furthermore, the addition of low and high rutin doses increased the TPC. The highest TPC was noted in BERGC-2H cake after dough fermentation-like process, whereas the result was almost two times higher than in BERGC-2. Higher TPC values were observed in ginger cakes after 72 h at constant 21 °C fermentation-like process. It can be related to the positive influence of fermentation process of dough on effective formation of antioxidants [34]. Moreover, all types of rye-buckwheat ginger cakes reached higher TPC values than did ginger nut biscuits [14]. It means that this innovative buckwheat-based product is a good source of phenolic compounds.

It is generally known that rutin is the main bioactive compound in buckwheat-based products [9], and for this reason, the rutin content in rye-buckwheat ginger cakes was analysed. The results of rutin content are presented in **Figure 1**. The rutin identification in RGC, obtained both with or without dough fermentation-like process, was related to the buckwheat honey usage in the recipe. Except for buckwheat honey, another crucial source of this flavonoid was light buckwheat flour and flour from roasted buckwheat groats. Therefore, rutin content increased almost twice in BERGC-1 and BERGC-2 cakes due to the 30 % substitution of rye flour by buckwheat flours. The highest rutin content was noted in BERGC-1H cake after dough fermentation-like process; this result was almost 25 times higher than in BERGC-1. In the case of cakes with omitted fermentation-like step, it was noted that BERGC-1 and BERGC-2 with low and high rutin doses have 7 times higher rutin content in BERGC-1L and 15 times in BERGC-1H. The analogous tendency was observed in BERGC-2L and in BERGC-2H, 12 times and 15 times, respectively. Moreover, a similar trend was noted in BERG-1 and BERG-2 obtained after dough fermentation-like process. Generally, the fermentation-like process caused some changes in dough, resulting in higher rutin content in cakes after this process. Compared to Filipčev et al. [14], the rutin content in rye-buckwheat ginger cakes (BERGC-1 and BERGC-2 with dough fermentation-like step) was higher than it was noted in ginger nut biscuits (wheat-buckwheat flour, 70:30).

Type of ginger cakes	TPC	DPPH	ABTS	PCL
Dough *without* fermentation-like preparation				
RGC	2.52 ± 0.10eG	5.15 ± 0.65fI	17.96 ± 0.87cE	3.45 ± 0.07fG
BERGC-1	3.85 ± 0.27dF	7.53 ± 1.14e	28.12 ± 2.08aA	7.95 ± 0.71bcC
BERGC-1L	3.79 ± 0.16dF	9.16 ± 0.10dE	23.94 ± 1.12bC	7.64 ± 0.07cdC
BERGC-1H	4.97 ± 0.16cD	9.37 ± 0.24dE	27.18 ± 0.74aA	10.36 ± 0.08aA
BERGC-2	4.66 ± 0.32cD	8.74 ± 0.77eF	23.48 ± 0.70bB	6.93 ± 0.12dD
BERGC-2L	5.52 ± 0.36bC	12.15 ± 0.36bC	8.64 ± 0.28dG	5.49 ± 0.56eE
BERGC-2H	7.20 ± 0.46aB	17.74 ± 0.29aA	24.49 ± 0.53bB	8.65 ± 0.79bB
Dough *with* fermentation-like preparation				
RGC	4.80 ± 0.14dD	6.87 ± 0.05fH	17.41 ± 0.87cE	4.84 ± 0.06fF
BERGC-1	4.91 ± 0.23cdD	7.20 ± 0.21efG	20.19 ± 1.16abCD	5.93 ± 0.80cE
BERGC-1L	5.71 ± 0.49bC	7.78 ± 0.28dG	21.25 ± 0.37abC	5.96 ± 0.53cE
BERGC-1H	5.80 ± 0.42bC	8.18 ± 0.08cF	21.62 ± 0.90aC	7.32 ± 0.42bC
BERGC-2	4.26 ± 0.14eE	9.40 ± 0.35cE	19.72 ± 0.36cD	4.91 ± 0.79cdF
BERGC-2L	4.63 ± 0.36deD	11.02 ± 0.45bD	14.23 ± 0.65bF	5.97 ± 0.62cE
BERGC-2H	8.43 ± 0.37aA	14.55 ± 0.68aB	21.03 ± 1.41abC	8.97 ± 1.17aB

Table 2. The total phenolic content (TPC) and antioxidant capacity of rye-buckwheat ginger cakes determined by DPPH, ABTS and PCL methods.

