

Antioxidant Properties, Acrylamide Content and Sensory Quality of Ginger Cakes with Different Formulations

Henryk Zieliński^{1*}, Zuzana Ciesarova⁴, Agnieszka Troszyńska¹, Alicja Ceglińska², Danuta Zielińska³, Ryszard Amarowicz¹, Małgorzata Przygodzka¹, Kristina Kukurova⁴

¹Division of Food Science, Institute of Animal Reproduction and Food Research of Polish Academy of Sciences, Tuwima 10, P.O. Box 55, 10-747 Olsztyn 5, Poland

²Warsaw University of Life Sciences, ul. Nowoursynowska 159c, 02-787 Warsaw, Poland

³University of Warmia and Mazury in Olsztyn, Plac Łódzki 4, 10-957 Olsztyn, Poland

⁴VÚP Food Research Institute, Priemysel'ná 4, P.O. Box 25, 824 75 Bratislava 26, Slovak Republic

Key words: rye flour, extraction rate, white wheat flour, ginger cake, antioxidant capacity, phenolic acids profile, acrylamide content, sensory quality

The antioxidant capacity, phenolic acids profile, acrylamide contents and sensory quality of ginger cakes formulated on dark and brown rye flours according to the traditional formula (type 1 and type 2), and on the mixed white wheat flour with dark and brown rye flours due to the currently used formulation (type 3 and type 4), were studied. The antioxidant capacity of the ginger batters and cakes was investigated by cyclic voltammetry (CV) and against 2,2-diphenyl-1-picrylhydrazyl radical (DPPH[•]). Phenolic acids profile was determined by HPLC whilst acrylamide by GC-MS method. The antioxidant capacity of traditional ginger cakes determined by CV and DPPH assays was higher when compared to those formulated on white wheat and rye mixed flours. All types of ginger cakes showed higher antioxidant capacity and phenolic acids content in relation to the respective batters. The higher content of acrylamide by 42 and 24% was noted in traditional ginger cakes of type 1 and type 2 as compared to that noted in ginger cakes of type 3 and type 4 (49±4 µg/kg). The overall sensory quality of traditional ginger cakes formulated on dark and brown rye flours (type 1 and type 2) was higher than of those formulated on white wheat and rye mixed flours (type 3 and type 4). The results of this study indicate the possibility of modulating the sensory and antioxidant properties of ginger cakes by the type and quality of flours in the formulation as well as by batter preparation and baking process.

INTRODUCTION

One of the major challenges faced by the food industry is the need to develop products which can contribute to the customer's desire for a health-protective diet. This task can be achieved when industry action is focused among others on antioxidants which are responsible for the functional properties of food [Trichopoulou *et al.*, 2007; Martínez-Villaluenga *et al.*, 2009]. Ginger cakes are a typical traditional food in Europe. The tradition of making the ginger cake remained in several countries as Russia, Lithuania, Estonia, Germany, Netherlands and Poland. The ginger cakes were made since XVII century in Toruń in Poland and their popularity lasts up till now. The very important feature of ginger cake is its ability to remain fresh and savory for a long time. The cake may be kept in cold and dry place even for a couple of months. Whole meal rye flour (dark flour, extraction rate of 100%) and brown rye flour (extraction rate of about 90%) are the most popular for traditional ginger cake baking since rye (*Secale cereale* L.) is recognised as an excellent raw material for healthy foods

[Bushuk, 2001; Michalska *et al.*, 2007]. Currently ginger cakes are usually formulated on mixed white wheat and rye flours, milk, eggs, caramelised sugar and honey. The traditional and currently produced ginger cakes are spiced with a big amount of cinnamon and ginger. Cinnamon has been shown to possess antioxidative properties, and the flavonoids, especially flavonol glycosides were responsible for the free radical scavenging activity of cinnamon extracts [Mancini-Filho *et al.*, 1998]. Ginger is a root spice from Indo-Malaysia, long time used in Oriental cuisine and heralded for its medicinal qualities. It soothes an upset stomach, invigorates the circulatory system and can help prevent the onset of the common cold. Ginger has been known to have antioxidant activity due to the presence of gingerol-related compounds and diaryl-heptanoids [Kikuzaki & Nakatani, 1993]. The use of honey is not valued as a flavorful sweetener, but is also considered a part of traditional folk medicine [Molan, 1999]. Studies have shown that honey has both antibacterial and anti-inflammatory properties, useful in stimulation of wound and burn healing, and treatment of gastric ulcers and gastritis [Postmes *et al.*, 1993]. Additionally, honey has been reported as a rich source of polyphenolic compounds and honeys from various floral sources exhibited a wide range of antioxidant activities

* Corresponding author: Tel.: +4889 523 46 82; Fax: +4889 524 01 96
E-mail: haziel@pan.olsztyn.pl (Prof. H. Zieliński)

[Frankel *et al.*, 1998; Gheldof & Engeseth, 2002]. It is possible that traditional ginger cakes may offer some health benefits for customers due to the presence of rye flours, honey and ginger spice in the formulation. Moreover, the formulation of ginger cakes may act as promoter of acrylamide formation due to ingredients in recipes containing besides others honey or the mixture of glucose and fructose. On the other hand, ginger cakes are more commonly consumed as mid-morning snacks and seasonally during the Christmas time, so the acrylamide exposure from these items cannot be omitted [Hedegaard *et al.*, 2008]. Therefore, analysis of this compound was included in this study.

The aim of the present research was to investigate the antioxidant capacity, phenolic acids profile, acrylamide content and sensory quality of ginger cakes formulated on dark and brown rye flours (type 1 and type 2, respectively) and on the mixed white wheat flour with dark (type 3) and brown rye flours (type 4) according to the traditional and currently used formulations, respectively.

MATERIALS AND METHODS

Reagents

Ferulic, caffeic, *p*-coumaric, sinapic and vanillic acids, 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 6-hydroxy-2,5,7,8-tetra-methylchroman-2-carboxylic acid (Trolox) were purchased from Sigma (Sigma Chemical Co., St. Louis, MO, USA). Acrylamide analytical grade was purchased from Serva Feinbiochemica (Heidelberg, Germany), 2,3,3-d3-labelled acrylamide 98% from Cambridge Isotope Laboratories Inc. (Andover, Maryland, United States), methanol and acetonitrile HPLC grade from Sigma-Aldrich (St. Louis, United States), ethylacetate 99.9% was from Chromasolve (Reidel-de Haën, Germany). Other reagents of reagent-grade quality were from POCh, Gliwice, Poland.

Characterisation of rye and wheat flours

Rye grain cv. Warko was obtained from a local plant breeding station in Poland. The dark and brown flours with extraction rates of 100% and 92% were obtained using Quadrumat Senior equipment (Brabender, Duisburg, Germany) whereas white wheat flour, floral honey and sugar were purchased at a local market in Olsztyn, Poland.

