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COMPARISON OF SOME CHEMICAL, TEXTURAL AND SENSORIAL PROPERTIES OF COMMERCIAL HAZELNUT-CACAO SPREADS

Suleyman Polat*
Department of Food Engineering, Faculty of Agriculture, Cukurova University, Balcalı, 01330, Adana, Turkey

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ABSTRACT
The lack of standard regulations for the formulation of hazelnut-cacao spreads makes them susceptible to food fraud.The present study examines the chemical, rheological and sensory characteristics of six different commercial hazelnut-cacao spreads coded as A, B, C, D, E and F. The color values for L*, chroma and hue angle were detected between 32.68-38.11, 13.76-17.18, 50.83-54.61, respectively. Sucrose was the only sugar type detected in the samples and its concentration was found between 53.63-57.60 g/100g spread. For textural analysis sample F was found firmer and stickier than other samples. Aldehyde, pyrazine, terpene, phenol, ketone, furan and acid compounds were detected as volatile aroma compounds and their relative concentrations showed significant difference between each other. The total phenolic content of the samples was detected between 346.81-643.09 mgGAE/kgDFW. Catechin (21.13-35.79 mg/kgDFW) and epicatechin (44.62-108 mg/kgDFW) were the major phenolic compounds of the tested spreads. Sensorial results showed that the samples B and D are the most preferred ones.
Keywords: Hazelnut-cacao cream, textural properties, sugar analysis, aroma compounds, phenolics

KAKAOLU-FINDIK KREMALARININ BAZI KİMYASAL, TEKSTÜREL VE DUYUSAL ÖZELLİKLERİNİN KARŞILAŞTIRILMASI

ÖZ
Kakaolu fındık kreması formülasyonu için herhangi bir standartın bulunmaması ürünü tağşiş ve taklite açık hale getirmektedir. Bu çalışmada piyasadan temin edilen altı farklı kakaolu-fındık kremasının (A, B, C, D, E ve F olarak kodlanmıştır) kimyasal, tekstürel ve duyusal özellikleri incelenmiştir. L*, chroma ve hue açısı için renk değerleri sırasıyla 32.68-38.11, 13.76-17.18, 50.83-54.61 arasında tespit edilmiştir. Örneklerde şekerlerden yalnızca sakkaroz tespit edilmiş olup, miktarları 53.63-57.60 g/100 g krema arasında bulunmuştur. Örneklerin tekstürel farklılıkları enstrümantal olarak uygulanan sürülebilirlik testleri ile belirlenmiş ve F örneği, diğer numunelere göre daha sert ve yapışkan bulunmuştur. Uçucu aroma bileşikleri olarak aldehit, pirazin, terpen, fenol, keton, furan ve asit bileşikleri tespit edilmiş ve bağıl konsantrasyonları birbirleri arasında anlamlı farklılık göstermiştir. Örneklerin toplam fenolik madde içeriği 346.81-643.09 mg GAE/kg DFW arasında, kateşin (21.13-35.79 mg/kg DFW) ve epikateşin (44.62-108 mg/kg DFW) baskın fenolik bileşikler olarak belirlenmiştir. Duyusal analiz sonuçları, B ve D numunelerinin en çok tercih edilenler olduğunu göstermiştir.
Anahtar kelimeler: Kakaolu fındık kreması, tekstür özellikleri, aroma bileşikleri, fenolikler

* *Corresponding author* / Yazışmalardan sorumlu yazar;
✉ polats@cu.edu.tr, ✆: (+90) 322 338 6173-108 🖷: (+90) 322 338 66 14

Suleyman Polat; ORCID no: 0000-0002-2112-3136

INTRODUCTION

Confectionery spreadable creams are on a continuous development, due to its high nutritive value and pleasant taste. Hazelnut-cocoa cream is one of the spreadable confectionary products that is mainly consumed in everyday breakfast or directly as snack or desert. During the production of hazelnut spread with cacao, firstly hazelnuts are roasted and brought to paste. According to formulation, the obtained hazelnut paste is mixed with additives such as sugar, milk powder, vegetable oils, cocoa and artificial flavorings. The formulation and amount of ingredients have an effect on quality parameters of hazelnut-cacao spread, as well as its consumers' acceptance (Čížková et al., 2013).