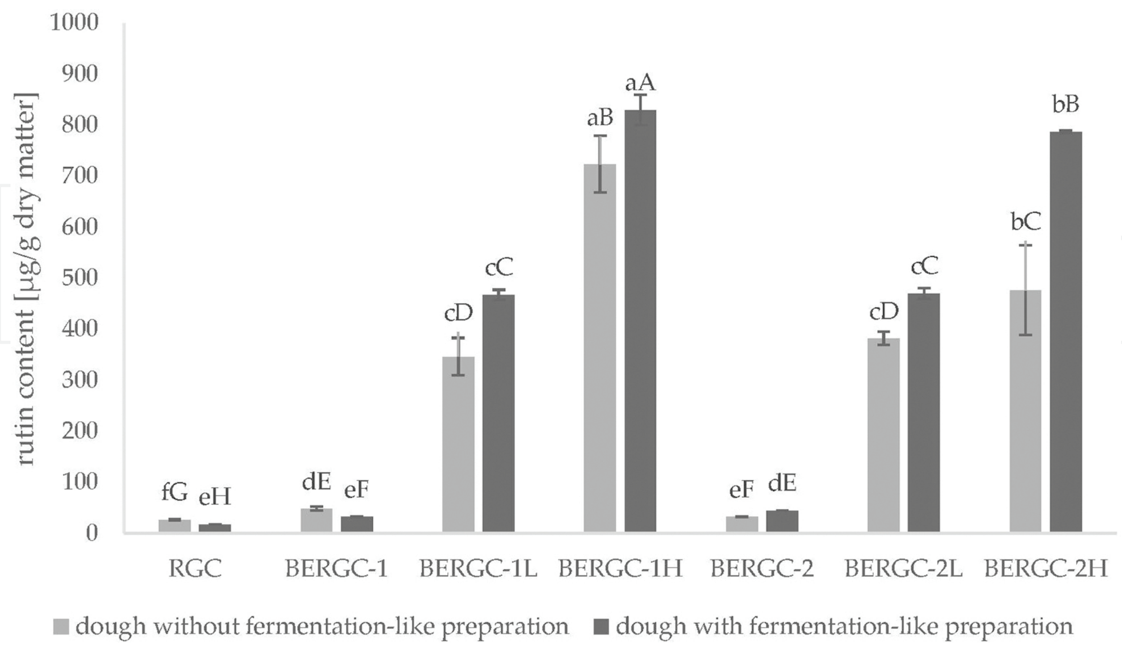

Figure 1. Rutin content in rye-buckwheat ginger cakes from dough obtained with or without fermentation-like preparation. Sample description under **Table 1**.

The 80 % methanol-water extracts of rye-buckwheat ginger cakes were examined for their free radical scavenging activity against $DPPH^{\bullet}$, $ABTS^{+\bullet}$ and $O_2^{\bullet-}$ radicals. The results are collected in **Table 2**. In DPPH method, the highest scavenging ability was noted in BERGC-2H without dough fermentation-like process. In general, higher antioxidant capacity was noted for ginger cakes made of flour from roasted buckwheat groats (BERGC-2) and in cakes from dough without fermentation-like treatment. These results are in accordance with Sedej et al. [35], in which authors maintained that buckwheat groat possesses the strongest DPPH scavenging ability. The 16 % increase of antioxidant activity values was noted in BERGC-2 compared to BERGC-1, 89 % in BERGC-2H to BERGC-1H. A similar increasing trend of antioxidant capacity vs. rutin addition was found for rye-buckwheat ginger cakes with dough after fermentation-like step. The antioxidant scavenging ability of rye-buckwheat ginger cakes against $DPPH^{\bullet}$ was higher than in ginger cakes evaluated from rye flours [33]. For the ABTS method (**Table 2**), the highest scavenging ability was noted in BERGC-1H without dough fermentation-like process. In this case, higher antioxidant capacity as 11 % was noted for ginger cakes made of light buckwheat flour (BERGC-1) and, as previously in DPPH method, in cakes from dough without fermentation-like treatment. The increase of almost 56 % in antioxidant activity values was noted in cakes after buckwheat flour incorporation to achieve BERGC-1 and 31% to BERGC-2 without fermentation-like usage. Then the influence of low and high rutin application was not observed. For cakes after dough fermentation-like process, the 16 % increase of antioxidant activity values was noted in cakes after buckwheat flour incorporation to achieve BERGC-1 and 13%—BERGC-2. The results were similar for BERGC-1H and BERGC-2H. At least, in PCL method the highest scavenging ability was noted, as well as for ABTS method, in BERGC-1H without dough fermentation-like process. Therefore, higher antioxidant capacity was noted for ginger cakes made of light buckwheat flour (BERGC-1) and, as previously in DPPH and ABTS method, in cakes from dough without fermentation-like treatment. The antioxidant activity values have 2.3 times increase in cakes after buckwheat flour incorporation to achieve BERGC-1 and two times in BERGC-2 (dough without fermentation-like step). Then the influence of low and high rutin application was not observed. For cakes after dough fermentation-like process, no spectacular increase of antioxidant activity values was noted in cakes after buckwheat flour incorporation BERGC-1 and BERGC-2. Furthermore, a significant increase of ability to scavenge superoxide anion radicals was observed after addition of high rutin dose, 23 % in BERGC-1H compared to BERGC-1 and 83 % in BERGC-2H in comparison to BERGC-2.