Rye flours were characterised as it was described by Zieliński *et al.* [2008]. White wheat flour was characterised with the following analyses: moisture, ash, protein and starch content. Protein content was measured following AOAC 979.09 method using Foss Tecator apparatus (Tecator, Sweden) and nitrogen-to-protein conversion factor was 5.7 [AOAC, 2000]. The starch content was determined by the polarimetric method [AACC, 2000]. Moisture and ash content of flours were analysed according to AOAC 15.950.01 and 15.955.03, respectively [AOAC, 1990]. All analyses were made in triplicate.

Ginger cake making process

The following types of ginger cakes were baked: type 1 formulated on dark rye flour, type 2 formulated on brown rye flour, type 3 formulated on mixed white wheat flour with dark rye flour and type 4 formulated on mixed white wheat flour

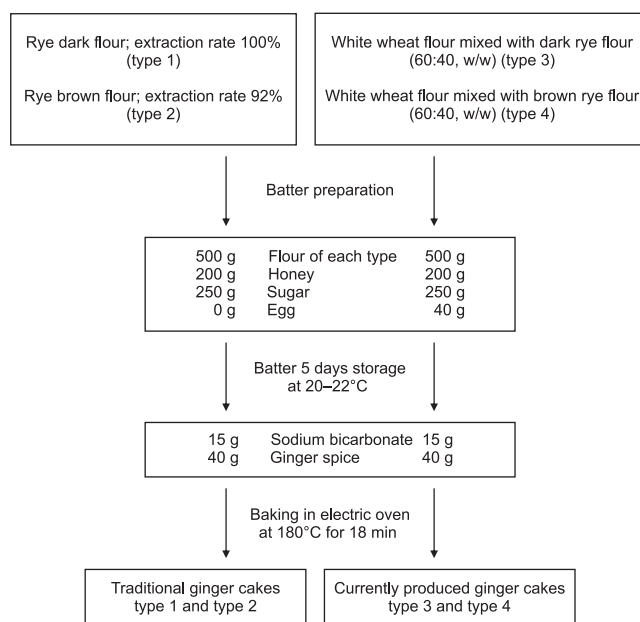


FIGURE 1. Simplified flow diagram of ginger cakes making process with different formulations.

with brown rye flour. The traditional ginger cake-making process (type 1 and type 2) involved batter preparation by mixing flour, honey and sugar. Eggs were included only in the currently used formulations (type 3 and type 4), and storage at 20–22°C for 5 days. Afterwards, soda and ginger spices were added. The batter was cut into 0.5-cm thick discs of 5.5 cm diameter that were baked at 180°C for 18 min in a DC-32E electric oven (Sveba-Dahlen, Fristad, Sweden). The simplified flow diagram of ginger cake making process is shown in Figure 1. At least 20 units of each type of ginger cakes were made. Ginger batters and cakes were freeze-dried and ground. The powdered samples were sieved through a 60-mesh screen and stored at –20°C until analysed.

Preparation of extracts from ginger batter and cake

The ginger batter and cake powder was extracted in triplicate with 80% aqueous methanol (1/10; w/v) for 2 h of shaking at 37°C. Samples were then centrifuged at 2600 × *g* at 4°C for 15 min in a Beckman GS-15 R centrifuge (Beckman Instruments, Inc., Palo Alto, CA, USA). The fresh 80% methanol extracts were used for the determination of the antioxidant capacity by cyclic voltammetry and DPPH assays, and further for phenolic acids profile by HPLC method.

Determination of the antioxidant capacity of the ginger batter and cake by cyclic voltammetry (CV) assay

A potentiostat/galvanostat (GAMRY, USA) was used for voltammetric experiments as it was recently reported in details [Zielińska *et al.*, 2010]. Cyclic voltammetric experiments were performed on 80% MeOH extracts of the batter and ginger cake mixed with 0.2 mol/L sodium acetate-acetic buffer (pH 4.5) at a ratio of 1:1 (v/v) in 80% methanol [Cosio *et al.*, 2006]. The measurements were performed at room temperature using apparatus cell (volume 200 μL), to which respective extracts mixed with

the buffer solution were introduced. Exactly 100 μL of each extract and 100 μL of buffer solution were used in the assay. The cyclic voltammograms were acquired in the range of -100 to +1200 mV at scanning rate of 100 mV s^{-1} at 2 mV intervals. For the test purpose, the total charge was measured below anodic wave curve of the voltammogram. The 80% methanol solutions of Trolox within the concentration range of 0.05–2.50 mmol/L were used and the results were expressed as $\mu\text{mol Trolox/g dm}$. The total charge under anodic wave of the background signal (solvent + supporting electrode) was subtracted from the total charge under anodic wave obtained for each sample measured within the range of +100 to +1100 mV. Triplicate samples were run for each set.

DPPH[•] radical scavenging assay

The DPPH[•] radicals scavenging activity assay was based on a modified method of Brand-Williams *et al.* [1995]. In this assay antioxidants present in the sample reduce the DPPH[•] radicals, which have an absorption maximum at 515 nm. The DPPH[•] solution was prepared by dissolving 10 mg DPPH in 25 mL 80% methanol. First, the extinction of the disposable cuvette with 250 mL of the methanolic DPPH[•] solution and 2.1 mL 80% methanol was measured as blank. Then, the 80% methanol extract (100 mL) of batter or cake was added to 250 mL of the methanolic DPPH[•] solution and 2 mL 80% methanol. The mixture was shaken vigorously and allowed to stand at room temperature in the dark for 20 min. The decrease in absorbance of the resulting solution was monitored at 517 nm for 20 min using a spectrophotometer (UV-160 1PC, Shimadzu, Kyoto, Japan). The Trolox standard solution (concentration 0.1–2.5 mmol/L) in 80% methanol was prepared and assayed under the same conditions. The DPPH[•] scavenging activity was expressed as Trolox equivalents, on the basis of percentage inhibition of absorbance at 515 nm of standards and samples.

Determination of phenolic acids profile

For phenolic acids profile, following the evaporation of methanol in a rotary evaporator at 45°C from the crude extracts, the remaining acids solutions were lyophilised. Separation of phenolic acids was carried out according to Amarowicz & Weidner [Amarowicz & Weidner, 2001]. An aqueous suspension of extract (5 mL) as mixed well 5 mL of 4 mol/L NaOH and hydrolysed for 4 h at room temperature under a nitrogen atmosphere. After acidification to pH 2 with 6 mol/L HCl, free phenolic acids and those liberated from esters were extracted 5 times into 15 mL of diethyl ether using a separatory funnel. Then ether was evaporated; the dry residue was dissolved in 2 mL of methanol and filtered through a 0.45 μm filter. The samples obtained in this way were injected onto a high-performance liquid chromatography (HPLC) column. Phenolic acids were analysed using a Shimadzu HPLC system (Shimadzu Corp., Kyoto, Japan) consisting of an LC-10AD pump, SCTL 10A system controller and SPD-M 10A photo-diode array detector. Phenolic acids separation was carried out by using a prepacked LiChrospher 100 RP-18 column (4 \times 250 mm, 5 μm ; Merck, Darmstadt, Germany). The mo-

bile phase water-acetonitrile-acetic acid (88:10:2; v/v/v) was delivered at a rate of 1 mL/min. The detection was monitored at 260 and 320 nm.

