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THE RELATIONS BETWEEN HYDROXYMETHYLFURFURAL CONTENT, ANTIOXIDANT ACTIVITY AND COLORIMETRIC PROPERTIES OF VARIOUS BAKERY PRODUCTS

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ABSTRACT
The aim of this study was to evaluate the relations between hydroxymethylfurfural (HMF) content, colorimetric properties (*L*, a*, b** and 100-*L**) and antioxidant activities of various bakery products. For this purpose, eighteen bakery products were divided four groups according to their product formulation and processing conditions, as breads, scones, biscuits and crackers and their properties were examined. The results were evaluated as statistically. The product formulation and processing conditions of bakery products effected on HMF, color properties and antioxidant activity. While the correlation between HMF and antioxidant activity was not found, the correlation between HMF and 100-*L** was determined statistically significant ($P < 0.05$). HMF values of samples ranged between 2.59 and 165.28 mg/kg, while the browning index (100-*L**) ranged between 23.1 and 42.9. According to results, the 'browning index (100-*L**) value can be used as an indirect approach for evaluation of browning reactions and HMF formation together.
Keywords: Bakery products, Maillard reaction, antioxidant activity, HMF

ÇEŞİTLİ FIRINCILIK ÜRÜNLERİNİN HİDROKSİMETİLFURFURAL İÇERİĞİ, ANTİOKSİDAN AKTİVİTESİ VE KOLORİMETRİK ÖZELLİKLERİ ARASINDAKİ İLİŞKİLER

ÖZ
Çalışmanın amacı çeşitli fırıncılık ürünlerinin hidroksimetilfurfural (HMF) içeriği, antioksidan aktivite ve renk özellikleri (*L*, a*, b** ve 100-*L**) arasındaki ilişkinin araştırılmasıdır. Bu amaçla, on sekiz fırıncılık ürünü, ürün formülasyonuna ve işleme koşullarına göre ekmek, çörek, bisküvi ve kraker olarak dört gruba ayrılmış ve özellikleri incelenmiştir. Sonuçlar istatistiksel olarak değerlendirilmiştir. Fırıncılık ürünlerinin ürün formülasyonu ve işlenme koşullarının, HMF, renk özellikleri ve antioksidan aktivite üzerinde etkili olduğu tespit edilmiştir. HMF ve antioksidan aktivite arasında korelasyon bulunamamasına rağmen, HMF ve 100-*L** arasındaki korelasyon istatistiksel olarak anlamlı bulunmuştur ($p < 0.05$). Örneklerin HMF değerleri 2.59 ve 165.28 mg/kg, esmerleşme indeksleri (100-*L**) ise 23.1 ile 42.9 arasında değişim göstermiştir. Çalışma sonucu "esmerleşme indeksi (100-*L**) değerinin, esmerleşme reaksiyonu ve HMF oluşumunun kantitatif tespitinde indirekt bir yaklaşım olarak kullanılabileceği tespit edilmiştir.
Anahtar kelimeler: Fırıncılık ürünleri, Maillard reaksiyonu, antioksidan aktivite, HMF