Sample description under **Table 1**. TPC is expressed in mg of rutin eq. per gram of dry matter. Antioxidant capacity is expressed in μmol of Trolox eq. per gram of dry matter. Values are means and standard deviations (n = 3).

3.2. The results of Maillard reaction products formed during buckwheat ginger cake baking

In **Table 3**, data of furosine, fluorescent intermediary compounds (FIC), carboxymethyllysine (CML) and melanoidin contents formed *via* Maillard reaction are summarised.

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Type of ginger cakes	Furosine (mg/g DM)	Total FIC (FI/mg DM)	CML (μg/g DM)	Melanoidins (AU)
Dough *without* fermentation-like preparation				
RGC	0.94 ± 0.08aA	132.8 ± 0.08eI	12.70 ± 1.20dE	0.40 ± 0.01eI
BERGC-1	0.54 ± 0.01bC	166.6 ± 3.05dG	15.60 ± 1.00cD	0.75 ± 0.01bB
BERGC-1L	0.58 ± 0.01bC	208.2 ± 5.08aC	15.90 ± 2.00bcD	0.76 ± 0.00bB
BERGC-1H	0.53 ± 0.07bC	187.6 ± 3.33cE	11.90 ± 0.90dE	0.91 ± 0.01aA
BERGC-2	0.52 ± 0.02bC	200.8 ± 11.53abCD	17.90 ± 1.20abC	0.42 ± 0.01eI
BERGC-2L	0.29 ± 0.02cD	202.2 ± 4.51abD	19.10 ± 0.60aC	0.50 ± 0.01dE
BERGC-2H	0.27 ± 0.01cD	198.2 ± 0.19bD	17.90 ± 1.20aC	0.62 ± 0.01cC
Dough *with* fermentation-like preparation				
RGC	0.49 ± 0.10cC	125.7 ± 5.62eJ	12.69 ± 1.15dE	0.40 ± 0.01fI
BERGC-1	0.80 ± 0.06bB	151.3 ± 2.09dH	27.63 ± 1.95aA	0.45 ± 0.00dG
BERGC-1L	0.14 ± 0.03dE	250.9 ± 1.29aA	18.67 ± 1.66cC	0.35 ± 0.00gJ
BERGC-1H	0.17 ± 0.01dE	230.7 ± 2.49bB	17.98 ± 0.88cC	0.49 ± 0.00bE
BERGC-2	0.76 ± 0.08bB	172.0 ± 0.01cF	24.36 ± 1.31bB	0.43 ± 0.00eH
BERGC-2L	0.98 ± 0.04aA	174.2 ± 6.62cF	23.84 ± 0.80bB	0.48 ± 0.00cF
BERGC-2H	0.47 ± 0.04cC	175.6 ± 6.25cF	22.96 ± 0.90bB	0.55 ± 0.00aD

Table 3. Data of furosine, fluorescent intermediary compounds (FIC), carboxymethyllysine (CML) and melanoidin contents formed via Maillard reaction.