Determination of acrylamide contents of ginger cakes

Acrylamide was extracted from homogenised sample by laboratory equipment Grindomix GM 200 (Retsch, Germany). Water extraction of acrylamide with preextraction to ethylacetate was used according to previously published methodology by Ciesarová *et al.* [2009] using RVC 2–33 IR (Christ, Osterode am Harz, Germany) for rotatory concentration of ethylacetate extracts. Modification for GC-MS analysis using methanol as a solvent for dissolution of dried ethylacetate extracts was applied. For acrylamide analysis Gas Chromatograph 7890A equipped with Mass Spectrometer MSD 5975 Inert (Agilent Technologies, Santa Clara, California, USA) and method published by Kolek *et al.* [2008] using negative chemical ionization was applied under the following chromatographic conditions: injection – split/splitless inlet, temperature: 250°C, volume: 2 μL , purge time: 0.4 min, purge pressure: 200 kPa, liner – single tapered; column DB-FFAP phase (30 m \times 0.25 mm \times 0.25 μm), temperature programme: 60°C (1 min), 10°C/min, 190°C (0 min), 50°C/min, 240°C (2 min), carrier gas: helium, constant flow: 1.0 mL/min; parameters of MSD: interface 250°C, ion source 230°C, quadrupole 150°C, SIM mode, dwell time 150 ms, negative chemical ionization (NCI) with methane as a reagent gas, fragments detected: 70.15 for acrylamide and 73.15 m/z for 2,3,3-d³-labelled acrylamide used as an internal standard.

Sensory evaluation

A 6-member trained panel experienced in discrimination and descriptive analysis on different food products performed assessments [ISO, 1998]. Quantitative descriptive analysis (QDA) was used to determine differences in the sensory characteristics of the ginger cakes [Lawless & Heymann, 1999]. Prior to the analysis, vocabularies of the sensory attributes were developed by the panel in a round-table session, using a standardised procedure [ISO/DIS, 1998]. For evaluation, approximately 30 g of each samples was presented to assessors in a 3-digit coded plastic containers covered by lids and in random order. The panellists evaluated the intensity perceived for each attribute on unstructured 10 cm line scales verbally anchored at each end. The results from the linear scale were subsequently converted to numerical values (from 0 to 10 units) by a computer. The assessments were carried out at a sensory laboratory room, which fulfils the requirements of the international standards [ISO, 1998]. The results were collected using a computerised system (Analsens System, IRZiBZ PAN, Olsztyn, Poland). The profiling analysis of all samples was run in duplicate (two sessions) preceded by an introductory session. Each assessor was provided with spring water and un-salted crackers and asked to cleanse their palate between tasting. The panellists were also asked to evaluate the overall quality of the ginger cakes on the basis of overall appearance, odour, taste and texture. An unstructured graphical scale was anchored on both ends: not accept (0) – fully accept (10).

Statistical analyses

The results of the chemical analyses are given as the means and the standard deviation of three independent measurements. Statistical analysis was performed using Student's t-test and a significance level was set at $p < 0.05$. The correlation analysis between the overall quality of ginger cakes and their antioxidant capacities was performed and the Pearson correlation coefficient was calculated.

The sensory attributes were analysed by ANOVA using Fisher's Least Significant Difference (LSD) test. Statistical analyses were performed using software package (StatSoft Inc., v. 7.1, Tulsa, OK, USA).

RESULTS AND DISCUSSION

Characterisation of rye and wheat flours

The recently reported quality tests showed clearly the effect of the rye flour extraction rate on protein, starch and ash content [Zieliński *et al.*, 2008]. The dark flour (extraction rate of 100%) contained the higher content of proteins and ash whereas the brown flour (extraction rate of 92%) contained the higher amount of starch. In contrast, white wheat flour contained lower content of protein (9.2 g per 100 g of flour), lower content of ash (0.5 g per 100 g of flour) and higher content of starch (74.9 g per 100 g of flour) when compared to the data reflecting the both types of rye flour. The content of dry matter (dm) of dark rye flour, brown rye flour and white wheat flour was 88.5, 88.3 and 87.3, respectively.

Antioxidant capacity of ginger batters and cakes by CV assay

CV method provides information describing the integrated antioxidant capacity without the specific determination of the contribution of each individual component. It is based on the analysis of the anodic current waveform which is a function of the reductive potential of a given compound in the sample and/or a mixture of components. The total antioxidant capacity of the sample is a function combining two sets of parameters. The first parameter is the biological oxidation potential whereas the second parameter is the intensity of the anodic current, reflecting the concentration of the components. Recently, it has been proposed that the area under the anodic current wave, related to the total charge, is a better parameter reflecting the antioxidant capacity of the sample [Chevion *et al.*, 1999; Kilmartin *et al.*, 2001; Cosio *et al.*, 2006; Zielińska *et al.*, 2010].

In this study, cyclic voltammograms of selected Trolox concentration were recorded and then the dependency of the total charge under the anodic wave as a function of increasing concentration of Trolox (0.05–2.50 mmol/L) was provided. The total charge below anodic wave of the background signal (solvent + supporting electrolyte) was subtracted from the total charge obtained for each Trolox concentration within the range of 100 – 1100 mV and then the standard curve was constructed to calculate the antioxidant capacity of the samples (data is not shown). The cyclic voltammograms of 80% MeOH extracts from ginger batters and cakes were recorded as shown in Figure 2. The observed anodic wave was broadened due to the response of several antioxidants with different

oxidation potentials [Kikuzaki & Nakatani, 1993; Frankel *et al.*, 1998; Woffenden *et al.*, 2001; Gheldof & Engeseth, 2002; Rizzi, 2003; Lindenmeier & Hofmann, 2004]. It was found that baking of traditional ginger cakes type 1 and type 2 caused an increase of antioxidant capacity by 50 and 69% when compared to the respective batters. The similar increase by 51 and 57% was observed in relation to the ginger cakes type 3 and type 4 formulated on the mixed wheat and rye flours. Traditional ginger cakes type 1 and type 2 based on dark and brown rye flours showed higher values of antioxidant capacity by average 64% than ginger cakes formulated on wheat and rye mixed flours (Table 1). The rank of antioxidant capacity of ginger cakes was as follows: type 2 > type 1 > type 3 > type 4. These findings indicate different reducing properties of compounds present in the traditional ginger cakes when compared to those formulated in accordance to the currently used formulation. It can be suggested that the higher antioxidant capacity of the traditional ginger cakes based on dark and brown rye flours may result from a higher level of phenolic compounds and neo formulated antioxidant

