Dynamics of 5-Hydroxymethylfurfural Formation in Shortbreads during Thermal Processing

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Abstract

Kowalski S., Lukasiewicz M., Juszczak L., Kutyła-Kupidura E.M. (2013): **Dynamics of 5-hydroxymethylfurfural formation in shortbreads during thermal processing**. Czech J. Food Sci., **31**: 33–42.

The analysis was carried out of 5-hydroxymethyl-2-furfural (HMF) formation during the baking of shortbreads. The investigation was done on three types of shortbread in which sucrose, glucose, or fructose were used as sweeteners. In all the samples the concentration of sugar was 20% (w/w). The cookies were baked in a laboratory oven at temperatures of 200, 215, 230, and 245°C. The samples for the HMF determination were taken at intervals from 5 to 18 min depending on the baking temperature. It was found that HMF formation can be described by exponential equation. The HMF formation was correlated with the colour changes of the cakes determined according to CIELab system. Different parameters of colour were investigated, however, only in the case of brightness difference may the correlation be treated as statistically important.

Keywords: HMF; sweeteners; cookies; colour changes

Thermal food processing may be classified as a unit operation in blanching, cooking, baking, frying, drying, pasteurisation, sterilisation, thawing etc. It involves raising the product to some final temperature (surface or inner) that depends on the particular objective of the process (Sun 2005). The process of baking is commonly used to obtain certain sensory or textural features, or to assure microbiological safety as well as to eliminate enzymatic activities for manufacturing shelf stable food products (Tewari & Juneja 2007). On the other hand, sensory attributes including aroma, taste, and colour are strictly correlated with chemical processes when higher temperature is used to prepare food products. Good examples are: bread, cereals, chocolate, coffee, nuts, malt, or grilled meat. Thermal operations taking place in food products are associated with the occurrence of non-enzymatic browning phenomena or so-called Maillard reaction (Richardson 2001). Processes like roasting and baking are connected with a very intensive thermal treatment. In some cases, the temperature and time of the process are highly correlated with the product dimensions. In bread baking, small products (about 45 g) can be processed for about 20 min at 240–250°C, while bigger ones (up to 1000 g) can be heated up to 60 min or longer at 220°C.

During the treatment, caramelisation of sugars as well as Maillard reactions take place especially on the product surface (Richardson 2001).The presence of 5-hydroxymethyl-2-furfural (HMF) in foods is usually the result of the Maillard reaction or caramelisation processes, especially when dehydration of monosaccharides in an acidic environment takes place (Yaylayan 1997; Perez Locas & Yaylayan 2008; Capuano & Fogliano 2011). When model compounds are used, i.e. there are no proteins or amino acids in the reaction media, the mechanism of HMF formation may be divided into two separate paths (Figure 1) (Perez Locas & Yaylayan 2008).