The formulations of the hazelnut-cacao spreads varied according to preference of market and brand. The hazelnut is basic raw material of the spreads and it can be consumed as a snack food or incorporated into confectionery food products due to its organoleptic characteristics. It mainly consist of protein, oil (monounsaturated and polyunsaturated fatty acids), vitamin and minerals that leads to high nutritional value. According to FAO statistics, approximately 742175 tons of hazelnut were grown worldwide in 2016. The five largest hazelnut producers in the world are Turkey (56.6% of world production, 420000 tons), Italy (16.2%, 120572 tons), United States (4.6%, 34473 million tons), Azerbaijan (4.6%, 33941 tons) and Georgia (4.0%, 29500 tons). The hazelnut paste contributes to the specific flavour, the rich taste and the creamier mouth feeling (by lowering the spreads' melting point) of the spreads (Bonvehi & Coll, 2009; Čížková et al., 2013). The spreadable hazelnut-cocoa creams generally contain cacao powder and cheap vegetable fats or oils (to improve spreadability). Lecithin is also used in the spread formulation, in order to provide a smooth texture and emulsifier properties (Lončarević et. al. 2016). The sugar represents major compound of the spread formulation. The properties of sugars not only make them useful as sweeteners but also for processing and the structural (rheological and textural) development of the spreads (Kokkinidou et. al., 2018). Milk powder such as roller-dried and spray-dried whole milk powders, high-fat powders, buttermilk powders, whey powders, and skim milk powder, represents another ingredient of the hazelnut-cacao spread. The type of milk powder significantly effects physical and organoleptic properties of the final product (Liang and Hartel, 2004).

There is no standard or regulation for production of hazelnut-cacao spreads, they can be produced according to different formulations. It is a delicious product for children in the developing age, sportsmen, workers who need to work hard due to its high content of sugar. It is produced in many countries and economically important product for many companies. Although there are many studies on physicochemical and sensory properties of cacao, cacao powder and hazelnut, there is no comprehensive study on the hazelnut-cacao spreads especially on the identification of the volatile compounds, phenolics and textural properties. Therefore, the aim of the present study was to characterize textural and sensorial properties, identify aroma compounds and to determine main polyphenols in six commercial hazelnut-cacao spreads.

MATERIAL AND METHODS

Six different hazelnut-cacao creams (sample A, B, C, D, E and F) were purchased from the supermarket. During the purchasing, it was considered that production date of samples which are produced from different companies, was in same month. All samples were 400 g and packaged with glass jar. For each brand two jars which had different production dates (there was 1 month between each production) were purchased. Samples' contents declared on label were given in Table 1. Acetonitrile and formic acid that are HPLC-grade were purchased from Merck and used after filtration through a 0.45-µm pore size membrane filter. Phenolic acids (gallic, protocatechuic and chlorogenic acids), flavanoids (catechin and epicatechin) and sucrose were purchased from Sigma–Aldrich.

Color analysis

Color analyses were carried out using a colorimeter (CR-400, Konica Minolta, Japan) equipped with illuminant D_{65}. The colorimeter was calibrated on before each measurement using a reference white ceramic tile. The color was determined in terms of CIE L*, a* and b* color scale from 3 different parts of the cacao-hazelnut samples. Hue angle (1) and chroma (2) were calculated from these values according to equations 1-2.

(1) $HueAngle=180/\pi\times\arctan b^*/a^*$

(2) $Chroma=(\sqrt{a^2+b^2})$

Table 1. The ingredients which declared on packaging label of hazelnut-cacao spreads

Sample	Ingredients
A	Sugar, vegetable (palm, sunflower, canola) oil, whey powder, cacao powder 7%, hazelnut 4%, milk powder 4%, emulsifier (soy lecithin, polyglycerol polyricinoleate), flavorings, salt.
B	Sugar, vegetable oil (palm), hazelnut 13%, skim milk powder %8.7, fat reduced cacao powder 7.4%, emulsifier (soy lecithin, sunflower lecithin), vanillin
C	Sugar, vegetable (palm) oil, hazelnut 13.5%, cacao powder 8%, demineralized whey powder, emulsifier (sunflower lecithin), salt, aroma
D	Sugar, vegetable oil (sunflower, shea, coconut), hazelnut 13%, skim milk powder, cacao powder 7%, whey powder, lactose, emulsifier (sunflower lecithin), natural flavoring (vanillin).
E	Sugar, vegetable oil (varying amounts of hazelnut, sunflower, cotton), hazelnut 16%, cacao powder 7%, skimmed milk powder, whey powder, lactose, emulsifier (soya lecithin), flavoring (vanillin)
F	Sugar, vegetable (cotton, sunflower) oil, hazelnut puree 13%, skim milk powder, cacao powder 7%, whey powder, lactose, cacao mass 0.8%, emulsifier (soya lecithin), flavorings (vanillin, hazelnut, chocolate)

Sugar analysis

Sugar analysis was performed using a LC-10A HPLC (Shimadzu, Kyoto, Japan) system with a refractive index detector (RID-10A) and an HPX-87H column (300 mm x 7.8 mm) (Bio-Rad, UK) kept at 35 °C. The analytical conditions used were as follows: flow rate 0.5 mL/min), eluent 3 mM H_2SO_4 +7% acetonitrile. After comparison of retention time with the standard, the peak was identified. The amount of sugar in the hazelnut-cacao samples was quantified using calibration curves obtained from different concentrations of sucrose. The extraction procedure of sugar was given below.