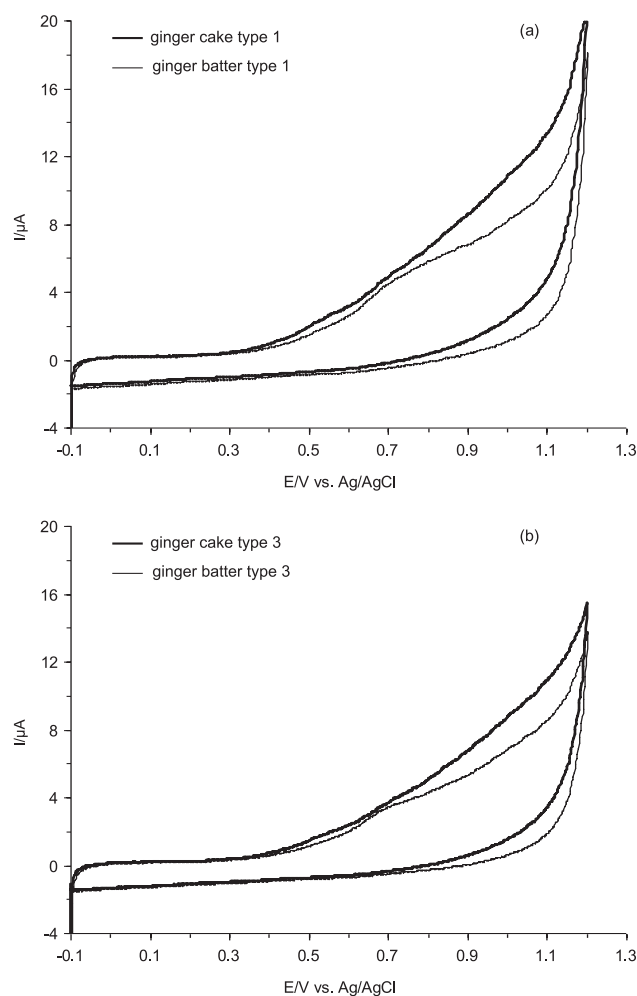


FIGURE 2. Cyclic voltammograms of 80% methanol extracts of ginger batters and cakes (a) type 1 according to the traditional formulation (b) type 3 according to the currently used formulation. Measurements were performed with extracts (100 mg/mL) mixed with 0.2 mol/L sodium acetate-acetic buffer (pH 4.5) at the ratio of 1:1 (v/v); scan rate 100 mV s⁻¹. The total charge under anodic current was calculated from 0.1 to 1.1 V.

TABLE 1. Antioxidant Capacity (AC) of ginger batter and cake measured by CV and DPPH assays¹.

Batter/cake	CV assay		DPPH assay
	Total charge below anodic wave (μC)	AC (μmol Trolox/g dm)	AC (μmol Trolox/g dm)
Type 1	batter	16.01 \pm 1.78	2.75 \pm 0.30 ^a
	cake	24.36 \pm 0.57	4.13 \pm 0.09 ^b
Type 2	batter	15.86 \pm 1.22	2.72 \pm 0.20 ^a
	cake	27.34 \pm 1.07	4.61 \pm 0.18 ^b
Type 3	batter	10.11 \pm 0.46	1.77 \pm 0.08 ^a
	cake	15.45 \pm 0.30	2.68 \pm 0.05 ^b
Type 4	batter	9.42 \pm 0.32	1.66 \pm 0.05 ^a
	cake	15.15 \pm 0.37	2.62 \pm 0.06 ^b

¹ Data expressed as mean \pm standard deviation (n=3). Means in a column for the indicated type of ginger batter and cake followed by the same letter are not significantly different ($p\leq 0.05$).

due to the baking process [Michalska *et al.*, 2008]. In this case a replacement of 60% of rye flours by white wheat flour may provide a lower content of phenolic compounds since white flours are known to be a poorer source of these constituents [Michalska *et al.*, 2007].

DPPH[•] radical scavenging activity of ginger batters and cakes

The 80% methanol extracts of the four types of ginger batters and the respective cakes were examined for their free radical scavenging activity against DPPH[•] radicals. Traditional ginger cake type 1 and type 2 based on dark and brown rye flours showed the same ability to scavenge DPPH[•] radicals (Table 1). The DPPH[•] scavenging activity of these traditional ginger cakes was higher by 12% in comparison to the scavenging activity of ginger cakes formulated on wheat and rye mixed flours. These findings indicate different free radical scavenging properties of compounds present in the traditional ginger cakes when compared to those formulated in accordance to the current recipe. It can be suggested that higher DPPH[•] scavenging activity of ginger cakes formulated on dark and brown rye flours may result not only from the higher level of phenolic compounds but also from the products of Maillard reaction [Michalska *et al.*, 2007, 2008; Zieliński *et*

al., 2010]. It was also found that baking of traditional ginger cakes type 1 and type 2 resulted in higher DPPH[•] scavenging activity by 74% when compared to the batters. Moreover, in the case of the ginger cakes type 3 and type 4 formulated on the mixed wheat and rye flours, the highest increase in DPPH[•] scavenging activity by 155 and 126% was noted, respectively. The antioxidant capacity of traditional and currently produced ginger cakes provided by DPPH assay was almost two and threefold higher than that determined by CV methods. The results from voltammetric experiments were correlated with DPPH[•] scavenging activity ($r=0.83$).

Phenolic acids profile of ginger batters and cakes

In this study the phenolic acids profile originated from extractable fraction was analysed by HPLC. Phenolic acids were recorded at 320 nm, vanilic acid was analysed at wavelength of 260 nm. In ginger batters and cakes almost the same profile of phenolic acids was provided. According to the retention times, vanilic, caffeic, ferulic, *p*-coumaric and sinapic acids were found (Table 2). Ferulic and sinapic were predominant among analysed acids in this material. Our findings on the contents of phenolic acid, determined as free and those liberated from esters, in ginger cakes were in agreement with data reported recently [Weidner *et al.*, 1999; Hansen *et al.*, 2002]. The rye flour extraction rate, replacement of 60% of rye flour by white wheat flour in the formulations, and baking affected the content of phenolic acids in products as shown in Table 2. The highest content and the most beneficial profile of phenolic acids was noted in the traditional ginger cakes whereas ginger cakes formulated on mixed wheat and rye flours showed almost twofold lower content of phenolic acids both in batters and cakes. The traditional ginger cakes formulated on dark and brown rye flours were a better source of phenolic acids. It can be due to the well known findings that phenolic acids are mainly localised in the outer part of cereal grains [Zieliński, 2002]. For example, ferulic acid in rye grain is the most abundant phenolic compound present in bran [Andreasen *et al.*, 2000]. Therefore, it can be concluded that the profile of phenolic acids can be modulated by the type and quality of flours as well as by batters preparation process [Andreasen *et al.*, 2000]. For this reason, consumption of traditional ginger cakes as typical whole meal rye products may increase the intake of beneficial ferulic (Table 4).

TABLE 2. Phenolic acids content (as free and those liberated from esters) in ginger batter and cake ($\mu\text{g/g dm}$)¹.

