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Fatty acid profile and quality specifications of chocolate spreads

Fettsäuremuster und Qualitätsspezifikationen von Nuss-Nougat-Cremes

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Summary

This study examined the characteristics of 13 samples from 10 different brands of chocolate spread that are sold in markets in Turkey. Humidity level, oil content, pH value, color values (L*, a*, b*), were determined, chocolate fat samples were tested for free fat acidity rate, peroxide value, iodine value and fat acids composition. The samples composed of 14 different fatty acids. Dominant fatty acids were palmitic acid (9.82–27.19 %), oleic acid (26.27–56.05 %) and linoleic acid (10.87–52.40 %). It was observed that saturated fatty acids (SFA) of the samples ranged between 17.01 and 32.03 %, monounsaturated fatty acids (MUFA) ranged between 19.74 and 57.00 % and polyunsaturated fatty acids (PUFA) ranged between 11.01 and 52.51 %. The analyses showed that contents of the samples complied with legal limits. The types of fatty acids used were determined to be remarkable due to their fatty acids composition.

Keywords: Chocolate spread, fatty acids, quality

Zusammenfassung

Die vorliegende Studie untersucht die Eigenschaften von 13 Proben 10 verschiedener Nuss-Nougat-Cremes aus Supermärkten in der Türkei. Bestimmt wurden die Feuchtigkeit, der Ölgehalt, der pH-Wert und die Farbwerte (L*, a*, b*). Das Fett der Nuss-Nougat-Cremes wurde auf den Gehalt freier Fettsäuren, die Peroxidzahl, die Jodzahl und die Fettsäurezusammensetzung analysiert. Die Proben enthielten 14 verschiedene Fettsäuren. Die dominierenden Fettsäuren waren Palmitinsäure (9,82–27,19 %), Oleinsäure (26,27–56,05 %) und Linolsäure (10,87–52,40 %). Es wurde beobachtet, dass die gesättigten Fettsäuren zwischen 17,01 und 32,03 % lagen, einfach ungesättigte Fettsäuren lagen zwischen 19,74 und 57,00 % und mehrfach ungesättigten Fettsäuren lagen zwischen 11,01 und 52,51 %. Die Analysen zeigten, dass die Inhalte der Proben die gesetzlichen Grenzwerte eingehalten haben. Bemerkenswert war bei den ermittelten Fettsäuren deren Zusammensetzung.

Schlüsselwörter: Ölgehalt, Fettsäuren, Qualität

Introduction

Chocolate is a cocoa-based emulsion that stimulates pleasure centers in the brain when it is consumed. Chocolate generally includes milk or milk powder in addition to cocoa (Afoakwa et al., 2007). In addition, chocolate can also include nuts and sweets, depending on the type of product (Mexis et al., 2010). Chocolate is consumed by people of all ages in all walks of life across the globe. Nowadays, consumers pay more attention to nutritious food (Borchers et al., 2000). A standard chocolate includes 47 % sucrose, 15.6 % milk powder, 15 % cocoa liquor, 22 % cocoa oil and 0.4 % lecithin (Minifie, 1989). Chocolate is a major source of minerals and proteins, due to its milk or milk powder component. It is also a major source of energy, due to its sugar and oil components. The ingredients in chocolate are important, especially for children during developmental ages. Despite its high contents of sugar and oil, chocolate is regarded as a healthy product, due to antioxidants and flavonoids such as epicatechin, catechin and procyanidins in cocoa. Epidemiological studies showed that high dietary consumption of flavonoids (subgroup of polyphenols) prevented coronary heart diseases (Hertog et al., 1995; Geleijnse et al., 1999; Engler et al., 2004).

Derivatives of milk are added to chocolate for the desired creamy pattern of chocolate, and include 80 % casein and 20 % whey proteins. Casein fraction acts as surface active component, and reduces the viscosity of chocolate; conversely, whey proteins increase viscosity. Dry milk with the addition of skim milk powder and full fat milk powder, contributes to aroma, texture and liquidity, depending on heat treatment and dehumidification conditions. Whey powder and lactose powder are used to reduce the sweetness of some chocolate products. Demineralized whey powder (DPST) is preferred in order to avoid off-flavor composition (Afoakwa et al., 2007).

