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Chemical and textural attributes of Hellim (Halloumi) cheese marketed in Turkey

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Summary

Chemical and textural properties of Hellim (Halloumi) cheese marketed in Turkey were determined in this research. Cheese samples were collected from manufacturers in Turkey and according to data obtained, water amounts of samples were changing in a wide range of 34.07-55.92 %, whereas the average pH values of the samples was 5.91±0.36. Cholesterol contents of the samples were low and changing among 7.54-14.79 mg/100 g. Average fat and protein amounts of samples were 25.43±1.7 (%), and 22.81±5.62 (%) respectively, and 30.31±1.15 (%) of the fat fraction was composed of unsaturated fatty acids. Main organic acids determined in samples were citric, lactic and propionic acids. Also, hardness, chewiness, adhesiveness, cohesiveness and gumminess scores of the samples were determined by TPA analysis and Hunter color scores were evaluated.

Key words: Hellim (Halloumi) cheese, dairy products, texture, organic acids, fatty acids

Introduction

Hellim (Halloumi) cheese is a traditional cheese belonging to Cyprus. Hellim is a popular and a widely-consumed dairy product especially in the eastern region of Mediterranean (Kaminarides et al., 2007). It is a semi-hard rindless cheese preserved in brine. The manufacture of Halloumi has been described by Anifantakis and Kaminarides (1983). The most characteristic peculiarity of the manufacture of this cheese is that after separation of the curd, the whey is heated to 80 to 90 °C for 30 min to coagulate the whey proteins that are used in the manufacture of Anari which is manufactured by using the whey which drains off during manufacturing of Halloumi. Additional fresh milk is added to the whey, and with boiling curds of Anari cheese is formed (Phelan et al., 1993; Recio et al., 2004). Hellim has a characteristic taste and an elastic texture, and it can be sliced easily.

Hellim cheese is also consumed after frying. Since it is very popular in the region, Hellim cheese is produced also in Turkey. But the number of the plants manufacturing Hellim is rather limited. To our knowledge, Hellim cheese is consumed in Turkey under 7 different trade marks, some of them are being produced in Turkey, the others are imported from Cyprus.

The aim of this research was to determine the chemical, textural and sensorial attributes of Hellim cheese which is marketed in Turkish markets under different trade marks.

Materials and methods

Seven Hellim cheese samples beleonging to these different trade marks were purchased in their own packages. Cheese samples were kept under refrigerator conditions at +4±1 °C until being analyzed. All analyses were repeated 2 times. The percentage of NaCl and total solid (TS) (%) was determined using the method of James (1995). Fat and protein contents of the samples were determined according to AOAC (1980).

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Lipid extraction

Lipids were extracted with diethyl ether as described by Renner (1993). Diethyl ether (Merck) was added to cheese samples and mixed well. After waiting for 5 minutes, mixture was filtered through filter paper (Whatmann No:2) from a funnel. Filtrate was centrifuged for 2 minutes at 6000 rpm to remove the undesired particles originated from cheese. Liquid phase of diethyl ether and oil was taken into centrifuge test tube and diethyl ether was removed using rotary evaporator (Rv 05-St, IKA Labortechnic, Sweden) at 40±1 °C. Then sample was flushed with nitrogen to remove remained ether from oil. Fatty acid methyl esters were prepared according to AOCS (1997). Sample (approximately 200 mg) was weighed into a stoppered-glass centrifuge vial. 0.5 mL of 2 N methanolic KOH and 2.5 mL of pure hexane were added into tube. Tube was shaken well about 30 s and centrifuged for 2 minutes at 6000 rpm. Upper phase was taken into a vial to be analyzed by GC.

Diethyl ether and methanol were from Riedel (Riedel-de Haën, Germany), and KOH and hexane was from Merck (Darmstadt, Germany). Reference standard of cholesterol and standard fatty acid methyl ester mixtures were purchased from Sigma Chemical Co. (St. Louis, MO, USA).

Determination of fatty acid composition

The instrumentation used for the analyses was as follows: a Hewlett-Packard GC (model 6890) equipped with Supelco SP-2380 fused silica capillary column (60 m×0.25 mm i.d., 0.2 μm film thickness; Supelco Inc., Bellefonte, PA, USA) and a flame ionization detector. The injection volume was 2 μL. The temperature of GC oven was programmed from 150 to 210 °C at the rate of 3 °C/min. The injector and detector temperatures were 250 °C. Nitrogen was used as the carrier gas and the flow rate was 1 mL/min. The split ratio was set at 1:100. The identification of the peaks was achieved by retention times and by comparing them with authentic standards analyzed under the same conditions. Peak areas of duplicate injections were measured with a HP computing integrator.