At the early stage of Maillard reaction, furosine was analysed due to its influence on nutritional protein damage in thermally treated food products [36]. According to obtained results, furosine was formed in all types of ginger cakes. In cakes from non-fermented-like dough, light buckwheat flour or flour from roasted buckwheat groats, limited formation of furosine was observed from 0.94 in RGC to 0.54 mg/g of dry matter in BERGC-1 and to 0.52 mg/g of dry matter in BERGC-2. Furthermore, the highest reduction of furosine, being about twofold, was noted in BERGC-2L and BERGC-2H. In cakes with dough after fermentation-like preparation, 63 and 55 % higher formation of furosine was noted in BERGC-1 and BERGC-2 than in RGC. These findings are in accordance with other studies where high protein content of light buckwheat flours and from roasted buckwheat groats was confirmed [38]. Then, the protective effect of rutin application was observed. In contrast, in BERGC-2L the polyphenolic protective effect was not observed. The most effective furosine decrease 4.7-fold and 1.6-fold was noted for BERGC-1H and BERGC-2H, respectively. Moreover, the lowest furosine content was determined in BERGC-1H with fermentation-like step during dough preparation. The furosine content formed in rye-buckwheat ginger cakes reported in this study was at the same level as previously described in enteral formula [37] and rye ginger cakes [33].

In the next step, the total fluorescence of intermediatory compounds (total FIC) formed at the advanced stage of Maillard reaction was studied. The formation of FIC is related to nutritional loss due to the formation of new molecules from lysine-free amino residues and reducing sugars [21]. These results are presented in **Table 3**. The total FIC were determined in all types of cakes within the range of 132.8–208.2 FI/mg in rye-buckwheat ginger cakes from non-fermented-like dough and 125.7–250.9 FI/mg in cakes from fermented-like dough. The addition of buckwheat flours to ginger cake recipe from dough after fermentation-like processing influenced the increasing total amount of FIC formation around 1.25 times and 1.51 times in BERGC-1 and BERGC-2, respectively. The lower formation of total FIC was noted after incorporation of high rutin dose compared to ginger cakes with low rutin dose. The most significant decrease 1.1-fold in BERGC-1H was noted. Similar findings were noted in ginger cakes prepared from dough after fermentation-like process. The buckwheat flour incorporation increased FIC formation 1.2-fold and 1.36-fold in BERGC-1 and BERGC-2, respectively. Then the application of low and high rutin content increased total FIC value up to 65 % in BERGC-1L. These results may suggest that FI compounds are more likely to be formed after the addition of phenolic compounds such as rutin. The FIC values remain at the same level after rutin application to cakes made of flour from roasted buckwheat groats (BERGC-2L and BERGC-2H).

In **Table 3**, the results of carboxymethyllysine (CML) content in rye-buckwheat ginger cakes enriched with rutin, made in two dough preparation procedures, are collected. The CML is known as a nonfluorescent intermediatory compound and characteristic marker of advanced Maillard reaction stage [38]. The CML was identified in all ginger cake samples. The addition of buckwheat flours to ginger cakes made of dough without fermentation-like step influenced increasing CML content around 1.22 times and 1.41 times in BERGC-1 and BERGC-2, respectively. Then, enrichment with rutin proceeded to achieve 24 % lower amount of CML in BERGC-1H than in BERGC-1, whereas no change was observed for BERGC-2H. In cakes evaluated from dough after fermentation-like step, the buckwheat flour addition increased around twofold CML content in BERGC-1 and BERGC-2. Then, addition of rutin decreased CML amount to 1.5 times in BERGC-1H. However, in cakes made of flour from roasted buckwheat groats, no effect was observed. In general, the lowest CML content was found in GC-1H (without dough fermentation-like preparation) 11.9 μg/g of dry matter. According to high values of CML content, it may be observed that fermentation-like preparation of dough negatively influenced intensified formation of CML. The restricted parameters of fermentation process, e.g. using specific bacterial strain and temperature, are required to control CML formation in further studies. Moreover, CML formation was linked to furosine content ($r = 0.63$), suggesting that loss of nutritional quality of elaborated rye-buckwheat ginger cakes was caused by Maillard reaction progressing at the advanced stage.

Sample description under **Table 1**. Furosine is expressed as mg/g of dry matter. Total FIC is expressed in fluorescence intensity (FI) per mg of dry matter. Melanoidin content is expressed as arbitrary units (AU). Values are means and standard deviations ($n = 3$).