Phenolic acid	Traditional formulations				Currently used formulations			
	Type 1		Type 2		Type 3		Type 4	
	Batter	Cake	Batter	Cake	Batter	Cake	Batter	Cake
Vanilic	2.3 \pm 0.2	4.4 \pm 0.4	4.4 \pm 0.4	trace	1.9 \pm 0.2	2.4 \pm 0.2	2.4 \pm 0.2	2.4 \pm 0.2
Caffeic	2.9 \pm 0.2	5.2 \pm 0.4	4.1 \pm 0.3	5.4 \pm 0.4	1.4 \pm 0.1	4.9 \pm 0.3	1.4 \pm 0.1	2.7 \pm 0.2
<i>p</i> -Coumaric	2.9 \pm 0.3	4.4 \pm 0.5	4.2 \pm 0.5	2.3 \pm 0.3	1.4 \pm 0.2	3.1 \pm 0.4	1.4 \pm 0.2	2.7 \pm 0.3
Ferulic	18.3 \pm 1.5	24.0 \pm 1.9	15.3 \pm 1.2	15.8 \pm 1.3	9.7 \pm 0.8	12.3 \pm 1.0	7.4 \pm 0.6	11.0 \pm 0.9
Sinapic	25.0 \pm 2.5	34.0 \pm 3.4	19.6 \pm 2.0	22.0 \pm 2.2	11.7 \pm 1.2	14.5 \pm 1.5	8.7 \pm 0.9	13.5 \pm 1.4
Total	51.4 \pm 0.9 ^a	72.0 \pm 1.3 ^b	47.6 \pm 0.9 ^a	45.5 \pm 1.1 ^a	26.1 \pm 0.5 ^a	37.2 \pm 0.7 ^b	21.3 \pm 0.4 ^a	32.5 \pm 0.6 ^b

¹ Data expressed as mean \pm standard deviation (n=3). Means in a row for the indicated batter and cake of each type followed by the same letter are not significantly different ($p\leq 0.05$).

The baking caused an increase in the content of caffeic, ferulic and sinapic acids resulted in an increased level of total phenolic acids in ginger cakes. The level of phenolic acids, taken as a sum of the individual acids content, showed a positive correlation with DPPH[•] scavenging activity ($r=0.75$). Therefore, the observed increase in antioxidant capacity occurring during baking might be explained by the increase of extractable phenolic acids content due to the influence of baking process. Additionally, our recent studies indicate that increased antioxidant capacity might be attributed to the formation of brown melanoidins which are the end products of Maillard reaction [Michalska *et al.*, 2008, Zieliński *et al.*, 2010].

Acrylamide content in ginger cakes

During baking of ginger cakes the acrylamide, as a potentially harmful compound, was produced in the process of the Maillard reaction. It has been proved recently that the type of flour can affect the Maillard reaction products formation [Capuano *et al.*, 2009]. Authors observed that whole-wheat and rye flour contributed to the acrylamide formation to a greater extent than wheat flour due to higher content of free asparagine as a main precursor of acrylamide and moreover due to higher content of dietary fibre and ash. In our study, the partial replacement of wheat flour in ginger cake formulations by brown and dark rye flour resulted in a slight increase in the content of this process contaminant as it is obvious from Figure 3. Both of ginger cakes prepared with the mix of wheat flour and dark or brown rye flour addition contained 49 ± 4 ng/g dm of acrylamide, which is a significantly lower amount in comparison to traditional samples of ginger cakes with dark rye flours (61 ± 5 ng/g dm) and brown rye flour (70 ± 11 ng/g dm) addition. Despite the higher content of acrylamide in ginger cakes with dark and brown rye flour addition, this acrylamide concentrations are still within guidance levels discussed at the Expert Committee Meeting “Industrial and Environmental Contaminants” of the European Commission, Health and Consumers Directorate General in October 2010. Recently, European Commission in January 2011 revealed the recommendation on investigations into the levels of acrylamide [Commission Recommendation, 2011]. Indicative

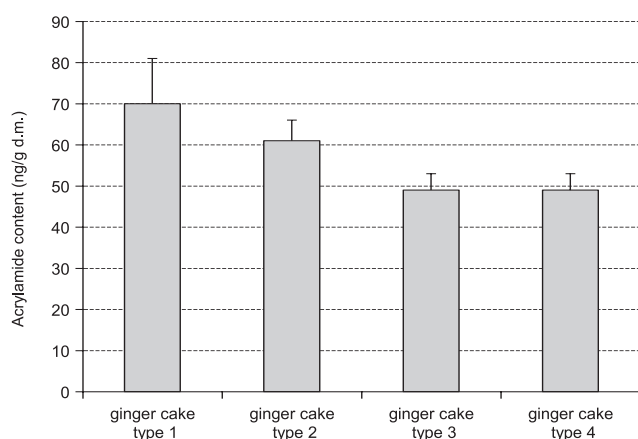


FIGURE 3. The level of acrylamide in traditional (type 1 and type 2) and currently produced ginger cakes (type 3 and type 4).

values have been set for 10 food categories: French fries ready-to-eat: 600 µg/kg; Potato crisps: 1000 µg/kg; Soft bread: 150 µg/kg; Breakfast cereals: 400 µg/kg; Biscuits, crackers, wafers, crisp bread and similar: 500 µg/kg; Roast coffee: 450 µg/kg; Instant coffee: 900 µg/kg; Baby foods: 80 µg/kg; Biscuits and rusks for infants and young children: 250 µg/kg; Processed cereal-based foods for infants and young children: 100 µg/kg.

Sensory evaluation of ginger breads

The literature describing the sensory perception of traditional ginger cakes based on rye flours with different extraction rates in the formulation is surprisingly sparse since currently the ginger cakes formulated on the mixed wheat and rye flours are dominant [Heiniö *et al.*, 2003]. To find attributes which influenced the sensory quality of ginger cake samples the quantitative descriptive analysis (QDA)

TABLE 3. The attributes and definitions used for descriptive analysis of ginger cakes.

	Attribute	Definition
<i>Appearance</i>		
1	colour	scale yields from light brown to dark brown
<i>Odour</i>		
2	honey	odour associated with buckwheat honey
3	spicy	characteristic odour elicited by a mix of spices (e.g. ginger, cinnamon, cloves)
4	cereal	odour typical of cereals (e.g. rye, wheat, oats) mixed in hot water
5	biscuit	odour typical of biscuit (e.g. Petit Beurre)
<i>Flavour/Taste</i>		
6	sweet	fundamental taste sensation evoked by sugars (e.g. sucrose)
7	honey	as for the corresponding odour (measured in the mouth)
8	spicy	as for the corresponding odour (measured in the mouth)
9	cereal	as for the corresponding odour (measured in the mouth)
10	caramel	characteristic flavour from sugarsubmitted to thermal processing (caramelisation)
<i>Aftertaste</i>		
11	sweet	residual taste sensation following consumption evoked by sucrose
12	ginger	a lingering ginger taste associated with spicy ginger
13	baking soda	a lingering baking soda taste in the mouth
<i>Texture (mouth feel)</i>		
14	hardness	force required to bite through the sample placed between the molars
15	meltiness	amount of work to melt samples to point of swallow
16	crispness	degree of disintegrates sample into pieces

Anchoring points: Odour/Taste: none – very intensive; Texture: low – high.