Extraction procedure

The samples were defatted before extraction of the sugar as described by Hu et al. (2016) with some modifications. Briefly, 2 g of hazelnut-cacoa cream sample was mixed with 10 mL of n-hexane in the PTFE tube, extracted for two times by shaking with Promax 1020 (Heidolph, Germany) at 22 °C, 150 rpm for 30 min. After each extraction, the mixtures were centrifuged for 10 min at 4000 rpm, and the supernatant discarded. After the second extraction, samples were dried in a vacuum dryer for 24 h at 22 °C. The defatting samples were diluted with water, and centrifuged to remove solid particles from supernatant. Then 125 μL sample was treated with 875 μL perchloric acid (3.25% v/v) to precipitated protein fragments for 10 min at 4 °C. After incubation, the mixture was centrifuged at 13000 rpm for 5 min at 4°C to pick up the supernatant (900 μL). The supernatant was neutralized with 90 μL 5 M KOH then vortexed and incubated 5 min at 4 °C. The resulted mixture was centrifuged at 4 °C for 2 min at 13000 rpm. Then 800 μL of supernatant phase was treated with 200 μL 2.25% perchloric acid at 4 °C for 5 min. The amount of sugar lost during the defatting process was calculated too.

Texture analysis

The spreadability test was applied on samples using with TA.XT texture analyzer to evaluate the textural properties. The test conditions were fixed 22±1 °C and 50±2 % relative humidity and the samples allowed to equilibrium of specified temperature before testing. The samples were put into the female cone and pressed it down carefully to eliminate air pockets. Excessive sample was removed with a knife, to leave a flat test area and excessive work was not be applied into the product. The test speed and post-test speed were 3 mm/s and 10 mm/s, respectively. The data was analyzed using Texture expert Version Software to measure the firmness, shear work, stickiness and work of adhesion (cohesiveness) in the samples.

Volatile aroma composition

The volatile compounds in the samples were determined using GC-MS (Agilent 7010 Triple Quad GC/MS) combined with solid-phase microextraction (SPME). For this purpose, 3 g of hazelnut-cacao sample was transferred into a 20 mL headspace vial and incubated at 50 °C for 10 min, then at 50 °C for 30 min while agitation at 250 rpm. After, a fiber [Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS)] was used to absorb the volatile compounds for 10 min. Following this, the volatiles were desorbed at 250 °C for 5 min in an injection port.

Elution conditions: a nonpolar HP-5MS 30m x 0.25mm ID, 0.25μm film column was used. The column temperature was programmed; first increased from 40 °C to 200 °C at a rate of 5 ºC/min (held at 2 min.), then to 280 °C at the rate of 10 ºC/min (held at 5 min). Helium was used as carrier gas and flow rate was 1.4 mL/min. The volatile compounds were identified using the mass spectral libraries of NIST 14 and Flovar 2. Their retention indexes were also confirmed by comparing with an online library.

Determination of phenolic compounds

Before the extraction of phenolic compounds, the fats were removed from hazelnut-cacao creams as described in sugar analysis. The phenolics were extracted with 80% methanol acidified with HCI from the defatted samples. Total phenolic content of the hazelnut-cacao creams was determined following the procedures performed by Singleton et. al. (1999). The chromatographic conditions were as described previously (Hu et. al., 2016) and it used with some modifications for the detection of phenolic compounds. The phenolic compounds were identified by comparing their UV–visible spectra and retention times with that of corresponding standards. Each extract was injected two times and the average results are expressed as mg/kg defatted spreads (mg/kg DFW).

Sensory analysis

The sensory evaluation of hazelnut-cacao samples was performed using the scoring and ranking tests. The scoring test was performed on a scale of 10 points, indicating color, odor, spreadability liking, firmness, adhesiveness and taste. Also, panelists subsequently graded the most preferred sample through to the least preferred using the ranking test. The samples were put carefully to standard glass jar and coded by 3-digit numbers to prevent panelists from being influenced by the brand. Sensory analysis was performed by 12 panelists who consume hazelnut-cacao cream and chocolates regularly, including three master students, three PhD candidate and six academic staff. An experimental setup was performed in sensory analysis laboratory at 22 °C and 50±2 % RH consisting of water cups, unsalted twice-baked breads, meal knifes and napkins (Meilgaard et al., 1999).

Statistical analysis

The findings of this study were subjected to analysis of variance using the SPSS 22 software programme (SPSS Inc., Chicago, Illinois, USA), and significant differences were determined by Duncan's multiple range test. However for ranking test that applied in sensory evaluation, Friedman T test and LSD rank was applied to find the most preferred samples.