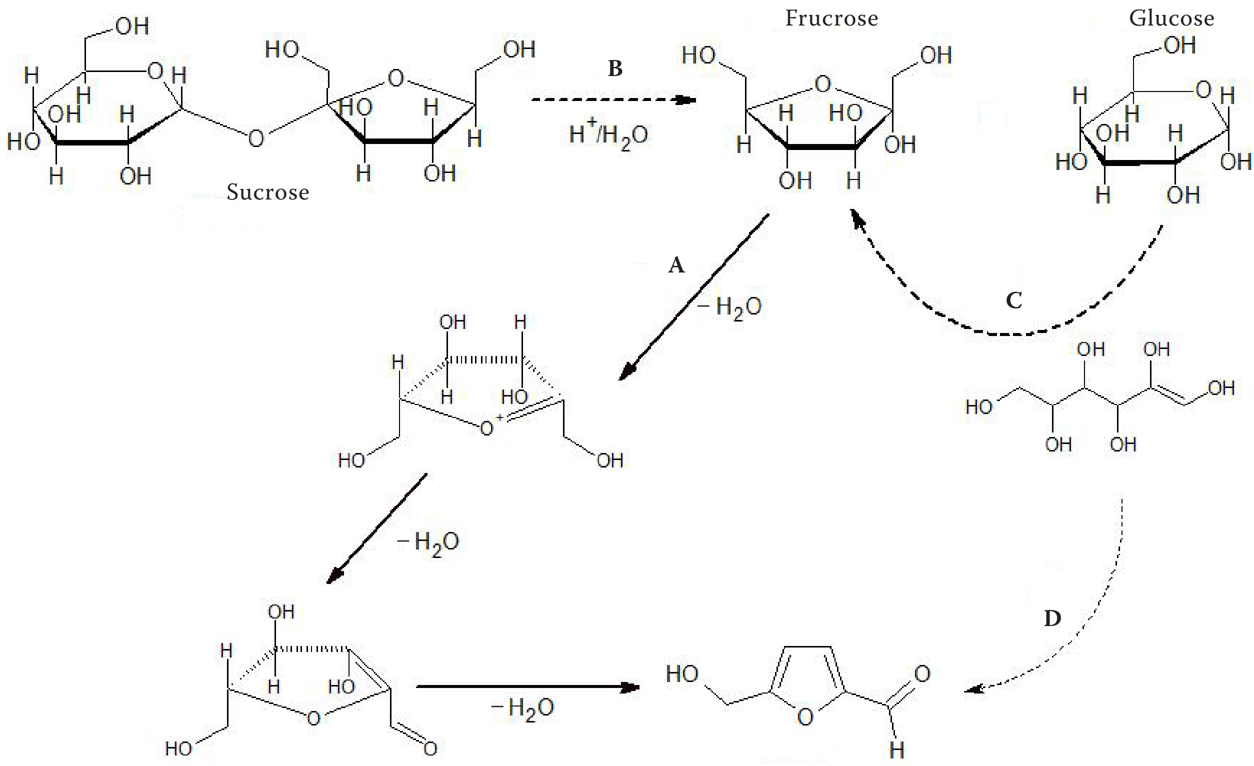

Figure 1. Simplified HMF formation mechanism: **A** – main mechanism of fructose dehydratation; **B** – inversion of sucrose; **C** – Lobry de Bruyn-Alberda van Ekenstein isomerisation; **D** – side path of glucose transformation (Antal *et al.* 1990)

One of them includes the transformation of fructofuranose ring, while in the second one an acyclic intermediate may be observed. The basic substrates for HMF production are monosaccharides i.e. fructose or glucose (Corma *et al.* 2007). Either of them may be used as a primary substrate or obtained in the process of disaccharide (sucrose) acidic hydrolysis, which leads to fructose/glucose equimolar mixture. It is known that the dehydration of fructose is more effective and faster than that of glucose (Perez Locas & Yaylayan 2004; Yaylayan 2006; Zhao *et al.* 2007). Glucose as an aldohexose may be involved in competing reaction pathways leading to nonfuran cyclic ethers by-products formation or may be isomerised into fructose according to Lobry de Bruyn-Alberda van Ekenstein transformation (Miljkovic 2009).

Despite many studies on the HMF effects on human health, an unambiguous interpretation exists of its influence on the human body. LD_{50} dose of 3.1 g/kg body weight in the case of oral administration was established based on studies on rats (Ulbricht *et al.* 1984). Potential cytotoxicity and carcinogenicity of this compound was also confirmed by numerous studies. According to these, harmful effects may be a direct result of HMF impact or the result of HMF transition to the 5-sulphooxymethylfurfural (5-SMF) and other metabolites (Delgado-Andrade *et al.* 2008; Bakhiya *et al.* 2009; NTP Technical Report 2010).

It is also worth pointing out that reports can be frequently found dealing with beneficial effects of HMF or its derivatives on the human body, or even therapeutic possibilities in the fight against cancer

Table 1. Ingredients used for shortbreads baking (all values in g)

Wheat flour	Saccharose	Fructose	Glucose	Confectionery fat	Sum of components
300	120	–	–	180	600
300	–	120	–	180	600
300	–	–	120	180	600

or H1N1 virus (Chuda *et al.* 1999; Utsunomiya *et al.* 2002; Ding *et al.* 2010; Wang *et al.* 2010; Sriwilaijaroen *et al.* 2011).