Determination of cholesterol content

Cholesterol was determined by the procedure described by Fletouris et al. (1998). One g of cheese was taken into a test tube and 5 mL of 2 N KOH was added into it. Tube was shaken well for 15 seconds then kept in a water bath at 80 °C for 30 minutes by shaking in 5 minutes intervals. Tube was cooled down under tap water and 1 mL of distilled water and 5 mL of hexane were added, then shaken for 1 minute and centrifuged for 1 minute at 2000 rpm. Upper phase was taken into a vial and analyzed by Hewlett-Packard GC (model 6890).

For preparation of cholesterol standards, the stock solution (2 mg/mL) was prepared by dissolving 20 mg of reference standard (Sigma Chemical Company, St. Louis, MO, USA) with hexane in a 10 mL volumetric flask. Working solutions were prepared by appropriately diluting aliquots from the stock solution with hexane to obtain solutions in the range of 10-80 μg/mL.

GC conditions used for analyses were as follows: ZB-1 silica capillary column (30 m×0.25 mm i.d., 0.1 μm film thickness; Phenomenex, USA). Oven temperature was set at 285 °C, injection port temperature at 300 °C, and flame ionization detector temperature at 300 °C. The flow rates were 2 mL/min for nitrogen, 30 mL/min for hydrogen, and 300 mL/min for air. The injection volume was 2 μL with a split ratio of 20:1 (Seçkin et al., 2009).

Calculation

The concentration of cholesterol (C) in analyzed samples was calculated according to the equation C=M x V x 2.5

where *M* is the computed mass (nanograms) of the analytic in the injected extract (1 μl), *V* the dilution factor, if any, that was applied.

Recovery

Percentage recovery was determined by adding a known concentration of cholesterol to selected samples during extraction. The amounts added were roughly 50 percent of the actual concentrations of the samples.

The concentration of cholesterol standard in the mixture was then determined in a way similar to the sample analysis. Recovery rates of >90 percent were achieved for the compound analyzed.

Organic acid determination

7 g of Hellim cheese was taken and then 40 mL of mobile phase (% 0.04 H_2SO_4) was added and mixed by ultraturrax for 1 min. Mixture was held in water bath at 40 °C for 1 h, then centrifuged at 6000 rpm for 5 min. Upper phase was filtered through filter paper (Whatman No:1) and filtrates were filtered again through Supelco Discovery DSC-18 filter (Seçkin et al., 2009).

20 μL aliquots of individual standards were injected to column and their retention times were determined. To obtain the calibration curves, a mixture of standards of certain concentrations were also injected into HPLC and their chromatograms were obtained. After injection of the samples, chromatographic peaks were identified by comparing retention times of samples to known standards.

A Perkin Elmer Series 200 Model HPLC apparatus equipped with a UV absorbance detector set at 214 nm was used. Chromatographic separation was performed on a Shodex RSpak KC-118 model ion-exchange organic acid column (300 x 8 mm i.d.). The mobile phases were 0.04% (w/v) of sulphuric acid in distilled HPLC grade water with a flow rate of 0.8 mL/min (Seçkin et al., 2009).

Textural profile analysis (TPA) of the samples

To determine the TPA values of Hellim cheese samples, the method of Awad et al. (2002) and TA.XT Plus Texture Analyser (Vienna Court, Surrey Gu7 YL, England) were used. Cylindrical samples of 2 cm in diameter and 2.5 cm in height were prepared by using aluminum cylindrical sampling equipment (Code no: P/35 and 35 mm in diameter). Pressing speed and total processing period were set at 1 mm/sec and 10 sec respectively. Compression was 80 %. Two compressions in a row were applied on the samples. According to the graphic obtained, textural profile attributes of the samples were determined according to Bourne (2002). Hardness, cohesiveness, chewiness, adhesiveness, springiness and gumminess values of the samples were determined. Chewiness of the samples was calculated by the multiplication of gumminess and springiness values.

Hunter color values (L, a*, b*) of the samples*

Hunter color values of the samples were determined according to Güleç et al (2008). L* represents the lightness of the color, a* represents the position of the color between green and red, whereas b* represents the position of the color between blue and yellow. 10 measurements were performed for each sample and average color values were determined by using colorimeter (Minolta CR310, Osaka, Japan).

Results and discussion

Physicochemical characteristics

Table 1 represents the mean characteristics and the cholesterol content of Hellim cheese samples. As seen, pH values of the samples were ranging among 5.37-6.45 and average pH value was 5.91±0.36. Milci et al. (2005) revealed that average pH values of Hellim cheeses made from ovine, bovine and caprine milk were 5.42, 5.30 and 5.32, respectively. According to the findings of Raphaelides et al. (2006), pH values of Hellim cheeses made from ovine and bovine milk were 6.31 and 6.65.