RESULT AND DISCUSSION

Color and sugar content

Color is one of the most important properties of foodstuffs that affects consumer prefer decision. Typically, the hazelnut-cacao spreads have a dark color, because they contain cacao powder at different ratio. According to label information, the cocoa contents of samples used in this study were between 7 and 8%, (Samples A, D, E and F contain 7%, B contains 7.4%, C contains 8%). A low value (0-50) on the L* scale indicates a dark color, and the chroma value defines the saturation of the color, in other words, its wilt or vividness and generally using for the quality of a color's purity, intensity or saturation. The L*, chroma and hue angle values of the samples were ranged between 32.68-38.11, 13.76-17.86 and 50.83-54.61 respectively. The lowest L* (32.68) and chroma (13.76) value were detected in the C sample that contains highest cacao powder (Table 2). However, statistically significant differences were detected in samples which contain same amount of cacao powder. This difference can be explained, either by the different temperatures used during the production of the samples, or the use of different quality of cocoa powders (affected by roasting temperature). The fermentation and roasting are the main operations that lead to the development of the characteristic brown color and produce compounds responsible for the distinctive aroma and flavor, during production process of cocoa powder. Time and temperature of the roasting process substantially affect the character of chemical changes such as Maillard reactions, caramelization, lipid oxidation, and oxidative degradation of phenolic compounds in addition to the physical changes occurring in cocoa beans (Żyżelewicz et. al., 2016; Sacchetti et al., 2016).

Table 2. Color values and sugar content of hazelnut-cacao spreads.

Sample	L*	Chroma	Hue°	Sucrose (g/100g)
A	35.52 ± 1.17^{b}	16.49 ± 0.57^{b}	54.29 ± 0.57^{a}	57.60 ± 1.51^{a}
B	38.06 ± 1.35^{a}	17.86 ± 1.02^{a}	50.83 ± 1.46^{c}	53.63 ± 0.92^{c}
C	32.68 ± 2.61^{c}	13.76 ± 0.69^{c}	52.41 ± 0.67^{b}	55.96 ± 1.80^{ab}
D	34.41 ± 2.46^{bc}	13.85 ± 0.60^{c}	52.35 ± 0.34^{b}	54.50 ± 0.44^{bc}
E	36.59 ±1.23^{ab}	16.52 ± 0.77^{b}	54.08 ± 0.56^{a}	54.17 ± 1.49^{bc}
F	38.11 ± 1.56^{a}	17.18 ± 0.48^{ab}	54.61 ± 0.36^{a}	55.51 ± 0.71^{bc}

Values followed by different letters are significantly different ($P < 0.05$) (Duncan's multiple range test).
Values are mean ± standard deviation

The sugar content analysis of the samples showed that all samples have high sugar content and sucrose was the only detected free sugar in the samples. The amount of the sucrose in samples ranged from 53.63 to 57.60 g/100 g which represents more than 50% of their total composition. The concentration of the sucrose demonstrated statistically significant differences between samples (Table 2). Indeed, the highest amount of sucrose was found in the sample C (57.60 g/100 g spread).

Textural properties

The hazelnut-cacao spreads have ideally features such as good spreadability, a rich creamy taste, and smooth homogeneous structure with no phase separation. The results of the spreadability tests for the samples are shown in Table 3. The firmness, shear work, stickiness and work of adhesion values of the samples were ranged from 1464.39-2492.78 g, 1094.88-2042.95 g s, -2048.90 – -3199.48 g and -357.90 – -712.05 g s respectively.

Table 3. Spreadability properties of the samples.

Sample	Firmness (g)	Shear work (g.s)	Stickiness (g)	Work of Adhesion (g.s)
A	1771.77 ± 178.22^{b}	1403.18 ± 147.59^{b}	-2617.37 ± 186.29^{ab}	-441.59 ± 36.37^{b}
B	1587.32 ± 141.09^{bc}	1094.88 ± 138.50^{b}	-2386.23 ± 187.84^{b}	-399.78 ± 37.88^{b}
C	1750.45 ± 422.51^{bc}	1188.65 ± 422.79^{b}	-2801.24 ± 335.47^{ab}	-467.41 ± 92.73^{b}
D	2229.00 ± 259.87^{a}	1785.11 ± 287.58^{a}	-2413.95 ± 128.84^{b}	-485.88 ± 184.94^{b}
E	1464.39 ± 77.97^{c}	1102.89 ± 85.75^{b}	-2048.90 ± 150.69^{b}	-357.90 ± 26.57^{b}
F	2492.78 ± 138.10^{a}	2042.75 ± 183.86^{a}	-3199.48 ± 302.85^{a}	-712.05 ± 117.41^{a}

Values followed by different letters are significantly different ($P < 0.05$) (Duncan's multiple range test).
Values are mean ± standard deviation

As seen in the Table 3, the lowest firmness value was obtained for the sample E, while the highest firmness value was obtained for the sample F. The firmness values of A, B and E were not statistically significant from each other ($P > 0.05$). F sample has the most stickiness value due to a greater force required to remove the probe and yielding a larger negative area. The results of the spread test revealed F as the firmest and the stickiest sample, thus more difficult to spread it. The spreadability differences between the samples can be explained by the different composition of the samples. The samples C and D contain sunflower lecithin while the samples E and F contain soya lecithin as emulsifier. The amount of fat and its type are other factors can affect the rheological properties of food. Lončarević et al (2016) studied the rheological properties of the spreadable cocoa creams containing lecithin from different origins (sunflower, rapeseed and soy lecithin). They reported that sunflower lecithin has lower viscosity than soy and rapeseed lecithin. The spreadability tests also revealed that, the samples C and D have higher standard deviation values for the textural identifier values (firmness, shear work, stickiness etc.) than other samples. The higher standard deviations can be explained by the lack of standard production. The spreadability test results may be helpful in the design of the optimal processing parameters for spread production.