Cocoa oil is obtained from the seeds of the cocoa tree, which contain 50–58% oil. The most characteristic feature of cocoa oil is that its melting temperature range is 32–36 °C. This makes it solid at room temperature, and allows the chocolate to melt without smearing in the mouth, leaving a refreshing taste (Franzke and Mörsel, 1996).

Cocoa oil is an expensive component which is specially preferred for bar chocolates, due to its aforementioned characteristics. However, cocoa oil reduces the spreadability of chocolate spreads. Generally, vegetable oils derived from palm kernel, sunflower seed and soya, which are in liquid phase at room temperature, are used to provide the desired viscoelastic structure of chocolate spreads. Spread chocolates have a large variety of oil in terms of type and quality, due to the absence of a legal restriction on this issue.

Chocolate includes a considerable amount of two saturated fatty acids (SFA), stearic (21.21 %) and palmitic acids (20.00 %), and one of the unsaturated fatty acids (UFA), oleic acid (23.03 %) (Mursu et al., 2004).

Some vegetable oils are similar to cocoa oil in terms of composition. Vegetable oils can be used in chocolates manufacture without any drawbacks. In particular, oils of the lauric acid group and palm kernel oil can be used instead of cocoa oil (Talbot, 1999). But according to EU and Turkey food legislations it's forbidden to use lauric acids in chocolate manufacture (Anonymous 2000, Anonymous 2003).

Materials and Methods

Material

This study examined 13 different chocolate spreads, produced by 6 national and 4 international brands, and sold in 350–500 g packages in markets in Turkey. The samples were collected randomly.

Method

Moisture content

The moisture content of the samples was determined by drying at 103 ± 2 °C overnight as per the air oven drying method (AOAC, 1990).

pH and titratable acidity

The analyses method is adapted from Jinap and Dimick (1990). pH and titratable acidity were determined after dispersing 10.0 g of the dehydrated product in 100 ml distilled water, allowing it to stand for 30 min and filtering. The pH was determined using a pH meter (Model HM-30S, TOA Instruments, Japan). Aliquots of the filtrate (10 ml) were titrated with 0.1 M NaOH using 1% phenolphthalein as an indicator. Acidity was calculated as oleic acid.

Fat content

Fat content was determined using a Soxhlet extractor, using petroleum ether as the extraction solvent (AOAC, 1990).

Color measurement

Color measurement was performed using a Minolta Chroma Meter CR-400 (Minolta, Osaka, Japan). The “L” (luminosity), “a” (redness) and “b” (yellowness) color measurements were defined according to the CIELab color space system, where “L” corresponds to light/dark chromaticity (from 0 % dark to 100 % light), “a” to green/red chromaticity (from –60 % green to 60 % red) and “b” to blue/yellow chromaticity (from –60 % blue to 60 % yellow). The instrument was calibrated with a white reference tile ($L = 97.10$, $a = 4.88$, $b = 7.04$) before the measurements (Francis, 1998).

Lipid Extraction and Preparation of Fatty Acid Methyl esters

Lipids were extracted with diethyl ether as described by Renner (1993). Fatty acid methyl esters were prepared according to AOCS method (AOCS, 1997).

Peroxide value

The peroxide value was derived by the AOCS method. Extracted fat (5 g) was placed in a 100-ml flask and dissolved in 30 ml of an acetic acid–chloroform solution (3:1). Then, 0.5 ml of a saturated solution of KI was added. This was left to stand in darkness for 2 min with gentle stirring, and then 30 ml of water was added. The liberated iodine was titrated with 0.01 N Na₂S₂O₃. When the brown color tended to disappear, 1 ml of a solution of soluble starch was added to give better control of the end point. Results were expressed as meq O₂ per kg of fat.