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INTRODUCTION

Bakery products are generally subjected to various treatments for 'surface browning' before or during the baking process. The surface browning is a quality criteria in terms of appearance and baking level. The caustic (NaOH) solution, glucose syrup, molasses syrup, egg yolk, steam are different methods which are mostly applied. The formation of the yellow-gold-brown colors often called as browning is result from non-enzymatic chemical reactions which produce colored compounds during baking, particularly Maillard reaction and caramelization (Capuano et al., 2009; Purlis and Salvadori, 2009). Caramelization is described as a complex groups of reaction, which are been due to direct heated of carbohydrates, particularly sucrose and reducing sugars, above 120 ºC (Fennema, 1996). When bakery products containing reducing sugars and amino groups are heated, caramelization and the Maillard reaction may take place simultaneously (Purlis and Salvadori, 2009). HMF is regarded as the intermediate component and melanoidin pigments as the last stage components of the Maillard reaction. When the pH is being above 5, HMF and other reactive components polarize and convert into nitrogenous forms that are insoluble and dark-colored. The formation products which contribute to the flavor and color formation are known as Maillard reaction products (MRP). While the HMF is regarded as a quality parameter for distinguishing honey adulteration, and is limited by 40 mg/kg (Anonymous, 2000), it is not a parameter for which evaluation of quality of bakery products, so it hasn't got a limit which can be evaluated. During the Maillard reaction, both beneficial (Wagner et al., 2002) and harmful compounds (HMF and acrylamide) can develop. *In vitro* studies show that they have harmful effects, such as mutagenic, carcinogenic and cytotoxic properties. In contrast, the Maillard reaction and products such as melanoidin have also been associated with the formation of antioxidative, anti-allergic and anti-microbial products (Chevalier et al., 2001; Lindermeier et al., 2002; Borrelli et al., 2003; Lindermeier and Hofmann, 2004; Miralles et al., 2007; Carmelina et ald., 2007; Purlis and Salvadori, 2009; Yildiz et al., 2010). The progress of browning reactions need to be quantified in order to control and determine browning level. Color formation has been measured using different experimental techniques, which can be divided into two main categories, direct and indirect methods in several studies (Purlis, 2010). The first group involves chemical and experimental methods that aim to measure the concentration of browning reaction products or the consumption of reactants, such as the measurement of concentrations of HMF and furfurals. However, indirect approaches focus on the color produced by the Maillard reaction and caramelization. The indirect techniques are based on a technological or sensorial approach, such as measuring the variation of color using a colorimeter or color sensor (Aitameur et al., 2000; Wählby and Skjöldebrand, 2002)

The number of studies have been performed to reveal relations between various factors about browning during baking. Non-enzymatic browning has been evaluated by color measurement (*L*, a** and *b**), HMF, baking time, and concentration of melanoidins in several studies (Jimenez et al., 2000; Wählby and Skjöldebrand, 2002; Hadiyanto et al., 2007). However, any study which was examined the relationships between HMF, color parameters and antioxidant properties of various bakery products has not found. The aim of the study was to evaluation of the relation between of these attributes moreover it was to provide an approach to indirect detection of HMF.

MATERIALS AND METHODS

Chemicals; Fifteen percent potassium ferrocyanide (w/v) (Carrez I) and 30% zinc acetate (w/v) (Carrez II) HMF standard were purchased from Merck (Germany). 1,1-Diphenyl 2-picryl hydrazyl radical (dpph), butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) were obtained from Sigma-Aldrich (Germany).

Samples; Eighteen bakery products were collected from supermarkets, patisseries, regional bakeries and homes in Turkey. They were divided into four groups in terms of their common properties. The groups were marked by letters and shown in Table 1.

Table 1. The product groups and their general properties

Product group		General Characteristics
A (biscuits) Unfermented, sweetened products	A1	Petit Beurre
	A2	Petit Beurre, sugar poured onto the surface before baking
	A3	Petit Beurre, glucose applied to the surface
	A4	Petit Beurre, enriched with some minerals and vitamins for consumption by babies
	A5	Petit Beurre, baked with direct heated oven
B (breads) Fermented products	B1	Fermented with bakery yeast, from the bakery (250 g)
	B2	Fermented with sourdough (Contained 25%), made with wheat flour with bran, baked in a stone oven (4000 g)
	B3	Rusk (dried bread) from B2
	B4	Fermented with sourdough (Contained 25%), made with wheat flour, homemade type, baked in the stone oven (1000 g)
	B5	Fermented with sourdough (Contained 25%), made with whole wheat flour, baked in a stone oven (1500 g)
C (scones) Fermented products	C1	Surface varnished with egg yolk, unsweetened dough, large size (125 g)
	C2	Surface varnished with egg yolk, unsweetened, small size (25 g)
	C3	Surface varnished with egg yolk, sweetened dough
	C4	Surface varnished with egg yolk and sugar, sweetened dough
D (crackers)	D1	Stick cracker from unfermented dough (surface treatment with NaOH solution and salt/sesame before baking, 0.8 mm diameter)
	D2	Stick cracker from unfermented dough,(surface treatment with NaOH solution and salt before baking, 0.4 mm diameter)
	D3	Snack cracker from fermented dough, laminated and molded (small fish form) (surface treatment with melted hydrogenated vegetable oil and salt before baking)
	D4	Snack cracker from fermented dough, laminated and molded (rectangular form) (surface treatment with melted hydrogenated vegetable oil and salt before baking)