Compounds like 5-hydroxymethyl-2-furfural or furosine are usually used for monitoring the intensity of changes detected during thermal processing of food. HMF has been widely used for this purpose (Delgado-Andrade *et al.* 2007; Cioroi 2008; Rufián-Henares *et al.* 2008; Morales *et al.* 2009; Mesías-García *et al.* 2010). On the other hand, HMF present in foodstuffs seems to be studied extensively also as a food contaminant with potential harmful properties (Lee *et al.* 1995; Hiramoto *et al.* 1996; Albala-Hurtado *et al.* 1998; Hidalgo & Pompei 2000; Fallico *et al.* 2003; Gökmen *et al.* 2008; Husoy *et al.* 2008).

Outside food technology, HMF is known as a compound in the scope of interest of chemical industry, among other things due to the numerous possibilities for its use in macromolecular compounds synthesis (Román-Leshkov *et al.* 2006; James *et al.* 2010).

The aim of the present study was to determine if the replacement of sucrose by different sugars (glucose or fructose) in the dough destined for the production of brittle biscuit word(s) missing. The investigation of HMF dynamics during baking was also done based on the known mono- and disaccharide reactions mechanisms. The research was focused on the influence of the sugar type and baking temperature on the quantity of 5-hydroxymethylfurfural formed during baking as well as on the colour changes of shortbreads.

MATERIAL AND METHODS

The research was carried out using samples of cookies baked in a laboratory oven (Miwe Condo, Arnstein, Germany) at different temperatures: 200, 215, 230, and 245°C, respectively. Three different sugars (glucose, fructose, sucrose) at a concentration of 20% (w/w) per dough were applied as cookies sweeteners (Table 1). For the dough preparation, wheat flour (type 550) and confectionery fat Kasia were used. After weighing, the ingredients were mixed and kneaded by hand to achieve a uniform dough mass. The dough was allowed to rest in the refrigerator for 30 minutes. After this period of time, shortbreads were formed (5 mm high and 50 mm diameter). At specific periods of the baking time, samples of cookies were taken and analysed for HMF content using high performance liquid chromatography (HPLC). The colour analysis of the cookies by means of CIELab system was done as well.

Chromatographic analysis. For chromatographic analysis, 1 g of ground cookies were weighed into 25 ml centrifuge tube with a cap. 10 ml of water was added as well as 2.5 ml trichloroacetic acid water solution (40% (w/v)) (Ameur *et al.* 2006). The sample was vortexed intensively for 5 minutes. The suspension was than centrifuged for 20 min at 12 000 rpm (4°C). The extraction process was repeated twice for the same sample except that 5 ml of water was used instead of 10 ml. Supernatants were collected in 25 ml volumetric flask and made up to the mark with water. Before chromatographic analysis, the samples were filtered through 0.45 µm disc filter.

HMF was determined by HPLC using a Knauer chromatograph equipped with spectrophotometric detection (Knauer, Berlin, Germany). The measurement parameters were as follows: eluent – water/methanol 9:1 (v/v), flow 1 ml/min, UV detection – 285 nm, column RP-18 Lichrosphere (250 × 4 mm, 10 µm particle size) (Knauer, Berlin, Germany), sample volume 20 µl. The measurements were done in duplicate.

Colour analysis. The colour analysis was performed in the CIELab system using a X-Rite Color i5 (X-Rite Inc., Grand Rapids, USA) spectrophotometer (illuminant D65, measurement geometry d/8, spectral range 400–700 nm). The analysis was done on ground cookies samples. The results (L^* – luminance, a^* – position between red (magenta) and green, b^* – position between yellow and blue) were correlated with HMF concentration. Total colour change ΔE was calculated as follows:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \quad (1)$$

where:

ΔL – brightness difference

Δa – redness difference

Δb – yellowness difference (Fernandez-Artigas *et al.* 1999)

Calculation of induction time and HMF formation dynamics. For the estimation of HMF formation induction time, the graphical method was employed. The point of intersection of two linear functions fitted to the experimental points was determined analytically.

For all the samples, the dynamics of HMF formation may be described using the exponential equation:

$$F(t) = ae^{bt} \quad (2)$$

where:
t – time
b – exponential factor– EF
a – pre-exponential factor – PEF

Statistical analysis. Statistical analysis was performed using Statistica Version 9.0 (StatSoft, Krakow, Poland). The analysis was done of the correlation between the colour parameters and HMF concentration. The significance of the correlation coefficients values was tested by t-Student test.