Aroma compounds

The relative concentrations of volatile aroma compounds identified on the analyzed samples are presented on Tables 4. A total of 23 aroma compounds in the B and D samples, 22 aroma compounds in the E, 20 for F, 18 for the A and C samples were identified. It was observed that there were statistically significant differences between the samples with regard to the relative concentration of aroma compounds (Table 4).

An extensive diversity of aroma compounds was detected in the samples, including 9 aldehydes, 9 pyrazines, 4 terpenes, 3 phenol; 2 ketones; 2 furans and 1 acid. The concentration of the total aldehydes was strongly altered by the manufacturer. The total aldehyde concentration was detected higher in the samples D, E and F (18.89-15.07%), when compared to the samples A, B and C (3.29-5.40 %). Benzaldehyde was available with the greatest amount of total aldehyde and followed by nonanal and hexanal in the samples (Table 4).

In fact, numerous researchers also evidenced that benzaldeyhde was the main predominant volatile compound of cacao powder (Krings et al., 2006; Li et al, 2012) and being responsible for almond, green aroma notes and bitter attribute. It was also detected in roasted hazelnut samples (Alasalvar et al., 2003). The nonanal was detected both in natural and roasted hazelnuts, and in cocoa powders which were alkalized or glucose added ones (Li et. al, 2012). The hexanal was reported as the most abundant odorant in the raw hazelnuts, and also detected in roasted hazelnut paste (Freitag and Schieberle 2012). Moreover it was detected in commercial cacao powders (Krings et al., 2006).

The pyrazines were important contributors to the cocoa aroma and they were characterized as the most odor-active compounds in a commercial cocoa mass and reported to be formed by Maillard reaction through Strecker degradation from various nitrogen sources such as amino acids (Frauendorfer and Schieberle, 2006). An involvement of Maillard sugaramine-type reactions could be claimed in connection with the formulation of hazelnut-cacao creams. The total pyrazines concentration was detected higher in the samples D, E (15.55-10.60%) compared to the samples A, B, C and F. The relative concentration of the total pyrazines was strongly altered by the manufacturer. Alasalvar et al. (2003) reported that the pyrazines contribute to desirable nutty, roasty (especially 2-ethyl-3,5-dimethylpyrazine), and sweet odors of roasted hazelnuts and their types and amounts were increased by roasted process. Most of the pyrazine compound detected in present study already detected or identified in roasted hazelnut or commercial cacao powders except the 2-methoxy-3-methyl pyrazine and acetyl pyrazine.

Table 4. Relative concentrations of the aroma compounds detected in hazelnut-cacao spreads (%)