HMF Determination

Extraction; The HMF determination of the samples was performed the method described by Capuano et al. (2009). 500 mg of ground samples were mixed with deionized water, and the tubes were shaken for 1 min. 0.25 mL Carez1 and 0.25 ml Carez2 solutions were added. The tubes were centrifuged at 594 xg and 4°C for 10 min. The supernatant was collected and filtered through 0.45 μm disk filter before injection.

HPLC procedure; For chromatographic separation, an HPLC (Thermo, USA) reversed-phase C_{18} column was used. The mobile phase was water/methanol (90/10). The injection volume was 20 μL, and the detector was set at 280-285 nm. The external HMF standard method was used for calibration at different concentrations. The standard samples were subjected to HPLC, from min to max concentration (0.1-1.0 mg/kg). The peak areas of each concentration were obtained, and the linear regression equation was calculated as y=6E+06x+192526, in which X is the standard concentration (HMF) and Y is the peak area (R^2=0.9974). The peak areas of samples were measured under the same condition, and their HMF concentrations (mg/kg) were

determined through the linear regression equation. Duplicate samples were analyzed.

Color *(L*, a and *b*)* Determination**

The color of the samples were measured by a colorimeter (Minolta, Italy) as *L*, a** and *b**. The 100-*L** parameter was regarded as 'browning index' by Resmini et al (1993) and Fernandez-Artigas et al. (1999). This term was named as 'color index' by Jimenez et al (2000).

DPPH Free Radical Scavenging Activity

The DPPH radical scavenging assay was used to determine the antioxidative activity of samples.
Extraction; Five grams of sample was taken into a flask (100 mL). It was mixed with 50 mL of 80% methanol at 37°C for 2 hours (Banu et al, 2010). The mixture was centrifuged at 9503 xg for 15 min. The supernatant was filtered through Whatman No. 1 filter paper, and used for the assay (Beta et al, 2005).

DPPH Radical Scavenging Assay; 0.2 mL extract, 0.5 mL DDPH radical solutions and 4 mL 80% methanol were mixed for 15 sec. The mixture was kept at room temperature in the dark for 30 min. At the end of the time, the absorbance was measured at 517 nm in a UV-VIS spectrophotometer (Optizen, Korea) (Karamac et al, 2002). The results were calculated as inhibition% (Gulcin, 2010) and Trolox equivalent.

Statistical Analysis

Statistical analyses were performed with SPSS (version 11,5 for Windows, SPSS Inc.) software. The results were given as mean±standard deviation. The data sets were evaluated with ANOVA (*Tukey*) and Pearson correlation analysis (p <0.05).

RESULTS AND DISCUSSION

HMF Content and Color Properties

The percentage of HMF recovery was determined with the standard addition procedure. HMF standard was added to sample A5 at five different levels between 15 and 75 mg/kg. Recovery ranged between 92.15% and 97.84%, and the mean value was determined as 94.68 ±2.85%.