In **Figure 2**, the results of FAST index are displayed. In ginger cakes prepared from fermented-like dough, the FAST values ranged from 461 to 1309 % and in cakes without previous fermentation-like preparation from 271 to 1477 %. The obtained results were at least twice lower than those described for ginger cakes made from rye flour [33]. The addition of buckwheat flours to ginger cakes made of dough without fermentation-like process showed FAST index value on the same level for BERGC-1 as in RGC, while for BERGC-2 FAST value was above twice higher. Then, enrichment with rutin proceeds to achieve 2.8 higher FAST in BERGC-1H than in BERGC-1, whereas no change was observed for BERGC-2H. In cakes evaluated from dough after fermentation-like step, the buckwheat flour addition decreased around 2.6-fold and 1.4-fold FAST in BERGC-1 and BERGC-2, respectively. Then, addition of rutin increased FAST values up to 5.4 times in BERGC-1H. Moreover, in cakes made of flour from roasted buckwheat groats, no significant effect of rutin supplementation was observed. An increase of FAST values was observed in using light buckwheat flour in ginger cake recipe. In contrast, in ginger cakes baked from flour from roasted buckwheat groats, no significant effect was observed. However, their FAST values were significantly higher than in raw buckwheat groats [33].

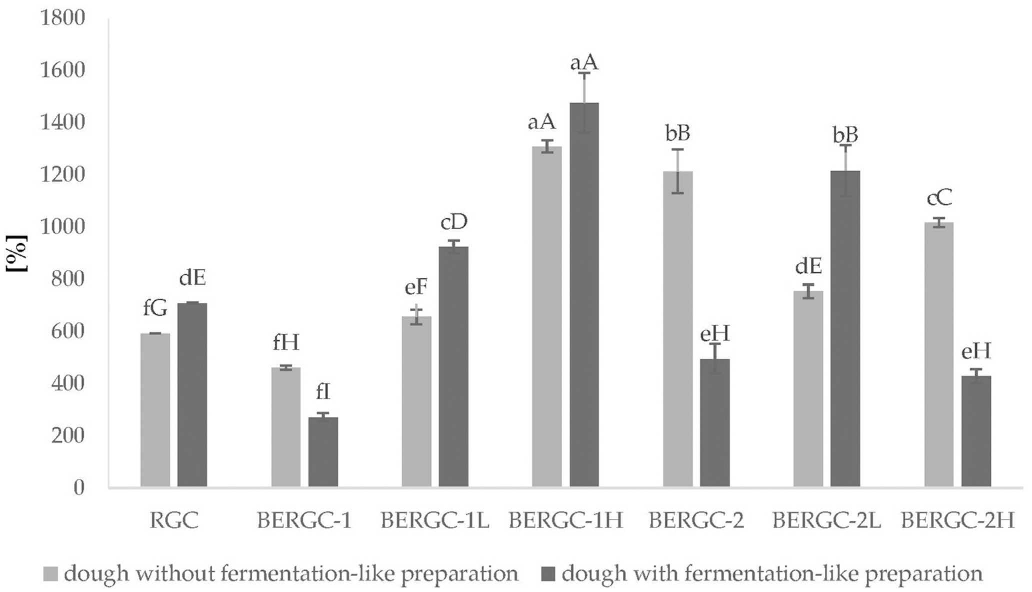

Figure 2. FAST index evaluation in rye-buckwheat ginger cakes obtained from dough with or without fermentation-like process.

The results of brown pigment formations as melanoidin, as the markers of the last stage of Maillard reaction, are shown in **Table 3**. As it may be observed, these brown polymers were formed in RGC as well as in new elaborated rye-buckwheat ginger cakes enriched with rutin. The addition of buckwheat flours to ginger cakes made of dough without fermentation-like process influenced on increasing melanoidin content by 88 % and 5 % in BERGC-1 and BERGC-2, respectively. Additional increase up to 21 % (BERGC-1) and 48 % (BERGC-2) was observed after rutin substitution. Therefore, the most advanced melanoidin formation process was observed in BERGC-1H. In cakes evaluated from dough after fermentation-like step, the results were similar. The obtained values noted in our study were slightly higher than those previously found in ginger cakes from rye flour, but they were twice as those in ginger cakes formulated on rye and wheat flours mix [39]. Moreover, melanoidin formation was found to be positively correlated with antioxidant capacity measured by ABTS test (r = 0.61) and PCL assay (r = 0.84) and DPPH (r = 0.94) as well as TPC and rutin content in cakes without fermentation-like process (r = 0.97 and 0.64). The slightly lower correlation coefficients for ginger cakes prepared from fermented-like dough were noted. Our findings are in accordance with previous studies, where positive correlation between melanoidin formation and antioxidant activity was proved [40].