No	RT	LRI	Compound	Samples					
				A	B	C	D	E	F
			Aldehydes						
1	1.42	595	Butanal	0.10 ± 0.07[b]	0.07 ± 0.03[b]	0.08 ± 0.03[b]	0.25 ± 0.10[a]	0.16 ± 0.08[ab]	0.13 ± 0.06[b]
2	1.92	669	3-methyl-Butanal	0.39 ± 0.10[bcd]	0.61 ± 0.25[bc]	0.12 ± 0.03[d]	1.89 ± 0.52[a]	0.74 ± 0.27[b]	0.27 ± 0.11[cd]
3	1.99	698	Pentanal	0.23 ± 0.21[bc]	0.32 ± 0.12[b]	0.09 ± 0.04[c]	0.87 ± 0.17[a]	0.42 ± 0.12[b]	0.22 ± 0.12[bc]
4	4.32	801	Hexanal	0.47 ± 0.17[b]	0.87 ± 0.39[b]	0.22 ± 0.08[b]	4.01 ± 1.33[a]	3.30 ± 1.02[a]	1.07 ± 0.22[b]
5	5.39	848	Furfural	1.35 ± 0.19[a]	0.76 ± 0.19[bc]	0.95 ± 0.58[abc]	0.73 ± 0.20[bc]	1.16 ± 0.51[ab]	0.44 ± 0.07[c]
6	8.04	902	Heptanal	0.17 ± 0.08[c]	0.15 ± 0.05[c]	0.05 ± 0.03[c]	0.79 ± 0.35[a]	0.52 ± 0.15[b]	0.12 ± 0.04[c]
7	10.51	966	Benzaldehyde	0.88 ± 0.14[c]	1.67 ± 0.35[c]	1.18 ± 0.39[c]	6.01 ± 0.29[b]	4.37 ± 0.32[b]	13.97 ± 2.00[a]
8	10.82	977	5-methyl-2-Furancarboxaldehyde	0.38 ± 0.06	ND	0.15 ± 0.03	ND	ND	ND
9	17.61	1108	Nonanal	0.31 ± 0.12[b]	0.95 ± 0.19b	0.45 ± 0.26[b]	4.34 ± 0.83[a]	4.40 ± 1.00a	0.48 ± 0.15b
			Total	4.28	5.40	3.29	18.89	15.07	16.7
			Pyrazines						
10	8.38	913	2,5-dimethyl pyrazine	ND	0.71 ± 0.40[a]	ND	1.11 ± 0.24[a]	1.89 ± 1.79[a]	1.35 ± 0.39[a]
11	8.58	916	2,6-dimethy pyrazine	ND	0.18 ± 0.14	ND	0.35 ± 0.78	ND	ND
12	5.10	826	2-Methyl pyrazine	0.73 ± 0.22[c]	0.59 ± 0.17[cd]	0.23 ± 0.08[d]	2.53 ± 0.48[a]	1.46 ± 0.26[b]	0.61 ± 0.17[cd]
13	11.14	985	2-methoxy-3-methyl pyrazine	1.48 ± 0.42	ND	0.18 ± 0.08	ND	ND	ND
14	12.55	1004	2-ethyl-5-methyl pyrazine	ND	0.37 ± 0.06[bc]	ND	1.29 ± 0.32[b]	3.80 ± 1.24[a]	0.19 ± 0.09[c]
15	12.64	1005	2,3,5-trimethyl pyrazine	4.00 ± 1.18[a]	0.21 ± 0.08[d]	0.72 ± 0.36[cd]	2.25 ± 0.63[b]	1.43 ± 0.25[bc]	0.73 ± 0.28[cd]
16	13.46	1025	Acetyl pyrazine	1.73 ± 0.36	ND	ND	ND	ND	ND
17	16.36	1085	2-ethyl-3,5-dimethyl pyrazine	ND	0.21 ± 0.01[b]	ND	0.90 ± 0.27[a]	1.02 ± 0.02[a]	ND
18	16.66	1090	Tetramethyl pyrazine	0.52 ± 0.27[b]	1.01 ± 0.20[b]	ND	7.12 ± 2.49[a]	1.00 ± 0.15[b]	ND
			Total	8.46	3.28	1.13	15.55	10.60	2.88
			Terpenes						
19	9.27	939	α-Pinene	ND	0.98 ± 0.49[a]	ND	0.88 ± 0.35[a]	0.36 ± 0.16[b]	0.07 ± 0.04[b]
20	12.85	1007	3-Carene	ND	0.25 ± 0.13[a]	ND	0.31 ± 0.11[a]	0.35 ± 0.09[a]	ND
21	13.77	1030	D-Limonene	0.34 ± 0.09[bc]	0.24 ± 0.09[bc]	0.04 ± 0.03[c]	0.62 ± 0.20[bc]	0.80 ± 0.12[ab]	1.40 ± 0.94[a]
22	17.13	1105	2,8-p-menthadien-1-ol	ND	0.24 ± 0.12[b]	ND	1.18 ± 0.67[a]	1.25 ± 0.19[a]	ND
			Total	0.34	1.71	0.04	2.99	2.76	1.47
			Phenols						
23	29.51	1394	Vanillin	23.16 ± 2.66[b]	72.74 ± 3.10[a]	73.43 ± 17.55[a]	0.98 ± 0.42[c]	3.74 ± 0.92[c]	62.11 ± 3.19[a]
24	31.39	1453	Ethyl Vanillin	31.91 ± 3.40	ND	ND	ND	ND	ND
25	33.67	1517	4-methylphenol	ND	ND	2.32 ± 0.15	ND	ND	4.17 ± 3.62
			Total	55.07	72.74	75.75	0.98	3.74	66.28
			Ketones						
26	13.99	1057	2-Acetyl pyridine	13.77 ± 2.91	ND	14.36 ± 13.29	ND	24.57 ± 7.30	ND
27	15.56	1065	Acetophenone	ND	ND	ND	ND	ND	5.69 ± 0.37
			Total	13.77	-	14.36	-	24.57	5.69
			Furans						
28	6.24	875	2-Furanmethanol	0.43 ± 0.09[a]	0.19 ± 0.14[a]	ND	0.17 ± 0.20[a]	ND	0.11 ± 0.05[a]
29	12.15	996	2-Pentyl furan	0.16 ± 0.04[c]	0.61 ± 0.21[b]	0.15 ± 0.08[c]	2.46 ± 0.48[a]	2.24 ± 0.18[a]	0.46 ± 0.20[bc]
			Total	0.59	0.80	0.15	2.63	2.24	0.57
			Acid						
30	1.62	602	Acetic acid	17.48 ± 3.55[c]	16.08 ± 1.80[c]	5.27 ± 2.52[d]	58.93 ± 9.82[a]	41.02 ± 3.68[b]	6.41 ± 0.94[d]

Values followed by different letters are significantly different ($p < 0.05$) (Duncan's multiple range test).
Values are mean ± standard deviation

Terpenes; α-pinene, 3-caren, d-limonene, 2,8-p-menthadien-1-ol were detected in the samples B, D, and E, while only d-limonene was detected in the samples A and C. The total terpenes were detected relatively at lower concentrations (2.99-0.04%) than other aroma compounds. Among the terpene compounds, the 3-carene was detected previously at different cacao beans (Qin et al. 2017) and roasted hazelnut (Alasalvar et al. 2003), the d-limonen in cacoa powders (Li et al. 2012) and the α-pinene in roasted hazelnuts.