Free Fatty Acids (FFA)

FFA was determined by titration method, and expressed as oleic acid, as described in AOAC method (AOAC, 1977).

Assignment of Fatty Acids Composition

Fatty acid compositions of oil samples that were extracted from chocolate samples were determined according to

AOAC (AOAC, 1990). According to this method, after the esterification of oil samples, they were injected to a gas chromatograph in order to determine the types and proportions of fatty acids.

Operating conditions of the gas chromatography apparatus are as follow:

Gas chromatograph: Agilent 6890N

Column: 60 m, 0.25-mm inner diameter, 0.25- μ m film thickness)

Column temperature: 190 °C

Detector: Flame Ionization Detector (FID)

Detector temperature: 240 °C

Carrier gas: Helium; flow rate 1.00 mL/min

Injection block temperature: 230 °C

Injection Amount: 1 μ L

Split rate: 1:80

Results and discussion

The results of analyses related to the rates of humidity, pH, titratable acidity, color and oil rates of chocolate samples; and the peroxide, free fatty acidity value and iodine number of oil samples obtained from chocolate samples via cold extraction method are shown in Table 1.

As seen in Table 1, the humidity of the samples ranges between 0.495 % (3) and 1.296 % (13). The humidity rate of spread chocolate generally ranges between 0.5 % and 1.5 %. An arenaceous and lumpy structure forms when sugar particles have high humidity. The humidity on the surface of the sugar particles prevents friction and increases absolute viscosity (Beckett, 2000).

After conching, producers should add extra 1 % oil for every 0.3 % decrease in the rate of humidity. This is important in terms of removing excessive free water (Beckett, 2000), because oil is by far the most expensive major component in chocolate.

The pH of the samples ranged between 6.18 % (1) and 7.36 % (7). Knowing the pH values of oil-free dry chocolate is important, particularly for preparing candy formula. For certain, the pH of chocolate products

differs from each other. The pH of natural chocolate products ranges between 5.5 and 6.0, whereas chocolates treated with alkaline range between 6.0 and 7.8. In the treatment of chocolate with alkaline, the type and concentration of alkaline and treatment time affect pH value (Altan, 2009).

Titration acidity ranges between 0.11 % (6,7) and 0.39 % (1,10). However, there is no standard limit related to these values. Therefore, as chocolate rich in oil, titration acidity was evaluated according to Turkish Food Codex vegetable oil notification 2012/29, in which the maximum permissible content of refined oil is 0.6 mg KOH/g. The acidity results were comply with this regulation.

Oil contents of the samples were between 29.12 % (1) and 39.18 % (12). The oil rate varies according to the process and required texture, and this affects the texture of the end product. Therefore, high quality chocolate tablets with have higher oil content and smaller particles than chocolate used for biscuit coating. The effect on viscosity of additional 1 % oil content depends on currently available amount and aforementioned viscosity parameters. If the oil content exceeds 32 %, viscosity does not change with addition of extra oil. However, in chocolate with 23 % oil content, 1, 1 % increase shows a striking effect, and plastic viscosity reduces nearly at the rate of 50 %. This change is more pronounced when the oil content is less than 23 %, and the chocolate – which is normally in mush consistency – develops a liquid phase (Afoakwa et al., 2007).

Peroxide value is an indicator of lipid oxidation. The peroxide values of the oil samples were between 0.817 meqO₂/kg (1) and 4.913 meqO₂/kg (9). The main reason of deterioration of chocolate and off-flavor composition is lipid oxidation (Antonio, 2003). Antonio (2003) reported that safe peroxide value of chocolates at the beginning of storage was 0.55 meqO₂/kg oil. Free Fatty Acid (FFA) is the main quality parameter of cooking oils. The Purified Food and Adulteration Act limits FFA to 3 % (Ranganna, 2005). The FFA values of oil samples were between 0.414 % (7) and 1.01 % (8). FFA values of all the samples were within the specified limits. In a previous study, FFA values of chocolates stored at 25 °C at 55–75 %

TABLE 1: Results of analyses of chocolate and extracted oil samples.