The results of HMF and color properties of the samples was given in Table 2. The results were evaluated between all samples and between the groups. *L*, a** and *b** values were depend on surface treatments and processes. *L** values of the bread samples were lower than biscuit (A) and cracker (D) samples. While the bread formulations didn't include any fat or oil, biscuits and crackers include in high ratio hydrogenated vegetable oil. Moreover, in the cracker production, the products surface generally are lubricated with spraying system at the end of the oven. Therefore, fat and oil content affects the *L** value.

The average *a** values of the groups A, B, C and D were 8.77, 8.96, 15.70 and 12.1, respectively. The *a** values of the C group samples were higher than those of the other groups. In the scone production, the egg yolk is generally applied to the surface of the products before baking. For that reason, the thick crust formation and the more browning at the surface were observed for the C group products. The egg white is a source of glucose, so it contributes to Maillard browning. The protein content of eggs and the carbohydrate content result from the formulation may have encouraged Maillard reaction. Basically, the reaction begins between a reducing sugar (e.g. glucose) and a compound with a free amino group of an amino acid or particularly the α-amino group of lysine in proteins. The condensation product (N-substituted glycosylamine) is then rearranged to form the Amadori product (1-amino-1-deoxy-2-ketose), which is subsequently degraded into different compounds depending on the pH of the system. Generally, at pH 4–7, HMF or furfural (from hexoses or pentoses, respectively) is formed (Purlis, 2010). The HMF values of products from C group were higher than those of other samples. HMF value was the highest level for C4 product, not only in C group but also among all the samples. The sugar content of the dough based on formulation and fermentation and the egg layer on the surface of the C4 samples might provide the source of the amino acids and simple carbohydrates necessary for the formation of HMF. Since the baking process of C4 sample taken a long time due to its

filling material, its HMF level might be higher than those of other samples. Besides the effects of the surface treatment ingredients, the long baking time and more heat treatment on the HMF level of the bakery products have also significant impact.

Table 2. HMF contents and color properties of the samples

Product group		*L**	*a**	*b**	HMF* (mg kg^{-1})	100-*L**
A	A1	57.01±4.82	11.15±0.55	28.31±0.56	20.66±2.22	42.99
	A2	69.83±1.71	6.33±1.99	31.84±1.32	6.72±0.24	30.17
	A3	65.27±2.04	9.54±1.71	32.82±0.60	9.63±0.78	34.73
	A4	65.09±1.52	8.98±1.23	35.84±0.51	16.37±1.65	34.91
	A5	57.99±0.88	17.87±0.39	23.55±0.74	36.56±3.01	42.01
B	B1	67.87±1.61	5.85±0.79	24.49±2.19	23.74±1.96	32.13
	B2	42.55±1.15	13.78±0.36	16.94±1.21	156.95±4.02	57.45
	B3	49.27±0.91	10.93±0.61	20.97±1.37	114.17±2.65	50.73
	B4	40.73±1.19	8.42±0.09	10.44±1.52	105.74±3.24	59.27
	B5	35.52±1.68	9.18±1.29	9.62±2.80	132.94±3.48	64.48
C	C1	41.28±1.60	16.59±0.43	12.17±1.51	31.57±2.25	58.72
	C2	48.67±1.23	16.78±1.32	22.49±1.10	13.14±0.78	51.33
	C3	36.33±0.68	12.40±0.96	5.41±0.43	49.45±1.03	63.67
	C4	34.43±2.37	16.55±2.39	14.14±4.48	165.28±2.23	65.57
D	D1	54.66±1.23	12.66±0.31	29.33±1.11	13.15±0.19	45.34
	D2	50.89±1.26	15.65±0.78	30.64±4.30	2.94±0.27	49.11
	D3	59.51±1.04	11.31±0.34	30.60±0.77	38.32±2.26	40.49
	D4	66.84±1.34	8.69±1.57	38.39±1.20	2.59±0.38	33.16

**means ± standard deviations*

The *a** values of D1 and D2 samples were higher than in which other cracker samples. In the stick cracker production line, the doughs generally are passed throught the heated NaOH bath for shiny and thick crust formation. This application has been effective on surface browning and *a** values of D1 and D2 products. HMF levels of the NaOH applied products were lower than those of many other samples. However, for D3 and D4 kind of products on last stage of the baking process, melted hydrogenated oil is sprayed onto the surface of the baked products. For that reason, the *L** value of D3 and D4 samples might be higher than the those of other cracker samples. The baking powder increases the alkalinity of the dough, and gives yellowish color to the structure of the end product. The *b** values of the samples of A and B groups, which contained baking powder, were higher than those of the other groups. The usage of baking powder improved the *b** values.