RESULTS AND DISCUSSION

HMF formation during shortbreads processing

Sucrose is the main sweetener that is commonly used in confectionary where baking goods are produced, however, glucose and fructose may also serve as efficient sweeteners. All of them are able to be converted into HMF. The increase in HMF content as a function of the baking time and temperature is shown for all sweeteners investigated in Table 2. According to the results obtained, we can state that in the case of fructose sweetened cookies, HMF content reaches the highest value at all temperatures investigated except 230°C. In general, HMF level drops in the order fructose > sucrose > glucose. The interpretation of this phenomenon is hidden in the reaction mechanism (Figure 1) and subsequent number of the reaction steps i.e. direct dehydration of fructose (one step), isomerisation of glucose into fructose and subsequent dehydration (two steps), hydrolysis of sucrose and parallel dehydration of fructose and isomerisation and dehydratation of glucose. The detailed mechanistic discussion was described in the introduction section.

Going into detail of HMF formation during baking, it may be stated that the increase in the baking temperature results in shortening the baking time as well as increasing HMF content in cookies (Table 2). In other research, it has been

Table 2. 5-Hydroxymethyl-2-furfural (HMF) content in investigated shortbreads

Temperature (°C)	Sweetener					
	fructose		glucose		sucrose	
	time of baking (min)	HMF (mg/kg)	Itime of baking (min)	HMF (mg/kg)	time of baking (min)	HMF (mg/kg)
200	7	2.99 ± 0.02	7	2.91 ± 0.40	7	4.26 ± 0.35
	9	4.22 ± 0.25	9	9.37 ± 0.75	10	7.80 ± 0.19
	12	37.44 ± 1.15	12	25.50 ± 2.01	13	24.56 ± 0.64
	15	137.76 ± 0.85	15	129.48 ± 17.77	16	221.82 ± 4.66
	18	577.60 ± 17.85	18	332.55 ± 19.96	19	563.61 ± 34.56
215	7	13.48 ± 0.47	7	15.56 ± 0.38	6	3.42 ± 0.16
	9	33.91 ± 4.71	9	53.52 ± 2.85	9	21.91 ± 0.87
	12	297.84 ± 3.88	12	288.28 ± 6.76	12	132.96 ± 7.31
	15	1655.76 ± 45.35	15	568.94 ± 33.02	15	652.67 ± 27.79
	18	4384.13 ± 249.45	18	1916.16 ± 61.41	18	2864.8 ± 153.34
230	5	1.68 ± 0.14	5	6.43 ± 0.59	5	8.60 ± 0.40
	7	21.20 ± 6.24	7	24.01 ± 1.97	8	39.63 ± 1.54
	9	74.10 ± 1.65	9	133.03 ± 4.26	11	422.44 ± 18.44
	11	904.91 ± 30.61	11	392.70 ± 0.58	14	2653.78 ± 66.09
	13	1880.69 ± 144.67	15	1085.68 ± 14.00	17	6713.30 ± 244.84
245	5	4.97 ± 1.00	5	5.92 ± 1.08	3	11.73 ± 1.67
	7	31.16 ± 0.52	7	36.15 ± 2.06	6	123.22 ± 6.98
	9	512.06 ± 13.22	9	177.74 ± 0.25	8	167.51 ± 4.04
	11	3146.64 ± 236.26	11	1212.06 ± 26.61	10	1980.78 ± 117.32
	13	4573.80 ± 15.21	13	3260.80 ± 8.80	12	3894.48 ± 137.59

found that at temperatures below 300°C (200 and 250°C, respectively) the amount of HMF is lower when sucrose is used as a sweetener in comparison with glucose and fructose. The research was conducted on cookies with 30% of sweetener in the dough (Ameur *et al.* 2007). The results obtained corroborate our observation although some differentiation between glucose and fructose is also important when focused on the reaction mechanism as described above. The observations made by Ameur *et al.* (2007) were also confirmed in a work on glucose-sweetened cookies done by Gökmen *et al.* (2007). The authors observed an increase in HMF concentration with temperature rising during baking (from 160 to 230°C).