SN	Chocolate Samples						Oil from Chocolate Samples			
	Moisture (%)	pH	Titratable Acidity (%)	Colour Values L*	a*	b*	Fat (%)	PV (meq/kg)	FFA (oleic acid %)	IN
1	0,500	6,18	0,39	32,24	12,83	13,63	29,12	0,817	0,781	70,64
2	0,931	7,12	0,25	30,44	12,08	12,08	38,45	1,980	0,712	103,45
3	0,495	6,76	0,28	28,85	12,43	12,36	30,67	1,599	0,789	103,91
4	0,817	7,19	0,19	29,76	12,21	12,14	35,51	1,782	0,618	100,86
5	0,859	6,83	0,16	32,14	12,31	12,67	34,73	2,283	0,734	98,58
6	0,755	7,14	0,11	29,24	11,30	9,96	33,01	2,509	0,420	99,04
7	0,729	7,36	0,11	27,90	11,19	9,63	31,43	1,191	0,414	98,60
8	0,839	6,42	0,33	27,40	11,80	10,17	39,12	1,724	1,010	106,10
9	1,083	6,68	0,25	30,09	10,41	10,02	36,54	4,913	0,894	121,32
10	1,043	6,67	0,39	33,18	12,26	13,94	32,18	1,619	0,752	102,77
11	1,110	6,66	0,22	30,94	11,64	12,49	30,43	7,156	0,912	102,77
12	0,929	7,05	0,20	27,75	10,34	9,18	39,18	1,735	0,913	110,20
13	1,296	6,87	0,25	30,03	10,37	10,34	31,05	4,781	0,748	122,50

*SN: Sample Number, TA: Titratable Acidity, PV: Peroxid Value, FFA: Free Fatty Acids IN: Iodine Number

TABLE 2: Fatty acid compositions of chocolate samples.

Fatty Acid	Sample Number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
C14	0,07	1,31	0,68	0,25	0,30	0,61	0,39	2,04	0,35	0,82	1,49	0,92	0,35
C16	27,19	10,42	22,95	9,82	10,98	10,63	10,95	22,36	11,94	24,74	12,64	15,52	11,26
C16:1	0,10	0,07	0,27	0,13	0,16	0,15	0,14	0,27	0,07	0,27	0,10	0,19	0,07
C17	0,06	0,04	0,06	0,05	0,04	0,06	0,04	0,06	0,04	0,07	0,05	0,06	0,04
C17:1	0,04	0,04	0,08	0,05	0,06	0,06	0,05	0,08	0,03	0,08	0,04	0,06	0,03
C18	4,17	6,33	3,94	5,78	5,40	5,50	6,03	6,55	4,86	5,30	5,62	4,24	4,59
C18:1	56,05	47,12	26,95	54,74	55,89	56,84	54,57	19,29	29,04	26,27	44,22	35,10	30,26
C18:2	10,87	33,54	43,56	22,93	21,04	18,25	20,60	48,58	52,29	41,51	34,53	43,12	52,40
C18:3	0,14	0,08	0,19	3,50	3,53	5,23	4,28	0,17	0,15	0,31	0,11	0,15	0,11
C20	0,30	0,25	0,37	0,75	0,75	0,77	0,83	0,23	0,26	0,24	0,27	0,21	0,20
C20:1	0,15	0,11	0,10	0,56	0,55	0,60	0,55	0,10	0,14	0,11	0,13	0,12	0,11
C22	0,09	0,47	0,65	0,95	0,85	0,96	1,23	0,16	0,56	0,20	0,53	0,24	0,42
C22:1	nd	nd	nd	0,27	0,34	0,24	0,23	nd	nd	nd	nd	nd	nd
C24	0,15	0,20	0,22	0,21	0,11	0,12	0,10	0,09	0,26	0,25	0,25	0,07	0,15
∑SFA	32,03	19,02	28,87	17,81	18,43	18,65	19,57	31,49	18,27	31,62	20,85	21,26	17,01
∑MUFA	56,34	47,34	27,40	55,75	57,00	57,89	55,54	19,74	29,28	26,73	44,49	35,47	30,47
∑PUFA	11,01	33,62	43,75	26,43	24,57	23,48	24,88	48,75	52,44	41,82	34,64	43,27	52,51