The vanillin was detected in all samples as a phenolic compound. It was already declared on labels of the samples B, D, E, and F as a flavor enhancer. 4-methylphenol was detected in the samples C and F. Previously, Burdack-Freitag and Schieberle (2012) have reported that the 4-methylphenol can be found in raw and roasted hazelnuts.

The 2-Acetyl pyridine was detected in the samples E (24.57%), C (14.36%) and A (13.77%). It was associated with fatty, dusty and nutty notes, and produced by the Maillard reaction and by nixtamalization process. The acetephonen was detected only in the samples F. It gives almond, floral, sweetish flavor to the products and has been detected in the sunflower spreadable cream containing cocoa (Rocalte et al. 2014). It has not been reported in studies based on cacao powders and hazelnuts, so possibly arises from sunflower oil content. The acetic acid was detected in all samples, especially as a predominant peak in the D (58.93%) and E samples (41.02 %).

Total phenolic content and composition of the samples

Table 6 lists the results of phenolic profile and total phenolic amounts of the samples. It was detected that there are statistically significant differences in the samples with regard to the total phenolic content. The highest total phenol content was determined for the samples B (643.09 mgGA/kg DFW) and D (632.35 mgGA/kg DFW) while the lowest total phenol content was determined in the sample F (346.81 mgGA/kg DFW).

The cacao powder and hazelnut represent the main sources of the bioactive compounds in hazelnut-cacao spreads. Polyphenols are categorized in different classes as phenolic acids, flavonoids, lignans, and stilbenes. The catechin and epicatechin which belong to the group of flavonoids called flavan-3-ols were detected as predominant phenolic compounds in the samples. The catechin, epicatechin, protocatechuic acid and chlorigenic acid concentrations of the samples were statistically different from each other. The highest catechin values were determined in the sample B (35.79 mg/kgDFW), while lowest values were determined in the sample F (21.13 mg/kgDFW). The epicatechin content changed between 44.62 and 108.0 mg/kg DFW in the spreads. The protocatechuic acid contents changed between 17.68 and 7.07 mg/kgDFW, where the highest values belonged to the sample E. According to samples' label, the E has the highest hazelnut content (16%). The protocatechuic acid was identified previously in hazelnuts and being reported as the most dominant phenolic acid in hazelnut skin (Shahidi et. al., 2007). Also, it was reported that its concentration increases with roasting because of the polymerized polyphenols degradation (Tas and Gokmen, 2017). The sample B showed the highest chlorogenic acid contents (20.49 mg/kgDFW), followed by the sample E (4.10 mg/kgDFW) where the F exhibited the lowest content as 0.99 mg/kgDFW. The phenolic content difference between samples can be explained by the samples' different formulation, variability of the cacao or hazelnut cultivars used in the creams, as well as different processing and storage parameters applied by manufacturers to raw materials. According to literature, the chemical composition of cacao powder changed depending on factors such as cultivar, growing region, maturity, storage conditions and processing (Oracz et. al., 2015). Moreover, varieties (Tas and Gokmen, 2017), roasting (Pelvan et. al., 2012) and removal of skin (Arcan and Yemenicioğlu, 2009) affect phenolic profile of hazelnut.

Sensory properties

The samples were evaluated in terms of color, smell, spreadability, firmness, stickiness, taste and the results are given in Figure 1. The panelist were asked to rate the sample color, smell, then to spread the sample on a unsalted bread and rate the spreadability liking, firmness, stickiness and finally to taste of the samples. There were no significant differences between the samples in the color attributes, while the highest score was given to the sample C. In terms of odor, the sample B had the highest score, although there was no significant difference between samples. The spreadability is an important property of semi-solid food texture and it is mostly defined to how easy a sample is uniformly distributed over a surface. The significant difference was detected between samples' sensorial spreadability attributes where the sample B holds the best score. The taste scores of samples also showed significant difference and sample B had the highest score while sample A had the lowest score (Figure 2). No significant differences were detected between the samples in the stickiness and firmness attributes in sensory evolution test. The ranking test results showed statistically significant difference (27.05>12.60) between samples where the observed order of preference was as B, E, C, D, A, and F ranked from the best to the worst. According to the result of the analysis (LSD), samples B and D were preferred more than other samples. Also panelist mentioned that taste and spreadability properties of the samples greatly influenced their choices. Based on sensory evaluation, the samples B and D properties can be used to provide further information about acceptability of new products which would be developed.