The dynamics of the sugar transformation into HMF may be described using the exponential equation. In some publications, the authors have described the dynamics of HMF synthesis using the first order kinetics (Ameur *et al.* 2006, 2007). In fact, the corresponding curves may suggest the first order kinetics although, as mentioned above, the reaction mechanism involves some intermediates and thus the process is a consecutive reaction and cannot be treated using simple kinetic equations. The question also arises about the validity of such an approach in which the kinetic constants are estimated to describe the reactions occurring during baking. According to the consecutive reaction properties, the induction time may be observed in the process (Figure 2). As can be seen, the induction time shortens as the temperature increases. The shortest induction time was observed in the case of fructose at higher temperatures. It may testify that the rate of fructose conversion into the first intermediate is the highest. On the other hand the induction times observed with sucrose are much longer due to the hydrolysis step (sucrose inversion into monosaccharides). It is also worth pointing out that at higher temperature (245°C) the induction time for glucose transformation is longer than that observed for sucrose. This may be the result of differences between two reactions rates. The inversion of sucrose is faster than the isomerisation of glucose into fructose according to Lobry de Bruyn-Alberda van Ekenstein transformation. In that case, the inversion reaction may be speeded up by the product (fructose) removal that is constantly consumed for the first transformation leading to HMF. This phenomenon was also observed by Gökmen *et al.* (2007) when a rapid increase in HMF content with decreasing pH accrued.

According to Eq. (2), exponential factors (EF) were estimated in sucrose based experiments (Table 3). The EF coefficient increases during the baking progress when the temperature is rising. It is an obvious phenomenon even in highly viscous reaction systems, i.e. dough. The values of a pre-expotential factors rise as well, however, their changes do not influence the process course as much as EF factors. The substitution of common sugar by fructose results in a faster HMF formation which mirrors in EF factors that almost reach the value above 0.9. An increase of the overall reaction dynamics is observed in this case. On the other hand, baking of cookies sweetened with glucose results in a far slower increase in HMF content when compared to sucrose based cookies, although in this case the exponential equation fits the experimental points as well. Exclusively at 245°C was EF higher than in the case of sucrose and equalled to 0.8067. The results obtained by fitting the experimental data confirm the differences between the reaction mechanisms discussed above. Therefore, the conclusion may be made that

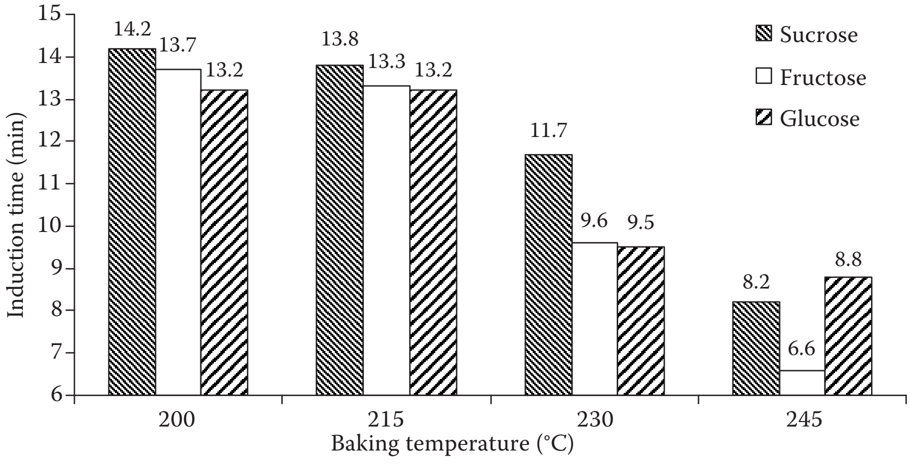

Figure 2. Induction time observed during shortbreads baking

Table 3. Dynamics of HMF formation

Sweetener		Temperature (°C)			
		200	215	230	245
Sucrose	EF	0.4372	0.5619	0.5842	0.6550
	PEF	0.1359	0.1335	0.4911	1.7193
	R^2 HMF vs. time	0.9635	0.9976	0.9829	0.9622
Glucose	EF	0.4306	0.4567	0.5224	0.8067
	PEF	0.1637	0.7972	0.7178	0.1208
	R^2 HMF vs. time	0.9915	0.9615	0.9393	0.9916
Fructose	EF	0.5030	0.5314	0.8901	0.9132
	PEF	0.0708	0.3002	0.0283	0.0695
	R^2HMF vs. time	0.9851	0.9848	0.9735	0.9515