was used which is often applied to study a variety of cereal products [Heiniö *et al.*, 2003; Kilhlberg *et al.*, 2004; Heenan *et al.*, 2008; Klensporf & Jeleń, 2008]. The QDA procedure elicited 16 attributes as follows: one for appearance; four for odour; five for flavour/taste; three for after taste and three for texture (mouth feel). Descriptive vocabulary and definitions used by trained assessors to sensory evaluate are summarised in Table 3. The mean sensory ratings for the samples and the analysis of variance are presented in Table 4. ANOVA showed that there were significant differences in the intensity of attributes such honey odour, spicy odour, biscuit odour, sweet taste, “honey” taste, “spicy” taste, “caramel” taste, ginger after taste and mouth feel (hardness, crispness) depending on the type of ginger cakes. No difference between the two replicate sessions was observed for analysed samples. The results of overall quality of ginger cakes are presented in Figure 4. The average overall quality of scores (in the scale of 10 units) for the traditional ginger cakes were 8.1 (type 1) and 7.8 (type 2) units whereas for the ginger cakes based on the currently used recipe 4.0 (type 3) and 5.1 (type 4). It indicates that the rye flour with extraction rate 100% as well as 92% might contribute to improve the sensory properties of ginger cakes. In order to observe the above differences in the samples more clearly, the sensory profiles based on the mean values of ginger cakes were displayed as spider diagrams in Figure 5. It can be seen that the sen-

sory profiles of traditional ginger cakes (type 1 and type 2) were very similar in the intensity of all analysed attributes. In both samples there dominated the sensory notes pleasant for the consumers such as honey odour, spicy odour, sweet taste, “honey” taste, “spicy” taste and “caramel” taste. In contrast, in the profiles of ginger cakes where rye flour was mixed with wheat flour (type 3 and type 4) these attributes were less intense. It suggests that probably a very mild flavour (odour and taste) did affect the sensory overall quality of ginger cakes type 3 and type 4. QDA proved that the addition of the white wheat flour for ginger cakes formula decreased the sensory quality of samples. Therefore, the ginger cake making process, in which the whole meal rye flour and rye flour with extraction rate of 92% are used, offers the consumers a traditional ginger cakes of a good sensory quality. Moreover, the other ingredients such as honey, sugar and ginger spice had also an important impact on the sensory properties of ginger cakes as honey and spice odour, sweet, honey, spice and caramel taste and ginger aftertaste were the main responsible descriptors. According to many reports, reducing sugars and amino acids affect ginger cake flavour through non-enzymatic Maillard browning reaction, Strecker degradation or simply by heat degradation [Gobbetti *et al.*, 1995; Hansen & Schieberle, 2005; Michalska *et al.*, 2008; Zieliński *et al.*, 2010]. Moreover, the sensory attributes of ginger cakes may also be influenced by the pentosans which comprise the water soluble non-starch polysaccharides, polymers of xylose and arabinose [Marklinder *et al.*, 1996]. The results of sensory analysis indicate that QDA was an adequate tool to describe and quantify ginger cake sensory attributes that are important to consumers.

In this study the correlation coefficient between the overall quality of ginger cakes and their antioxidant capacity determined by CV and DPPH assay had the value of $r=0.93$ and $r=0.96$, respectively. The weaker correlation was noted between the overall quality of ginger cakes and level of phenolic acids ($r=0.75$). The last finding indicates the lack of link between sensory properties of ginger cakes and phenolic acids since they are not implicated in Maillard reaction.

TABLE 4. Descriptive analysis of results based on the analysis of variance (ANOVA) and least significant difference (LSD) test performed on the four types of ginger cakes.

Attribute	Ginger cake samples			
	Traditional formulation		Currently used formulation	
	type 1	type 2	type 3	type 4
1 colour	4.0 ^a	4.1 ^a	3.9 ^a	3.7 ^a
2 honey o.	5.8 ^c	5.0b ^c	2.4 ^a	3.4 ^{ab}
3 spicy o.	6.3 ^b	5.4 ^b	2.6 ^a	3.1 ^a
4 cereal o.	2.6 ^a	3.2 ^a	2.0 ^a	1.6 ^a
5 biscuit o.	1.0 ^a	0.7 ^a	3.5 ^b	2.7 ^b
6 sweet t.	7.4 ^b	7.5 ^b	4.5 ^a	5.7 ^a
7 honey t.	6.6 ^b	6.2 ^b	2.7 ^a	3.9 ^a
8 spicy t.	7.0 ^b	6.2 ^b	2.6 ^a	3.4 ^a
9 cereal t.	1.8 ^a	2.1 ^a	2.5 ^a	1.9 ^a
10 caramel t.	5.4 ^b	5.1 ^b	1.9 ^a	2.7 ^a
11 sweet aftertaste	6.2 ^b	5.5 ^{ab}	3.3 ^a	4.8 ^{ab}
12 ginger aftertaste	6.5 ^b	5.9 ^b	1.8 ^a	2.9 ^a
13 baking soda aftertaste	1.5 ^a	1.3 ^a	2.2 ^a	2.5 ^a
14 hardness	5.5 ^b	5.7 ^b	3.4 ^a	2.9 ^a
15 meltiness	6.0 ^a	5.6 ^a	5.6 ^a	5.9 ^a
16 crispness	1.3 ^a	1.4 ^a	6.8 ^b	6.0 ^b

Means marked in each rows with the same letters do not have significant differences (Fisher test, $p < 0.05$). o - attributes of odour, t - attributes of taste; full scale: 0–10 conventional units.

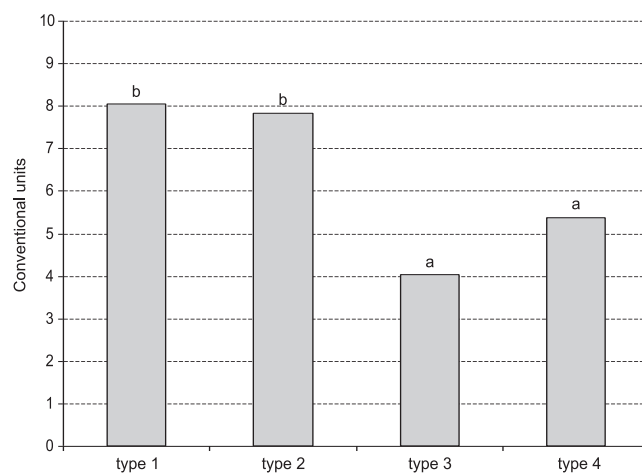


FIGURE 4. The overall quality of ginger cakes. Results reported as arbitrary units. Bars with the same letters do not have significant differences (Fisher test, $p < 0.05$).