Table 1. Average chemical composition of Hellim cheese sam

	Min-Max	Average
pH	5.37-6.45	5.91±0.36
Water (%)	34.07-55.92	45.65±6.91
Ash (%)	4.83-7.98	6.11±1.20
Protein (%)	13.19-30.95	22.81± 5.62
Fat (%)	23.00-28.00	25.43±1.72
Salt (%)	2.60-4.80	3.40±0.08
Cholesterol (mg/100 g)	7.54-14.79	11.93±2.23

Table 2. Hunter color values (L*, a*, b*) of Hellim cheese samples

	Min-Max	Average
L*	86.21-90.97	89.20±1.46
a*	-9.00 - -6.24	-7.90±1.07
b*	18.80-23.38	20.20±1.70

According to findings in thus research, total water amount of the samples were among 34.07 % and 55.92 % and average water content was 45.65 %. Milci et al. (2005) found that average water amounts of Hellim cheeses made from ovine, bovine and caprine milk were 49.9 %, 50.85 % and 50.34 %, respectively. On the other hand, Raphaelides et al. (2006) reported that the water contents of Hellim samples were 47.40 % and 43.72 % for cheeses made from bovine and ovine milk.

Ash contents of the Hellim samples were ranging among 4.38 % and 7.98 %, and the average ash content was 6.11±1.20. Milci et al. (2005) reported that the average ash content of the Hellim cheese produced by using bovine, ovine or caprine milk was 6.52 %. Fat contents of the samples were found among 23.00 % and 28.00 %. The average fat content was 25.43±1.72 %.

Salt contents of the samples were changing among the values of 2.60 % and 4.80 %, whereas the average value of salt was determined as 3.40±0.08 %. According to findings of Milci et al. (2005), salt contents of Hellim cheeses made from different types of milk were between 4.27 % and 6.45 %. On the other hand, protein contents of the samples were changing among 13.19 % and 30.95 %. Average protein content was 22.81±5.62 %.

Lowest cholesterol content detected in the samples was 7.54 mg/100 g whereas the highest one was 14.79 mg/100 g. Average cholesterol content found was 11.93±2.23 mg/100 g.

As seen in Table 2, Hunter color parameters (L*, a*, b*) were determined for Hellim cheese samples. Minimum L* value was 86.21, whereas the maximum L* value was 90.97. Average L* value of the samples was 89.20±1.46. a* value of the samples were ranging among -9.00 and -6.24. Average a* value was -7.90±1.07. Average b* value of the samples was 20.20±1.70 changing among the values 18.80 and 23.38.

Organic acid profile of Hellim cheese samples

Organic acid profile of Hellim cheese samples was given at Table 3. Total organic acid contents of the samples were among 59.34-570.69 mg/g and the average organic acid content was found as 320.91 mg/g. Oxalic, malic, citric, lactic, formic, acetic, propionic and butyric acids were detected in all samples, whereas pyruvic and fumaric acids were not detected in any of the Hellim cheese samples. Hellim samples have an average oxalic acid content of 0.20 mg/g ranging among 0.002 and 0.46 mg/g. Citric acid contents of the samples were between 19.75 and 56.94 mg/g, whereas the average malic

Table 3. Organic acid profile of Hellim cheese samples (mg/g)

Organic acid	Min-Max	Average
Oxalic	0.002-0.46	0.20
Citric	19.75-56.94	37.96
Malic	1.43-14.55	5.80
Lactic	7.37-476.79	227.62
Formic	0.046-9.05	1.71
Acetic	0.40-0.99	0.60
Propionic	21.24-31.44	21.39
Butyric	3.39-63.76	25.63
Total	59.34-570.69	320.91

Table 4. Fatty acid composition of Hellim cheese samples (%)

Saturated fatty acids in Hellim cheese samples													
Fatty acid	C4:0	C6:0	C8:0	C10:0	C11:0	C12:0	C13:0	C14:0	C15:0	C16:0	C17:0	C18:0	Total
Amount (%)	2.26±0.24	1.74±0.13	1.20±0.05	2.91±0.25	0.06±0.02	3.47±0.32	0.09±0.02	11.56±0.39	1.30±0.15	31.56±1.37	0.62±0.05	12.27±1.63	69.05±0.80
Unsaturated fatty acids in Hellim cheese samples													
Fatty acid	C14:1	C15:1	C16:1	C17:1	C18:1cis	C18:1 tr	C18:2 tr	C18:2 cis	C18:3	20:1	20:2	22:4	Total
Amount (%)	0.91±0.24	0.01	1.67±0.15	0.32±0.04	24.50±1.27	0.03±0.02	0.02±0.01	2.23±1.02	0.18±0.1	0.25±0.2	0.09±0.02	0.1±0.12	30.31±1.15

acid content was 5.80 mg/g. Organic acid content of the samples were mainly composed of lactic acid which has an average value of 227.62 mg/g. Samples were determined to have a low amount of formic acid ranging between 0.046 and 9.05 mg/g. Similarly, average acetic acid content of Hellim cheeses was 0.60 mg/g. Average propionic and butyric acids contents of the samples were determined as 21.39 mg/g and 25.63 mg/g, respectively.