*C14:0 (Miristik asit), C16:0 (Palmitik asit), C16:1 (Palmitoleik asit), C17:0 (Heptadekanoik asit), C17:1 (Heptadesenoik asit), C18:0 (Stearik asit), C18:1 (Oleik asit), C18:2 (Linoleik asit), C18:3 (Linolenik asit), C20:0 (Araçdik asit) C20:1 (Eikosenoik asit), C22:0 (Behenik asit), C22:1 (Erusik asit), C24:0 (Lignoserik asit). ** ∑SFA: Total saturated fatty acids, ∑MUFA: Total mono unsaturated fatty acids, ∑PUFA: Total poli unsaturated fatty acids

relative humidity were found to be 1.25 % and 1.41 %, respectively (Yadav et al., 2011).

Iodine numbers of oil samples were between 70.64 (1) and 122.5 (13). Iodine number shows the level of unsaturation of oils.

Results related to the fatty acid contents of chocolate samples are shown in Table 2. GC analysis showed that the main fatty acids were palmitic acid (9.82–27.19 %), oleic acid (26.27–56.05 %) and linoleic acid (10.87–52.40 %). Saturated fatty acids (SFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acid contents of the samples were calculated as 17.01–32.03 %, 19.74–57.00 % and 11.01–52.51 %, respectively.

Palmitic acid was the main saturated fatty acid in all samples (9.82–27.19 %). Tarkowski and Kowalczyk (2007) investigated the fatty acid composition of milk chocolates sold in Poland, and reported that the dominant fatty acids were palmitic, stearic, oleic and linoleic.

Conclusion

It was seen that there are insufficient legal regulations and information in the literature on the composition of chocolate spread. When the results were evaluated according to general food and oil notifications, it was seen that current products complied with the general parameters. Free-fatty acid rates are one of the main quality indicators, and give information on the oxidation of the product. In terms of peroxide number, all the samples were matching the consumable limits. It was also seen that fatty acids were not present at levels that would affect the sensual qualities of the product or have any health implications. The low peroxide value was possibly due to the antioxidant activity components originating from chocolate, especially phenolic substances.

Investigation of the fatty acid compositions of the oil samples extracted from the chocolate samples showed that none of the samples contained cocoa oil; all of the samples contain palm stearin oil. All of the samples except for sample (10) contained hazelnut oil. All the samples except for four (4, 5, 6, 7) include sunflower seed oil and most samples (except 8, 9, 10, 12, 13) include canola oil. It was assumed that cocoa oil was omitted due to cost and the required consistency. Hazelnut oil was supposed to come from the hazelnut in the product formula. The wide range of total saturated fatty acids contents (17.02–32.03 %) is an important indicator that the products had potentially different effects on consumers' health.

References

- Afoakwa EO, Paterson A, Fowler M (2007):** Factors influencing rheological and textural qualities in chocolate – a review. *Trends in Food Science & Technology* 18: 290–298.
- Altan A (2009):** Özel Gıdalar Teknolojisi. Çukurova Üniversitesi Ziraat Fakültesi: Adana, Turkey, 51–52 (in Turkish).
- Anonymous (2000):** European Community Directive 2000/36/EC of the European Parliament and of the Council of 23 June 2000 relating to cocoa and chocolate products intended for human consumption.
- Anonymous (2012):** Turkish Food Codex Vegetable Oil Regulation. 2012/29 (in Turkish).
- Antonio V (2003):** Browning of white chocolate during storage. *Food Chemistry* 69: 473–479.
- AOAC (1977):** Free Fatty Acids; Association of Official Analytical Chemists: Washington DC, USA, Ca 5a-40.
- AOAC (1990):** Official methods of analysis (15th ed.); The Association of Official Analytical Chemists: Washington.
- AOCS (1990):** Fatty acids in oils and fats. AOCS Official Methods of analysis, 15th edition, Helrich, 2, 963–964.
- AOCS (1997):** AOCS Official Method, Ce 2-66 1–2.