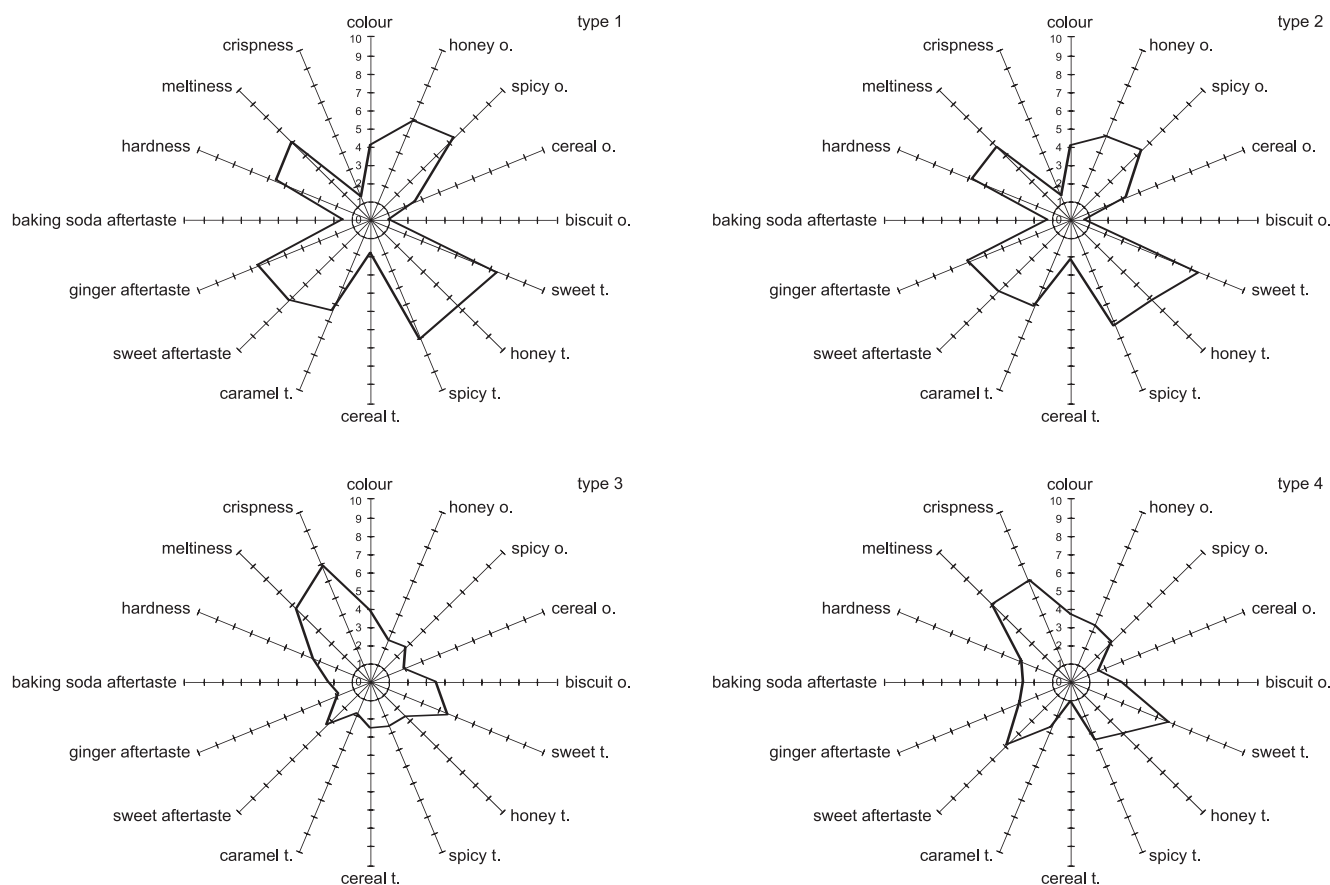


FIGURE 5. Sensory profiles of ginger cake samples: type 1 – based on rye dark flour, type 2 – based on rye brown flour, type 3 – based on white wheat flour mixed with dark rye flour (60:40, w/w), type 4 – based on white wheat flour mixed with dark rye flour (60:40, w/w).

CONCLUSIONS

The antioxidant capacity of traditional ginger cakes formulated on dark and brown rye flours and determined by CV and DPPH assays was higher when compared to those currently formulated on white wheat and rye mixed flours. These differences were related to the higher level of phenolic acids in traditional ginger cakes. All types of ginger cakes showed a higher antioxidant capacity and phenolic acids content in relation to the respective batters. The overall sensory quality of traditional ginger cakes formulated on dark and brown rye flours (type 1 and type 2) was higher than those formulated on white wheat and rye mixed flours. The results suggest that traditional ginger cakes based on dark and brown rye flours should be wider recommended in human nutrition despite of the slightly higher level of acrylamide.

ACKNOWLEDGEMENTS

This research was supported by the joint research collaboration project SK-PL-0051-09/7988/2010.

REFERENCES

1. AACC. Approved Methods of the American Association of Cereal Chemists. In: American Association of Cereal Chemists, 2000. Inc. St. Paul, MN.
2. Amarowicz R., Weidner S., Content of phenolic acids in rye caryopses determined using DAD-HPLC method. *Czech J. Food Sci.*, 2001, 19, 201–205.
3. Andreasen M.F., Christensen L.P., Meyer A.S., Hansen A., Content of phenolic acids and ferulic acid dehydrodimers in 17 rye (*Secale cereale* L.) varieties. *J. Agric. Food Chem.*, 2000, 48, 2837–2842.
4. AOAC. Official Method 979.09. In: Official Analytical Chemists, 2000. Washington, DC.
5. AOAC. Official Methods of Analysis (15th edn). In: Association of Official Analytical Chemists, 1990. Washington, DC, 777–779.
6. Brand-Williams W., Cuvelier M.E., Berset C., Use of a free radical method to evaluate antioxidant activity. *Lebens. Wiss. Technol.*, 1995, 28, 25–30.
7. Bushuk W., Rye production and uses worldwide. *Cereal Foods World* 2001, 46, 70–73.
8. Capuano E., Ferrigno A., Acampa I., Serpen A., Açar Ö.Ç., Gökmen V., Fogliano V., Effect of flour type on Maillard reaction and acrylamide formation during toasting of bread crisp model systems and mitigation strategies. *Food Res. Int.*, 2009, 42, 1295–1302.
9. Chevion S., Chevion M., Chock P.B., Beecher G.R., The antioxidant capacity of edible plants: extraction protocol and direct evaluation by cyclic voltammetry. *J. Med. Food* 1999, 2, 1–11.
10. Ciesarová Z., Kukurová K., Bednářiková A., Morales J.F., Effect of heat treatment and dough formulation on the formation