Fatty acid profiles of Hellim cheese samples

Fatty acid profiles of Hellim cheese samples are given as Table 4. Palmitic acid content of Hellim samples was among the values of 29.74 % and 33.23 % whereas the average palmitic acid content was 31.56 %.

Average myrsitic acid and stearic acid content of the samples were 11.56 % and 12.27 % respectively. Myristic acid contents of the samples were changing among the values of 11.23 % and 12.28 %, whereas the stearic acid contents of the samples were among 9.09 % and 14.14 %. As seen from Table 4, unsaturated fatty acids, myristoleic, palmitoleic acid, cis-oleic, and cis-linoleic acids were found in oil fraction of cheese samples at average amounts of 0.91%, 1.67 %, 24.50 % and 2.23 % respectively. Average saturated fatty acids amount of cheese samples was 69.05±0.80 % whereas the unsaturated fatty acid amount was 30.31±1.15 %.

Textural characteristics of cheese samples

As seen from Table 5, average hardness of cheese samples was 8.71 kg, whereas the hardness values of the samples were changing among the values 2.5 kg and 22.83 kg. It was determined that there is a significant and negative correlation among the water amounts and hardness values of cheese samples ($P<0.05$).

Cohesiveness values of cheese samples were changing between 0.65 and 0.97 and the average cohesiveness was 0.84. Awad et al. (2002) reported that the difference among the cohesiveness values of cheese samples was originated from the difference in manufacturing technique and the raw material used. On the other hand, it is known that the storage time and ripening period affect the cohesiveness value of cheese.

Table 5. Textural attributes of Hellim cheese samples

	kg		kg.s	s	kg.s	kg
Sample	Hardness	Cohesiveness	Adhesiveness	Springiness	Chewiness	Gumminess
1	6.62	0.89	3.28	9.95	58.63	5.91
2	7.73	0.84	0	9.98	64.6	6.48
3	8.42	0.65	0	9.95	63.65	6.4
4	4.2	0.95	36.77	9.99	39.69	3.97
5	8.64	0.87	17.61	9.95	74.75	7.51
6	22.83	0.68	0	9.98	155.11	15.55
7	2.5	0.97	67.37	9.96	23.24	2.33
Mean	8.71	0.84	17.86	9.97	68.52	6.88
SD	6.63	0.13	25.75	0.02	41.94	4.20

Average adhesiveness value of Hellim cheese samples was 17.86 kg.s, and was changing in a wide range (0 kg.s and 67.37 kg.s). On the other hand, springiness values of the samples were among 9.95 s and 9.99 s. There were no differences among the springiness values of Hellim cheeses sold under different trade marks ($P>0.05$).

Highest gumminess score obtained for Hellim samples was 15.55 kg, whereas the lowest score was 2.33 kg and the average gumminess score obtained was 6.88 kg. Chewiness scores of the samples were changing in a wide range of 23.24 kg.s - 155.11 kg.s, whereas the average chewiness score was 68.52 kg.s.

Conclusion

As seen from the results of the research, due to high differences among the analysis results of both textural and chemical attributes of cheese samples, it can be concluded that, there is no standard production technique and quality criteria for the optimization of the final product, in Turkey. It is though that data obtained can be used as a status report for dairy research area.

Kemijska i teksturalna svojstva Hellim (Halloumi) sira na tržištu u Turskoj

Sažetak

U istraživanju su utvrđena kemijska i teksturalna svojstva Hellim (Halloumi) sira koji se prodaje na tržištu u Turskoj. Uzorci sira prikupljeni su od proizvođača u Turskoj, a prema prikupljenim podacima količina vode uzoraka bila je u širokom rasponu od 34,07 do 55,92 %, dok je prosječna pH vrijednosti uzoraka bila 5,91±0,36. Sadržaj kolesterola u uzorcima bio je nizak i mijenjao se u rasponu od 7,54 do 14,79 mg/100 g. Prosječne vrijednosti udjela masti i proteina bile su u rasponu od 25,43±1,7 (%), odnosno 22,81±5,62 (%). Postotak od 30,31±1,15 (%) od frakcije masti čine nezasićene masne kiseline. Glavne organske kiseline utvrđene u uzorcima bile su limunska, mliječna i propionska kiselina. Također, rezultati tvrdoće, "žvakljivosti", adhezivnosti, kohezivnosti i gumenosti uzoraka određeni su TPA analizom a Hunter bojom su ocijenjeni.

Ključne riječi: Hellim (Halloumi) sir, mliječni proizvodi, organske kiseline, masne kiseline

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