EF – exponential factors; PEF – pre-exponential factor; HMF – 5-hydroxymethyl-2-furfural; R^2 – correlation coefficients

if a low level of HMF is needed, only glucose may be the sugar substitute in the cookies preparation. Fructose is sometimes recommended for diabetics because it does not influence the insulin formation (Grant *et al.* 1980). Fructose has also a low glycemic index of 19 ± 2, as compared with those calculated for glucose (100) and sucrose (68 ± 5) (Atkinson *et al.* 2008). Based on the results of the experiments, it may be stated that the benefits of fructose substitution are covered by some drawbacks including higher levels of HMF that is known as potentially harmful. On the other hand, fructose is also more than by seventy percent sweeter than sucrose (Hanover & White 1993), so the substitution using this monosaccharide at lower concentrations would lead to an acceptable HMF content.

Colour changes during shortbreads processing and their correlation with HMF content

With all the investigated shortbreads, the colour changes during baking as the results of HMF formation were investigated. Detailed colour analysis showed a positive linear correlation between the total colour change (ΔE) and HMF content (Table 4). The correlation coefficient increased with increasing temperature with all sweeteners except

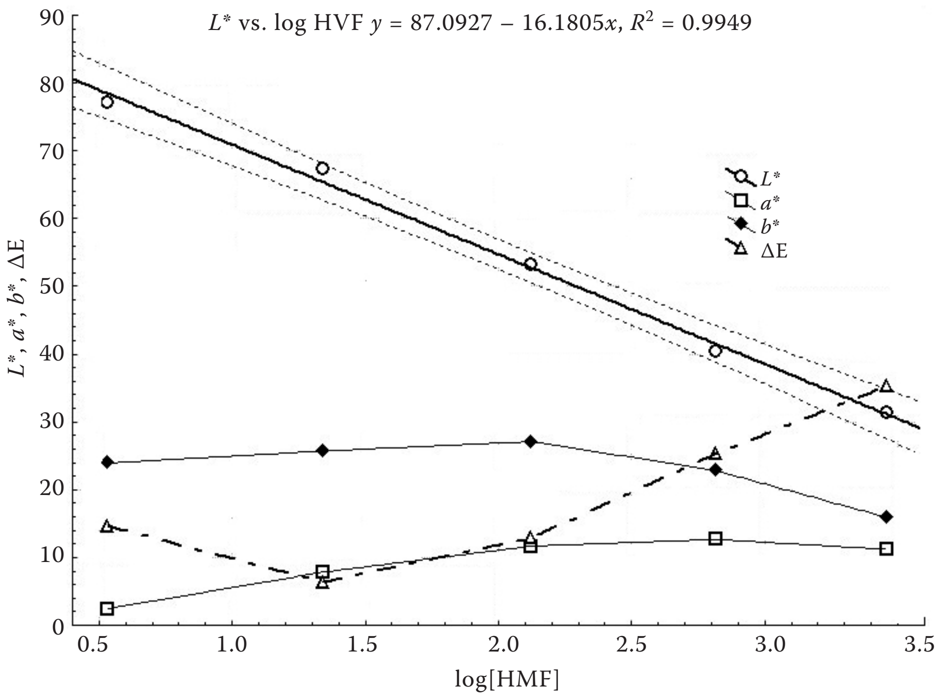

Figure 3. Colour parameters vs. logarithm of HMF concentration for sucrose sweetened shortbreads (215°C). Dotted lines represent confidence interval at α = 0.05