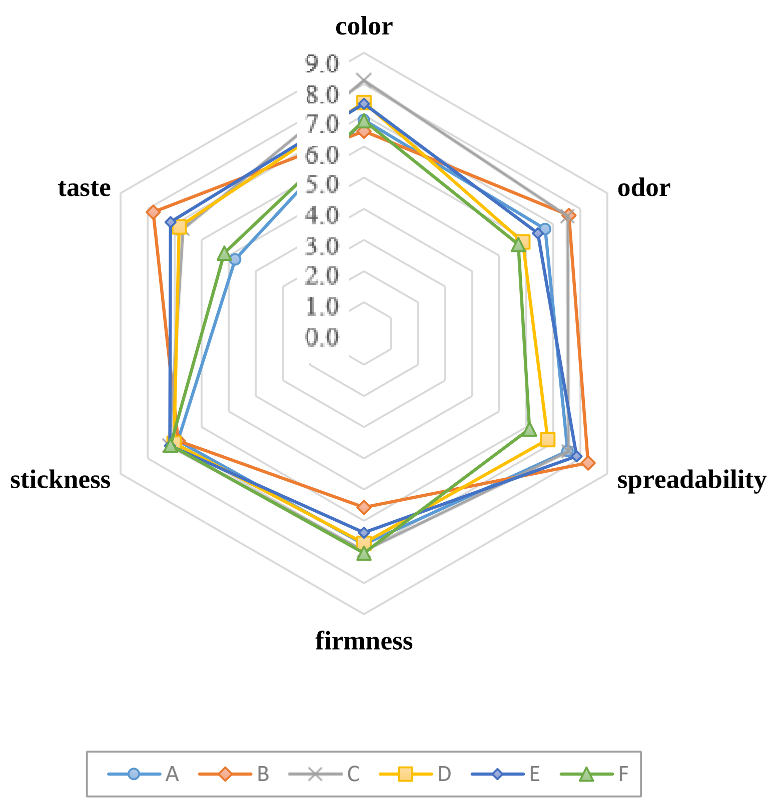

Figure 1: The results of sensory analysis as a spider web diagram.

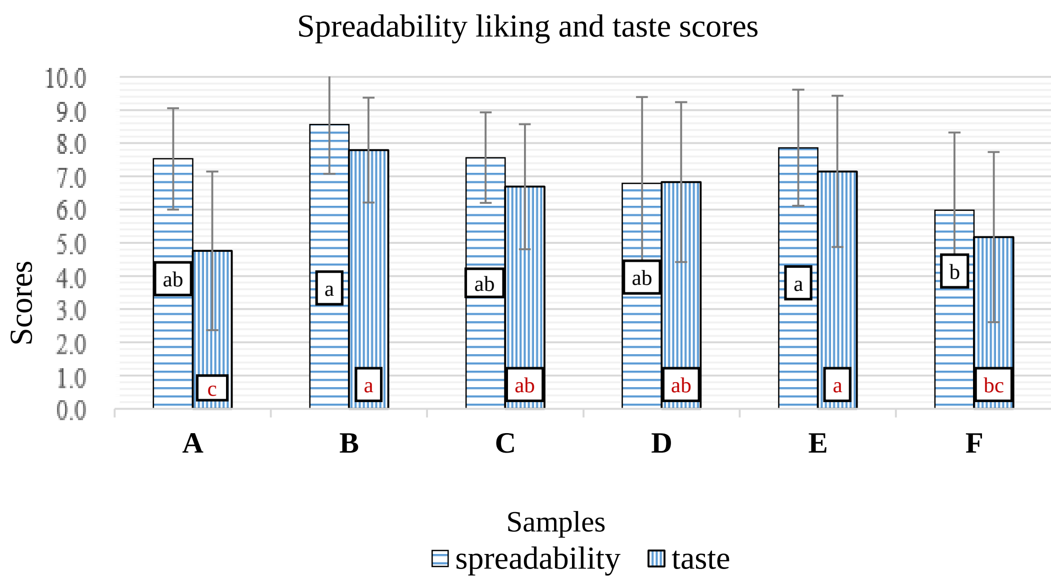

Figure 2. Spreadability liking and taste scores of the hazelnut-cacao spreads.

CONCLUSION

The absence of standard regulations in the field of hazelnut-cacao spread production affects the final product quality which may reduce the nutritional properties of the product, and if the formulation was not optimized and its ingredient concentrations were not controlled, it may make the consumer health at risk too. Textural properties of the samples showed significant difference between each other. The cacao powder and hazelnut are the important raw materials for the hazelnut-cacao spreads due to their bioactive contents. Catechin and epicatechin were detected as dominant phenolic compounds in all samples. Additionally, protocatechuic acid and chlorogenic acid were identified in the samples. From all aroma compounds discovered in the samples, vanillin was the most predominant aroma compound for the samples B, C and F, while it was acetic acid for the samples D and E. According to sensorial analysis, sample B got higher scores by panelists for spreadability liking and taste. The results of this study can be used for further development of hazelnut-cacao spreads and prevent the cheating in this field. For future investigations, it can be suggested to study quantitatively the aroma and aroma active compounds of hazelnut-cacao spreads, since these parameters could give better results for the characterization of products.

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