- of Maillard reaction products in fine bakery products – benefits and weak points. *J. Food Nutr. Res.*, 2009, 48, 20–30.
11. Commission Recommendation of 10/01/2011 on investigations into the levels of acrylamide in food C(2010)9681, 1–7 (2011). Available from: [[Http://ec.europa.eu/food/food/chemicalsafety/contaminants/recommendation_10012011_acrylamide_food_en.pdf](http://ec.europa.eu/food/food/chemicalsafety/contaminants/recommendation_10012011_acrylamide_food_en.pdf)].
 12. Cosio M.S., Buratti S., Mannino S., Benedetti S., Use of an electrochemical method to evaluate the antioxidant activity of herb extracts from the *Labiatae* family. *Food Chem.*, 2006, 97, 725–731.
 13. Frankel S., Robinson G.E., Berenbaum M.R., Antioxidant content and correlated characteristic of 14 monofloral honeys. *J. Apic. Res.*, 1998, 37, 27–31.
 14. Gheldof N., Engeseth N.J., Antioxidant capacity of honeys from various floral sources based on the determination of oxygen radical absorbance capacity and inhibition of *in vitro* lipoprotein oxidation in human serum samples. *J. Agric. Food Chem.*, 2002, 50, 3050–3055.
 15. Gobetti M., Simonetti A., Corsetti A., Santinelli F., Rossi J., Damiani P., Volatile compound and organic acid productions by mixed wheat sour dough starters: influence of fermentation parameters and dynamics during baking. *Food Microbiol.*, 1995, 12, 497–507.
 16. Hansen A., Schieberle P., Generation of aroma compounds during sourdough fermentation: applied and fundamental aspects. *Trends Food. Sci. Tech.*, 2005, 16, 85–94.
 17. Hansen H.B., Andersen M.F., Nielsen M.M., Larsen L.M., Bach-Knudsen K.E., Meyer A.S., Christensen L.P., Hansen A., Changes in dietary fiber, phenolic acids and activity of endogenous enzymes during rye bread-making. *Eur. Food Res. Technol.*, 2002, 214, 33–42.
 18. Hedegaard R.V., Granby K., Frandsen H., Thygesen J., Skibsted L.H., Acrylamide in bread. Effect of prooxidants and antioxidants. *Eur. Food Res. Technol.*, 2008, 227, 519–525.
 19. Heenan S.P., Dufour J.-P., Hamid N., Harvey W., Delahunty C.M., The sensory quality of fresh bread: Descriptive attributes and consumer perceptions. *Food Res. Int.*, 2008, 41, 989–997.
 20. Heiniö R.-L., Liukkonen K.H., Katina K., Myllymaki O., Poutanen K., Milling fractionation of rye produces different sensory profiles of both flour and bread. *Lebens. Wiss. Technol.*, 2003, 36, 577–583.
 21. ISO 8586–1. Sensory analysis – General guidance for the selection, training and monitoring of assessors – Part 2: Experts. International Organization for Standardization, Geneva, Switzerland, 1998.
 22. ISO 8589. Sensory analysis – General guidance for the design of test rooms. International Organization for Standardization, Geneva, Switzerland, 1998.
 23. ISO/DIS 13299. Sensory analysis – Methodology – General guidance for establishing a sensory profile. International Organization for Standardization, Geneva, Switzerland, 1998.
 24. Kikuzaki H., Nakatani N., Antioxidant effects of some ginger constituents. *J. Food Sci.*, 1993, 58, 1407–1410.
 25. Kilhlberg I., Johansson L., Kohler A., Risvik E., Sensory qualities of whole wheat pan bread – influence of farming system, milling and baking technique. *J. Cereal Sci.*, 2004, 39, 67–84.
 26. Kilmartin P.A., Zou H., Waterhouse A.L., A cyclic voltammetry method suitable for characterizing antioxidant properties of wine and wine phenolics. *J. Agric. Food Chem.*, 2001, 49, 1957–1965.
 27. Klensporf D., Jeleń H., Effect of heat treatment on the flavor of oat flakes. *J. Cereal Sci.*, 2008, 48, 656–661.
 28. Kolek E., Šimko P., Šimon P., Jorík V., Šimúth T., Influence of D-glucose polymers on acrylamide elimination during heating – a model study. *J. Food Nutr. Res.*, 2008, 47, 200–204.
 29. Lawless H.T., Heymann H., Sensory Evaluation of Food: Principles and Practices. 1999, Chapman and Hall, New York, pp. 341–372.
 30. Lindenmeier M., Hofmann T., Influence of baking conditions and precursor supplementation on the amounts of the antioxidant pronyl-L-lysine in bakery products. *J. Agric. Food Chem.*, 2004, 52, 350–354.
 31. Mancini-Filho J., Van-Koijij A., Mancini D.A.P., Cozzolino F.F., Torres R.P., Antioxidant activity of cinnamon (*Cinnamomum zeylanicum*, Breyne) extracts. *Boll. Chim. Farm.*, 1998, 137, 443–447.
 32. Marklinder I., Haglund A., Johansson L., Influences of lactic acid bacteria on technological, nutritional, and sensory properties of barley sour dough bread. *Food Qual. Prefer.*, 1996, 3, 285–292.
 33. Martínez-Villaluenga C., Horszwald A., Frias J., Piskula M.K., Vidal-Valverde C., Zieliński H., Effect of flour extraction rate and baking process on vitamin B1 and B2 content and antioxidant activity of ginger based products. *Eur. Food Res. Technol.*, 2009, 230, 119–124.
 34. Michalska A., Ceglińska A., Zieliński H., Bioactive compounds in rye flours with different extraction rates. *Eur. Food Res. Technol.*, 2007, 225, 545–551.
 35. Michalska A., Amigo-Benavent M., Zieliński H., Del Castillo M.D., Effect of baking on the formation of MRPs contributing to the overall antioxidant activity of rye bread. *J. Cereal Sci.*, 2008, 48, 123–132.
 36. Michalska A., Ceglińska A., Amarowicz R., Piskula M.K., Szawara-Nowak D., Zieliński H., The antioxidant contents and antioxidative properties of traditional rye breads. *J. Agric. Food Chem.*, 2007, 55, 734–740.
 37. Molan P.C., Why honey is effective as a medicine. I. Its use in modern medicine. *Bee World*, 1999, 80, 80–92.
 38. Postmes T., Van der Bogaard A.E., Hazen M., Honey for wounds, ulcers, and skin graft preservation. *Lancet*, 1993, 341, 756–757.
 39. Rizzi G.P., Electrochemical study of the Maillard reaction. *J. Agric. Food Chem.*, 2003, 51, 1728–1731.
 40. Trichopoulou A., Soukara S., Vasilopoulou E., Traditional foods: a science and society perspective. *Trends Food Sci. Tech.*, 2007, 18, 420–427.
 41. Weidner S., Amarowicz R., Karamać M., Dąbkowski G., Phenolic acids in caryopses of two cultivars of wheat, rye and triticale that display different resistance to pre-harvest sprouting. *Eur. Food Res. Technol.*, 1999, 210, 109–113.
 42. Woffenden H.M., Ames J.M., Chandra S., Relationships between antioxidant activity, color, and flavor compounds of crystal malt extracts. *J. Agric. Food Chem.*, 2001, 49, 5524–5530.
 43. Zielińska D., Szawara-Nowak D., Zieliński H., Determination of the antioxidant activity of rutin and its contribution to the antioxidant capacity of diversified buckwheat origin material by updated analytical strategies. *Pol. J. Food Nutr. Sci.*, 2010, 60, 315–321.

44. Zieliński H., Low molecular weight antioxidants in the cereal grains. *Pol. J. Food Nutr. Sci.*, 2002, 11, 3–9.
45. Zieliński H., Amigo-Benavent M., Del Castillo M.D., Horszwald A., Zielińska D., Formulation and baking process affect Maillard reaction development and antioxidant capacity of ginger cakes. *J. Food Nutr. Res.*, 2010, 49, 140–148.
46. Zieliński H., Michalska A., Ceglińska A., Lamparski G., Antioxidant properties and sensory quality of traditional rye bread as affected by the incorporation of flour with different extraction rates in the formulation. *Eur. Food Res. Technol.*, 2008, 226, 671–680.

Received March 2011. Revision received and accepted May 2011.
Published on-line on the 18th of January 2012.