- Beckett ST (2000):** The science of chocolate. Royal Society of Chemistry Paperbacks: Cambridge, UK.
- Borchers AT, Keen CL, Hannum SM, Gershwin ME (2000):** Cocoa and chocolate: composition, bioavailability, and health implications. *Journal of Medicinal Food* 3: 77–103.
- Daniewski M, Mielniczuk E, Jacorzynski B, Pawlicka M, Balas J, Filipek A (1999):** Fatty acids in chocolate and chocolate products. *Roczniki Panstwowego Zakladu Higieny* 50 (4): 369–383.
- Engler MB, Engler MM, Chen CY, Malloy MJ, Browne A, Chiu EY et al. (2004):** Flavonoid-rich dark chocolate improves endothelial function and increases plasma epicatechin concentrations in healthy adults. *Journal of the American College of Nutrition* 23 (3): 197–204.
- Francis FJ (1998):** Colour analysis In *Food Analysis*. Nielson, S. S.; An Apsen Publishers: Maryland, Gaithersburg, USA, 559–612.
- Franzke C, Mörsel T (1996):** Fette und Fetterzeugnisse. Allgemeines Lehrbuch der Lebensmittelchemie; Franzke, C.; Behr's Verlag: Hamburg, Germany, 449 (in German).
- Geleijnse JM, Launer LJ, Hofman, A, Pols HA, Witteman, JC (1999):** Tea flavonoids may protect against atherosclerosis: The Rotterdam study. *Archives of Internal Medicine* 159: 2170–2174.
- Hertog MGL, Kromhout D, Aravanis C, Blackburn H, Buzina R, Fidanza F, et al. (1995):** Flavonoid intake and long-term risk of coronary heart disease and cancer in the Seven Countries study. *Archives of Internal Medicine* 155: 381–386.
- Jinap S, Dimick PS (1990):** Acidic characteristics of fermented and dried cocoa beans from different countries of origin. *Journal of Food Science* 55: 547–550.
- Mexis SF, Badeka AV, Riganakos KA, Kontominas MG (2010):** Effect of active and modified atmosphere packaging on quality retention of dark chocolate with hazelnuts. *Innovative Food Science and Emerging Technologies* 11: 177–186.
- Minifie B (1989):** Chocolate, Cocoa, and Confectionary; Chapman and Hall: New York, NY.
- Mursu J, Voutilainen S, Nurmi T, Rissanen T, Virtanen JK, Kaikkonen J et al. (2004):** Dark chocolate consumption increases HDL cholesterol concentration and chocolate fatty acids may inhibit lipid peroxidation in healthy humans. *Free Radical Biology and Medicine* 37 (9): 1351–1359.
- Ranganna S (2005):** Handbook of Analysis of Quality Control of Fruit and Vegetable Products; Tata Mc Hill Publication: New Delhi, India.
- Renner E (1993):** Milchpraktikum; Justus-Liebig-Universität: Giessen, Germany.
- Talbot G (1999):** Chocolate temper. *Industrial chocolate manufacture and use* (3rd ed.); Beckett, S. T., Eds.; Blackwell Science: Oxford, 218–230.
- Tarkowski A, Kowalczyk M (2007):** Fat and fatty acids chosen in chocolates content. *Roczniki Panstwowego Zakladu Higieny* 58: 351–356. (in Polish)
- Yadav P, Pandey JP, Garg SK (2011):** Biochemical changes during storage of chocolate. *International Research Journal of Biochemistry and Bioinformatics* 1(10): 242–247.

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