3.3. The inhibitory activity of buckwheat ginger cakes against advanced glycation end-product (AGE) formation

The inhibitory ability of rye-buckwheat ginger cake extracts, prepared from dough without or with fermentation-like step, against AGE formation was evaluated using in vitro BSA-MGO and BSA-glu model systems. The obtained results are presented in **Figures 3** and **4**.

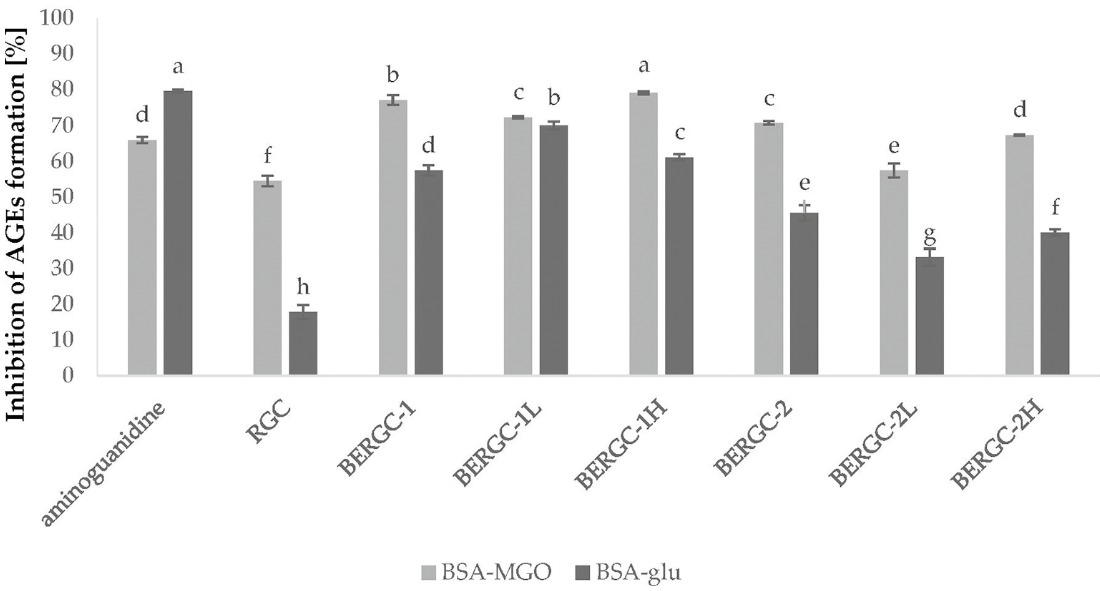

Figure 3. Inhibition of AGE formation in rye-buckwheat ginger cakes from dough without fermentation-like preparation. Sample description under **Table 1**.

Firstly, it was found that in BSA-MGO model in cakes, prepared without fermentation-like preparation, the AGE inhibitory activity increased after usage of buckwheat flours almost 42 and 30 % in BERGC-1 and BERGC-2, respectively (**Figure 3**). Their inhibitory activity values were higher than for aminoguanidine, a medicine used during medical treatment against diseases related to AGE accumulation in human tissues [29]. The enrichment of rye-buckwheat ginger cakes with rutin increased inhibitory activity and the highest value was noted in cakes with high dose of rutin (BERGC-1H). The application of light buckwheat flour in ginger cake formula (BERGC-1) offered also higher values of AGE inhibitory activity than in flour from roasted buckwheat groat incorporation (BERGC-2). In BSA-glu model, also the usage of buckwheat flours almost 23 and 56 % increased inhibitory activity of BERGC-1 and BERGC-2, respectively. However, in this model system, inhibitory effect of aminoguanidine was higher reaching 80 %. Also, the addition of low and high rutin dosages did not increase the inhibitory