The HMF contents of the samples (Table 2) ranged from 2.59 mg/kg (D4 sample) to 165.28 mg/kg (C4 sample). Although any surface treatment was not performed for bread samples, HMF contents of bread samples were generally higher than those of other products. The sourdough fermentation used in bread making might be effective on HMF formation. Such as,

the B1 sample didn't contain sourdough, thus its HMF level and *a** value were found to be lower than those of other bread samples. The product formulation or the content of the dough is a critical factor for browning development. The sugar content and the type of sugar are the main variables affecting color formation in bakery products. HMF formation increases by depend on sugar content, but depending on baking conditions, sugar or starch degradation proceeds in different ways. For instance, during sourdough fermentation, lactic acid bacteria produce organic acids such as lactic acid and acetic acid that affect the enzyme activity of the dough. Many lactic acid bacteria have their own enzyme activity and convert starch into simple sugars. Additionally, more drastic baking conditions such as excessive heating or a longer baking time are important in terms of HMF formation (Wählby and Skjöldebrand, 2002). All samples in group B were baked in traditional stone oven which was taken long time period, except for sample B1. Hence their HMF level were found severely higher than other products.

Antioxidant Activity

Because reductants and/or melanoidins formed in browning reactions exhibit antioxidative activity based on reducing power and metal chelating capability (Morales and Jimenez-Perez, 2001; González-Mateo et al., 2009)

The antioxidant activity values measured by DPPH radical scavenging assay as inhibition (%) and Trolox equivalent were given in Table 3. The inhibition (%) values of A,C and D groups were higher than that of the bread samples (B groups), as shown in Table 3. This result was attributed to two reasons. Biscuits, crackers or scones formulations are multi-component systems composed of raw materials, different ingredients and additives. Some of these materials contain natural antioxidative compounds and emulsifiers because of their natural composition. Another reason is that the formulations of these products include hydrogenated vegetable oils and emulsifiers that contain chemical antioxidants.

Table 3. Antioxidant activity of the samples

Product group		Inhibition %	Trolox Equivalent y = 3.7714x + 0.0105 (μg mL^{-1})
A	A1	44	131.03±2.63^{a}
	A2	29	84.23±5.44^{c}
	A3	45	132.36±3.01^{a}
	A4	34	100.94±3.19^{b}
	A5	22	63.42±3.37^{d}
B	B1	23	67.53±4.69^{b}
	B2	29	83.97±0.56^{b}
	B3	44	130.37±11.82^{a}
	B4	14	39.29±1.12^{c}
	B5	24	70.05±5.25^{b}
C	C1	29	85.42±3.75^{b}
	C2	30	88.47±1.34^{b}
	C3	59	174.91±2.07^{a}
	C4	63	187.51±15.75^{a}
D	D1	71	212.03±4.69^{a}
	D2	53	156.09±2.81^{b}
	D3	18	51.09±5.44^{c}
	D4	38	112.73±13.50^{d}

