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Some Physicochemical Characteristics and Aroma Compounds of Izmir Tulum Cheese Produced with Different Milk Types

Farklı Süt Çeşitleri ile Üretilen İzmir Tulum Peynirlerinin Bazı Fizikokimyasal Özellikleri ve Aroma Bileşikleri

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ABSTRACT

In this research some characteristics including physical, chemical, and volatile compounds of Izmir Tulum Cheese; a Turkish artisanal cheese were studied. A total of 37 samples, 21 produced from cow's milk (CM), 16 produced from the mixture of cow's, sheep's and goat's milks (MM) were analyzed. The pH, titratable acidity, dry matter contents, fat and fat-in-dry matter, salt and salt-in-dry matter, total nitrogen, protein, Water Soluble Nitrogen (WSN), Soluble Nitrogen in Trichloroacetic acid (TCA-N), Proteose-Peptide Nitrogen (PPN) values of 21 cheese samples produced from cow's milk (CM) varied between 4.11-4.92, 0.522-1.408%, 49.920-68.648%, 17.50-30.50%, 35.06-51.98%, 2.340-4.563%, 3.75-8.66%, 3.29-4.29%, 20.99-27.37%, 0.47-1.21%, 0.32-0.91%, 0.12-0.46%, respectively. In addition, characteristics stated above for a total of 16 cheese samples produced from cow's, sheep's and goat's milk (MM) varied between 4.01-4.75%, 0.86-1.447%, 54.587-71.854%, 24.00-32.00%, 33.59-52.71%, 1.872-5.265%, 3.02-9.65%, 3.37-4.31%, 21.50-27.50%, 0.56-1.29%, 0.34-1.03%, 0.12-0.60%, and 14.51-33.78, respectively. Volatile aroma compounds of Izmir Tulum Cheese samples were determined by gas chromatography (GC) using a solid-phase microextraction technique. The GC data were analyzed by principal component analysis based on their volatile profiles. Free fatty acids, esters, aldehydes, and ketones became prominent as aroma fractions in Izmir Tulum Cheese samples. It was also determined that the composition properties of aroma compounds were affected by milk type and production method.

ÖZET

Bu çalışmada geleneksel bir türk peynir çeşidi olan İzmir Tulum Peyniri'nin fiziksel ve kimyasal gibi bazı karakteristik özellikleri ile aroma maddeleri çalışılmıştır. 21 adet inek sütünden ve 16 adet ise inek, koyun ve keçi sütü karışımından üretilen olmak üzere toplam 37 peynir örneği analiz edilmiştir. Yalnızca inek sütü kullanılarak üretilen 21 adet pH, titrasyon asitliği, kuru madde içeriği, yağ ve kurumaddede yağ, tuz ve kurumaddede tuz, toplam azot, protein, suda çözünen azot, trikloroasetik asitte çözünen azot, proteoz-pepton azotu değerleri sırasıyla 4.11-4.92, %0.522-1.408, %49.920-68.648, %17.50-30.50, %35.06-51.98, %2.340-4.563, %3.75-5.26, %3.29-4.29, %20.99-27.37, %0.47-1.21, %0.32-0.91, %0.12-0.46 arasında değişiklik göstermiştir. Buna ek olarak, inek, koyun ve keçi sütü karışımlarından üretilen toplam 16 peynir örneğinde bu değerler sırasıya 4.01-4.75, %0.86-1.447, %54.587-71.854, %24.00-32.00, %33.59-52.71, %1.872-5.265, %3.02-9.65, %3.37-4.31, %21.50-27.50, %0.56-1.29, %0.34-1.03, %0.12-0.60 ve 14.51-33.78 arasında değişiklik göstermiştir. İzmir Tulum Peynirlerinin aroma maddesi profilleri katı faz mikroekstraksiyon tekniği ile gaz kromatografisinde belirlenmiştir. Gaz kromatografisinden elde edilen veriler uçucu profillerine dayalı temel bileşenler analizi ile analiz edilmiştir. Tulum peyniri örneklerinde serbest yağ asidi, ester, aldehit ve ketonlar temel aroma fraksiyonları olarak öne çıkmış ve aynı zamanda aroma maddesi kompozisyon özelliklerinin süt çeşidi ve üretim yöntemlerine göre etkilendiğini göstermiştir.

INTRODUCTION

Cheese manufacturing began in ancient times with the practice of transporting milk in animal stomachs and bladders. Over the centuries, cheese making has been modified and refined. Today, at least 800 different types of cheeses have been identified worldwide. Many cheese varieties which are known only in restricted geographic areas in the world are produced and consumed locally in small quantities. There are over than 190 different cheese types produced and consumed in Turkey today and most of them are traditional cheese belonging to a specific geographical province; however, three of them (White Pickled, Kashar and Tulum cheeses) are the most popular cheeses (Hayaloglu et al., 2007; Cakmakci et al., 2008; Karagozlu et al., 2016). Tulum cheese, a kind of local cheese produced in Turkey, has not been well known elsewhere. It is preferred for its characteristic taste and flavor (Gurses and Erdogan, 2006). Izmir Brined Tulum is manufactured from raw ewes' milk or mixtures of ewes' and goats' or cows' milk in the Aegean region of Turkey, especially in Izmir, Aydin, Manisa, Muğla and Denizli provinces and is also very popular in other regions of Turkey (Hayaloglu et al., 2007).