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ability. Then, in BSA-MGO model system but in cakes baked from fermented-like dough, 30 % of light buckwheat flour addition increased the AGE inhibitory ability from 59 to 65 %, while no change was obtained after flour from roasted buckwheat groats addition. Therefore, in BSA-MGO model system, the highest values of inhibitory activity of ginger cakes were noted for BERGC-2H. The same results were obtained in BSA-glu model system, whereas the highest inhibitory activity was achieved in BERGC-2H (48 %). According to these results, it has been confirmed that the antiglycation activity was strongly correlated with polyphenolic compound content and the scavenging ability measured for rye-buckwheat ginger cakes obtained from fermented-like dough. It may be summarised that the effect of rutin enrichment was clearly seen in cakes obtained with fermented-like dough, even if the inhibitory activity was slightly lower than those cakes produced from non-fermented dough. Our findings are confirmed in previous studies of antiglycation and antioxidative activities of buckwheat breads [29]. These breads substituted by light buckwheat flour inhibited at 40 % the AGE formation and breads baked from flour from roasted buckwheat groats at 60 % measured in BSA-glu model system, in BSA-MGO at 20 % and 40 %, respectively [29]. Moreover, the high AGE inhibitory potential of coriander, which is an ingredient of spice mix, may contribute to the total antiglycation ability of rye-buckwheat ginger cakes [41].

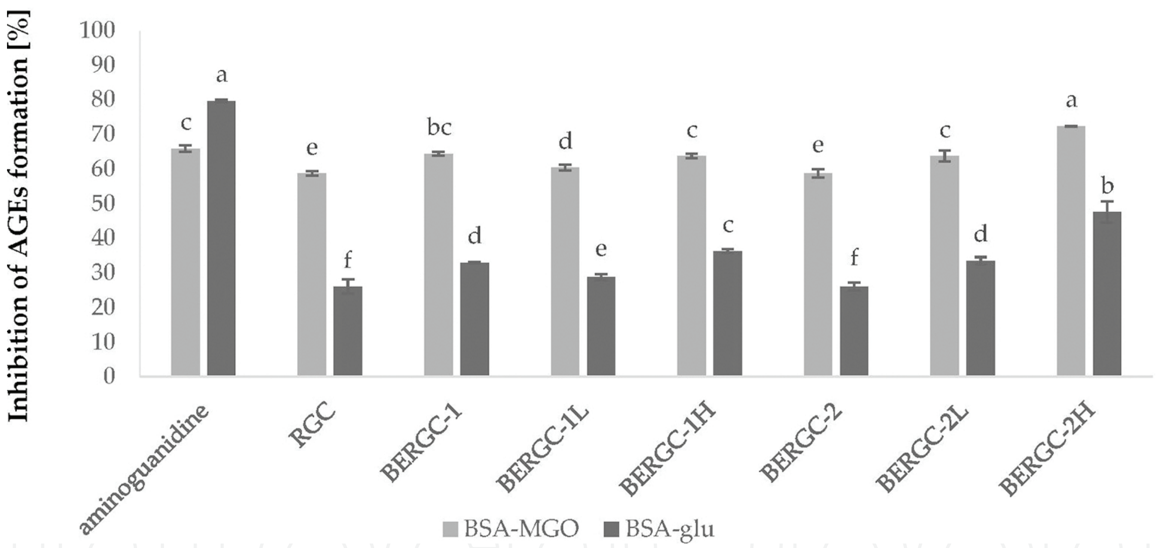

Figure 4. Inhibition of AGE formation in rye-buckwheat ginger cakes from dough obtained with fermentation-like preparation. Sample description under **Table 1**.

4. Conclusions

The new functional product as rye-buckwheat ginger cakes enriched with rutin has been elaborated, and data of total phenolics; rutin contents; antioxidative capacity measured by ABTS, DPPH and PCL methods; and characterisation of Maillard reaction markers have been provided. Moreover, the inhibitory activity against AGE formation using in vitro model systems BSA-MGO and BSA-glu has been studied. The enrichment of rye-buckwheat ginger cakes with rutin improved their increased total phenolic content and antioxidant properties. The protective effect on furosine formation has been observed, whereas melanoidin formation has been stimulated. In contrast, the loss of nutritional quality of rye-buckwheat ginger cakes enriched with rutin has been noted due to the formation of CML and FI compounds at the advanced stage of MR. Moreover, high antiglycation potential of rye-buckwheat ginger cakes enriched with rutin has been confirmed. The relationship between antiglycation ability and rutin content and antioxidant capacity has been found. The addition of buckwheat flours as well as rutin supplementation in ginger cakes has influenced the increase of AGE inhibitory potential.

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