**means ± standard deviations*

a–d: Means with different superscripts in the same column

The bread samples of group B collected from the region did not include any additives. The group B samples had lower inhibition % and Trolox equivalent level than the other groups. The B1 sample fermented by *Saccharomyces cerevisiae* as yeast, and exhibited lower antioxidant activity and HMF level. However, HMF levels and antioxidant activities of the sourdough breads (B2, B3 and B4) were higher than those of the other samples. The lactic and acetic acids are the major organic acids of sourdough fermentation. Their primary effects are on to taste and aromatic profile. The secondary effects are on to acidification and enzyme activity. When the pH value decreases below 4.5 thanks to sourdough fermentation, the maltogenic amylase becomes inhibited, but glucoamylase activity continues to produce glucose from starch and maltodextrin. (Brandt, 2006). According to the HMF formation mechanism, the simple monosaccharides promote the reaction. The increase of HMF levels in sourdough breads might be related to this mechanism. It was stated that the degradation of Amadori products at low pH values or the hexoses in the acidic conditions cause HMF formation (Hodge, 1953). During sourdough fermentation, the acidification increases rapidly and pH decreases below 4.5. This degradation might be another reason that the sourdough bread samples possess higher HMF content.

Evaluation of Correlations of Product Groups

The Maillard reaction known as non-enzymatic browning creates colorful or colorless reaction products, depending on several factors such as pH, types of reactants, temperature and water activity (Hidalgo and Zamora, 2000). The HMF is the middle stage, and melanoidins are the last stage products of the Maillard reaction. Since melanoidin compounds were being the "browning color pigments" and were presumed being their antioxidant activities, the relations between colorimetric properties in terms of *L*, a*, b** values, browning index and HMF, antioxidant activity were evaluated. The results obtained were compared within the groups, and then all results obtained from the samples were compared together for the evaluation (Table 4).

Table 4. R^2 and *p* values of *L*,a*,b**, HMF and inhibition % for product groups

		Product groups									
		A		B		C		D		For all samples	
Compared properties		R^2	**p*	R^2	**p*	R^2	**p*	R^2	**p*	R^2	**p*
100-*L**	HMF	0.884	0.042	0.917	0.028	0.908	0.029	0.050	0.950	0.746	<0.001
*L**	Inhibition %	0.164	0.792	0.042	0.947	-0.948	0.048	-0.531	0.469	-0.217	0.386
*L**	HMF	-0.884	0.042	-0.917	0.028	-0.908	0.029	0.050	0.950	-0.746	<0.001
*a**	Inhibition %	0.932	0.021	0.481	0.412	-0.383	0.617	0.451	0.549	0.468	0.058
*a**	HMF	-0.295	0.630	0.876	0.049	0.100	0.900	-0.137	0.863	0.156	0.537
*b**	Inhibition %	0.615	0.269	0.504	0.386	-0.494	0.506	-0.312	0.688	0.048	0.851
*b**	HMF	-0.884	0.041	-0.599	0.286	-0.177	0.823	-0.431	0.560	-0.67	0.002
HMF	Inhibition %	-0.571	0.315	0.222	0.720	0.880	0.124	-0.607	0.393	0.008	0.976

**P <0.05 statistically significant*

In a study conducted by Jimenez et al., (2000) the bakery products collected from various regions of Spain were divided into nine classes and examined their HMF content and formation mechanisms. HMF contents of all samples were found between 4.1 and 151.2 mg/kg, and the browning index (100-*L**) between 30.17 and 65.57. Although the linear correlation between HMF and browning index (100-*L**) was not found by Jimenez et al. (2000), the correlation coefficient (R^2=0.746) between HMF and 100-*L** of mean values for all samples was found to be statistically significant (*p*

<0.05) in this study (Table 4). Moreover, the linear correlations were observed between HMF and browning index (100-*L**) for the A, B and C groups (R^2=0.884, 0.917 and 0.908 respectively). However, any correlation was not determined between them (R^2= -0.050) for the cracker samples (D group). The formulation of biscuit doughs generally contain high sugar ratio. Furthermore, sugar or glucose syrup is generally applied to surface of the some biscuit types. Also the starch converts to simple sugars during the fermentation of bread and scone doughs. Hence, except D group products, all the other groups contained sugar compounds that could be used directly or indirectly for the Maillard reaction. Therefore, the correlations between HMF and browning index were found as significant in the other product groups except crackers, according to general evaluation of the results.