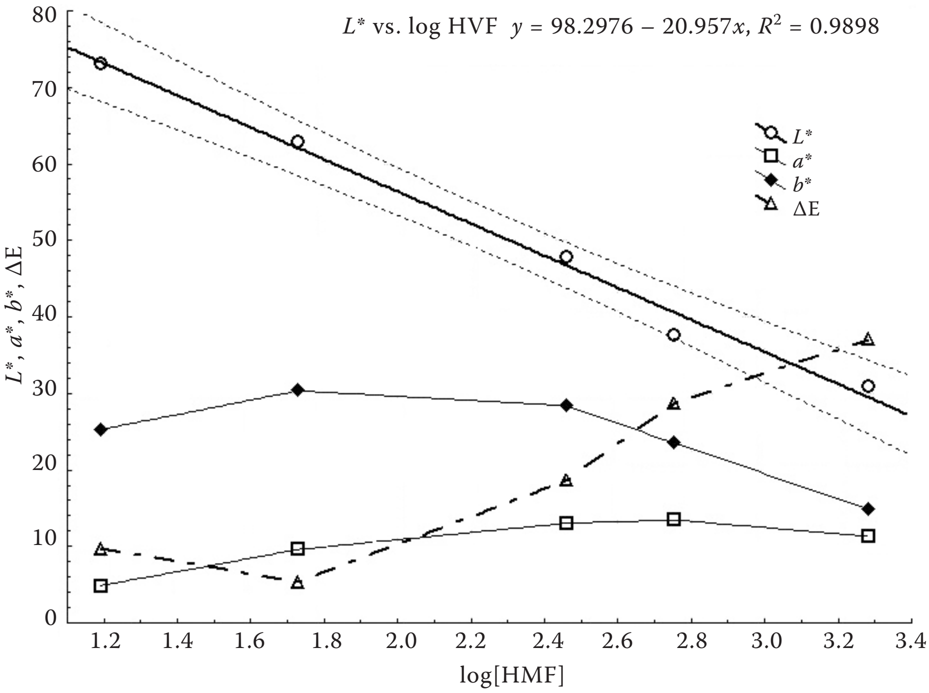

Figure 4 Colour parameters HMF concentration dependence for glucose sweetened shortbreads (215°C). Dotted lines represent confidence interval at α = 0.05

fructose at 230°C. The increase in temperature was strongly correlated with HMF content in the sample and also influenced the cookies colour. According to Gökmen *et al*. (2008), the total colour change of about 10 is expected for all the range of goods. On the other hand, the value higher than 25 testifies to browning the cookies surface (Gökmen *et al*. 2008). In our studies, the value of Δ*E* higher than 25 was connected with HMF concentration over 500 mg/kg in the case of glucose and fructose, and 630 mg/kg in the case of sucrose-based shortbreads (Figures 3–5).

The positive correlation was established not only in the case of Δ*E*. The *b** parameter was found to correlate also with HMF in the samples, especially at temperatures above 200°C. This parameter describes blue-yellow colour changes. The decrease of *b** means that the yellow colour of raw dough disappears during baking. The *L** also revealed a significant (negative) correlation with HMF

Table 4. Correlation factors for 5-hydroxymethyl-2-furfural and colour parameters changes during baking of shortbreads

Linear correlation coefficient (*r*) between the HMF content and colour parameters		Temperature (°C)			
		200	215	230	245
Sucrose	*L**	–0.8740*	–0.7909*	–0.8922*	–0.8714*
	*a**	0.7237*	0.4046	–0.0707	0.1762
	*b**	–0.1645	–0.9461*	–0.9896*	–0.9884*
	ΔE	0.8656*	0.8916*	0.9387*	0.9868*
Glucose	*L**	–0.9595*	–0.8106*	–0.8633*	–0.8641*
	*a**	0.8697*	0.3639	0.6084	0.1548
	*b**	0.4430	–0.9292*	–0.5621	–0.9270*
	ΔE	0.7237*	0.8867*	0.9383*	0.9381*
Fructose	*L**	–0.7956*	–0.8809*	–0.8136*	–0.9092*
	*a**	0.6773*	0.3121	0.6656*	0.4816
	*b**	–0.0740	–0.9769*	–0.7213*	–0.9942*
	ΔE	0.9039*	0.9047*	0.8358*	0.9717*