Tulum cheese is one of the most important types of Turkish traditional cheeses. Its name appears to derive from the word "tulum" which means animal skin- bag. The cheese is matured for 90–100 days in these skin bags. In recent years, some producers used tins for the maturation process of this cheese. In this situation, the cheese is called "Teneke Tulum" (canned Tulum). These two types of Tulum cheeses have been classified as hard cheese according to their total solids content (Kinik et al., 2005). However, Izmir Tulum Cheese is completely different from Classic Tulum Cheese because of its method of production and its characteristics. The only similarity between these two varieties of cheese is being produced in animal skins. In spite of the fact that ewe's milk in particular is preferred for the production of Izmir Tulum Cheese, in general a mix of ewe's, goat's and cow's milk is used (Figure 1). The production of both types takes place between the months of March and July, when milk is plentiful (Kamber, 2008).

The physico-chemical characteristics and aroma compound profiles of Turkish Cheeses, such as White Pickled, Kashar and Tulum Cheeses have been well examined; however, a few researches has ever been carried out on Izmir Tulum Cheese. Therefore, in this study, it was aimed to determine some physicochemical properties and aroma compounds of traditional Izmir Tulum Cheeses that are offered for consumption in Izmir.

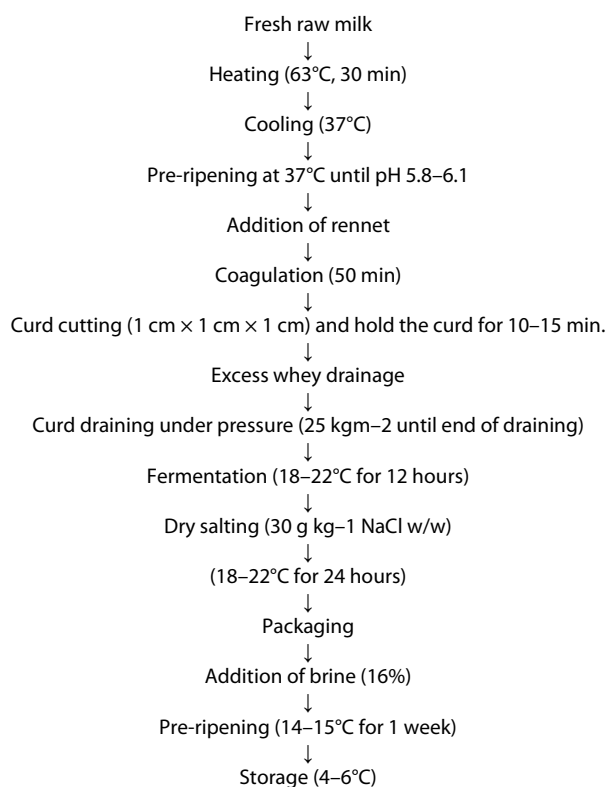


Figure 1. Traditional Izmir Tulum Cheese production

MATERIAL and METHODS

Materials

Thirty seven Izmir Tulum Cheese samples produced from only cow milk mixtures of cow's, sheep's or goat's milk mixtures were collected randomly from several markets in Aegean region of Turkey. The samples were about 1000 g, transported in sterile plastic bags to the laboratory under aseptic and refrigerated conditions (4°C). The analyses were initiated immediately after the samples were brought to the laboratory under cold storage conditions. Before the analyses, the samples were taken to the cold room and the edge of the cheese blocks and each obtained sample was homogenized in a blender.

Physicochemical Analyses

The dry matter contents of the cheese samples were measured by the gravimetric method; acidity was determined titrimetrically as lactic acid % (Kosikowski, 1982). Salt was measured according to the method described in TSE 591 (Anonymous, 2006) and the fat was determined by the Gerber method using Van-Gulik butyrometer (Anonymous, 1978). The pH of cheese was measured using a pH value with a combined electrode (Hanna pH 211 Microprocessor, Portugal). Total nitrogen (TN) levels of cheeses were determined by Kjeldahl method (AOAC, 1990) using

approximately 1 g of cheese. The water-soluble fraction (WSN) was prepared essentially as described by Ardö and Polychroniadou (1999), using 20 g of cheese with 100 ml pure water. The mixture was homogenized for 5 min using a SilentCrusher M Ultraturrax (Heidolph Instruments, Germany). Water-soluble N content of the cheese extract was determined by the Kjeldahl method, using 10 ml of cheese extracts (AOAC, 1990; Katsiari et al., 2000). Additionally, proteose peptone nitrogen (PPN) content was calculated by the derivation of NPN content from WSN content (Gripion et al., 1975).