At the beginning of the study, HMF was thought to be possibly related to the *a** value because of the melanoidin pigments. However, the correlation between HMF and *a** values didn't found statistically significant for the any sample groups except B in this study. For B group, the correlation was determined as R^2=0.876 (Table 4). The long time and high temperature baking conditions were required for the production of B group products. There is a close relation between heat treatment and color properties of bakery products. In the bread baking process, increased *a** values can be a marker of melanoidin formation resulted from HMF.

During fermentation, a decrease in pH affects browning reactions positively, because H^+ is needed for Amadori arrangement and Maillard browning. Moreover, the fermentation level influences the color formation. More intermediate product and browning compounds form in breads obtained from fermented dough according to ones produced with unfermented dough (Martinez Anaya, 1996). This pneumonia explains the importance of acidity in the Maillard reaction and in the formation of Maillard reaction products. In contrast, no great change is anticipated in HMF levels in alkaline conditions. When the dough system is being alkaline thanks to usage of some chemicals such as baking powder ($NaCO_3$), the appearance of the bakery products can turn to yellowish color. This can be determined as high *b** value with colorimetric measurement. This pneumonia explained the negative correlation between b* value and HMF of the samples in the group A contain baking powder. (Table 4).

The antioxidant activities of Maillard reaction products can be explained in terms of the excellent radical scavenging properties of melanoidins and their reactions with oxygen (O_2) and hydroxide (OH) (Hayase et al., 1998). Although the several studies have reported that HMF possesses antioxidative effects (Morales and Jimenez-Perez, 2001; Turkmen et al., 2006), this was not supported by the present data in this study, because the statistically significant correlation was not determined between antioxidative activity and HMF (R^2=0.008) (Table 4).

The negative correlation was observed statistically significant (*P* <0.05) between *L** value and Inhibition % for group C (R^2= -0.948). Although the surfaces of scones were coated with egg before baking, this application was not performed in any sample groups. Many egg lipids such as phospholipids, egg proteins such as ovotransferrin, ovalbumin and phosvitin, as well as certain micronutrients such as vitamin A, vitamin E, carotenoids and selenium all have antioxidant properties (Nimalaratne and Wu, 2015). The proteins and fats in egg cause different effects. The protein promotes browning, while the fat in the egg yolk gives a shiny appearance to crusts. Since the egg yolk and egg white contain protein, egg bestows a shiny/brown appearance to crust with heat treatment, although antioxidant activity decreases during baking. For that reason, a negative correlation was observed between *L** value and antioxidant activity in the D group samples. A recent study showed that various domestic cooking methods, such as boiling and frying, reduce antioxidant activity (Remanan and Wu, 2014).

CONCLUSION

One of the aims of this study was to determine HMF levels for bakery products and to elicit findings for food research. The HMF content of samples was determined as max. 165 mg/kg. Although, at the beginning of the study, HMF was thought to be related to *a** value, because of the melanoidin pigments, no consistent conclusions were possible regarding the relation between HMF and *a** on the basis of our findings. However, the significant correlation was determined between HMF and the browning index (100-*L**). It is thought to be that the 100-*L** value can be used for quantifying the progress of browning reactions and HMF formation as an indirect approach. HMF levels were increased by surface treatments (sucrose, honey, egg, etc.), some process conditions, such as long fermentation time and heat treatment, long baking time, and the sugar content in the formulation. For instance, the highest HMF was determined for D4 samples because of their surface treatment with egg yolk/sucrose mixture, and of fermented dough and longer baking time than other D samples. The samples examined in this study were collected from various sources. The results obtained in present study ensured an impression about relationship between HMF, antioxidant activitiy and color properties according to various bakery products. However, further studies are needed for obtaning clear results using specific samples produced by under controlled process conditions and with formulations.

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