*correlation coefficients statistically significant at $P < 0.05$

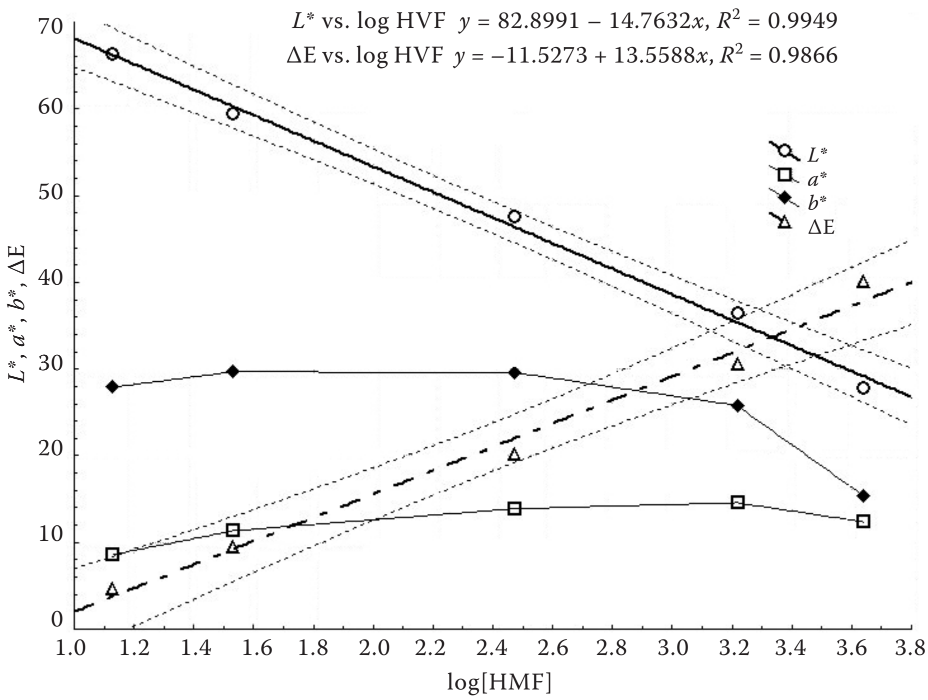

Figure 5. Colour parameters HMF concentration dependence for fructose sweetened shortbreads (215°C). Dotted lines represent confidence interval at α = 0.05

formation during baking. In baking, the cakes become darker according to the carbohydrate transformation including caramelisation. On the other hand, we found that luminance L^* correlated very strongly with the logarithm of HMF concentration (Figures 3–5). At all temperatures, R^2 were at least 0.99. The relation between L^* and HMF content gives the opportunity to link the changes in the cookie colour with thermal degradation and dehydration of sugars in even as viscous environment as the dough. However, it is also known that in food may HMF undergo several further transformation steps including polymerisation or degradation to simple acids (oxopentanoic acid and formic acid) (Lewkowski 2001). In this complicated series of side reactions, only HMF and melanoid polymers are able to influence the product brightness due to their natural colour. According to the results obtained, the overall luminance may be the measure of HMF content and the relation is adaptable for confectionary sugar as well as for glucose and fructose. Additionally, in the case of fructose, a strict logarithmic relationship existed between ΔE and HMF concentration (Figure 5). The phenomenon confirms the fructose path in the discussed dehydration mechanism. In baking, the changes in luminance and the overall colour take place. With other sugars, the luminance changes as well because some parts of the sugars are converted into fructose by means of hydrolysis or isomerisation. But the colour relations take place in further steps of the process due to interferences of colourless compounds (sucrose or glucose) at low temperature. It can also mean that the hydrolysis or isomerisation steps are the slowest and the overall reaction of the transformation of sugars into HMF depends on their rate (the overall sugars to HMF transformation reaction depends on their rate) i.e. the slow step is considered as the rate determining step. The last discussed factor in CIELab system was a^*. The coefficient shows the changes of colour in the range of green to magenta. In the cakes investigated, no correlation was found for this factor except at the lowest temperature. In fact, the baking of cakes does not influence the respective colour domain, thus a^* remains nearly stable during baking.

CONCLUSIONS

The investigation conducted allows to estimate the correlation between the colour and HMF content in shortbread cookies. The results allow to establish that the luminance of cookies is strictly linked with HMF content regardless of the sweetener used for the dough preparation which may lead to the creation of a new and simple tool for HMF content estimation. On the other hand, total colour change in shortbreads sweetened with fructose reveals a strong linear correlation with HMF concentration. The differences in total colour/HMF relations probably lie in the HMF formation mechanism. The distinction in the reaction mechanisms involved in sucrose, glucose, or fructose transformation to HMF was confirmed by changes in both the colour parameters and induction times. The induction times observed in the process suggest that sugar-HMF reaction cannot be described by simple kinetics, being a complex transformation with several consecutive reaction steps. On the other hand, the differences in HMF formation open the gate for glucose as a sweetener in shortbreads like cookies when a low level of HMF is needed. The replacement of sucrose by fructose, however, needs further study focused on the sweetening power-HMF relationship.

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Received for publication February 28, 2012
Accepted after corrections June 4, 2012

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