Volatile Aroma Compounds Analysis

The volatile compounds of Tulum cheeses were determined with a solid-phase-microextraction (SPME) method using a fiber (57348-U, Supelco Inc., Bellefonte, PA, USA) coated with the sorbent material, divinylbenzene/carboxen/polydimethylsiloxane. Volatile compounds of Tulum cheeses were determined using gas chromatography (GC) (Clarus 600, Perkin Elmer Inc., Massachusetts, USA) equipped with flame ionization detector. A BP-20 wax capillary column (SGE International Pty. Ltd., Victoria, Australia; 30m x 0.25 mm i.d.x 0.25 µm film thickness) was used. Frozen cheese samples, stored at -20 °C, were defrosted at 4 °C before the day of analysis. Cheese surfaces were removed, samples were cut from the inside part of the cheese and then, grated. Three grams cheese was weighed into a 20-ml vial and a PTFE/butyl septum

was sealed with an aluminum crimp seal. Samples were equilibrated at 65° C at 500 rpm for 30 min. Then, fibre was inserted into the vial with using SPME fibre holder. The samples, agitated at 500 rpm, were held with fiber at 65° C for 30 min. After 30 min the fibre was inserted into the GC injector and held for 6 min. The injector port temperature was 250° C. The temperature of GC oven was programmed as follows: held at 40 °C for 6 min, then the temperature was raised to 100°C with 5 °C/min and held for 2 min. After raised to a final temperature of 250 °C (10 °C/min, held for 4 min), carrier gasses were He with 1 ml/min and H₂ with 1 ml/min flow rates. The analysis was performed in two repetitions. The identification of our chromatographic peaks was carried out by comparison of their retention times using appropriate standards (Sigma Chemical Company, St. Louis, MO, USA) (Ercan, 2009).

RESULTS and DISCUSSION

The pH and Titratable Acidity

The pH and titratable acidity of Izmir Tulum Cheese samples are shown in Table 1 for CM (cow milk) cheese and MM (mix milk) cheese. The pH values ranged from 4.11 to 4.92 for CM with average value of 4.36 and 4.01 to 4.75 for MM with average value of 4.40. Similar pH values were observed in both cheese produced from cow milk and the cheese produced from the mixed milk.

Table 1. pH and acidity (lactic acid%) values of Izmir Tulum Cheeses (n=37)

Izmir Tulum Cheese samples made from cow's milk			Izmir Tulum Cheese samples from mix milk type		
Sample No	pH	Acidity (LA%)	Sample No	pH	Acidity (LA%)
1	4.36	0.961	2	4.75	1.138
6	4.26	0.943	3	4.55	1.253
11	4.92	0.677	4	4.26	0.979
13	4.32	0.846	5	4.48	1.260
19	4.22	1.408	7	4.36	0.900
21	4.41	1.098	8	4.60	1.447
22	4.24	1.058	9	4.30	1.109
23	4.33	1.217	10	4.48	0.983
24	4.24	1.195	12	4.33	0.986
25	4.49	0.846	14	4.61	1.080
26	4.37	0.72	15	4.23	0.972
27	4.21	1.192	16	4.54	0.990
29	4.18	0.835	17	4.28	0.860
30	4.36	0.781	18	4.31	0.871
31	4.32	1.278	20	4.32	1.048
32	4.11	1.307	28	4.01	1.156
33	4.24	1.055			
34	4.43	0.814			
35	4.16	1.12			
36	4.81	0.522			
37	4.51	0.886			
Average	4.36	0.989	Average	4.40	1.065
Maximum	4.92	1.408	Maximum	4.75	1.447
Minimum	4.11	0.522	Minimum	4.01	0.860

The pH value of the cheeses was lower than those of other studies on tulum cheeses (Hayaloglu et al., 2007; Bayar, 2008; Aslaner, 2008). Titratable acidity of Izmir Tulum Cheese samples had maximum 1.408% and minimum 0.522% made from CM, maximum 1.447% and minimum 0.860% made from MM. The average titratable acidity of Izmir Tulum Cheeses made from CM and MM were 0.989% and 1.065%, respectively. Anonymous (2006) suggests that titratable acidity values of tulum cheeses should not exceed 3% as lactic acid in cheeses. The titratable acidity values of Izmir Tulum Cheese did not exceed 3.0% as lactic acid in cheeses. Hayaloglu et al. (2008) determined that tulum cheese had maximum 1.53% and minimum 0.54% lactic acid. Aslaner (2008) found that titratable acidity values of tulum cheese samples between 0.594-1.296%

Dry Matter, Salt and Fat Contents

Dry matter, salt and fat contents of CM and MM Izmir Tulum Cheese samples were given in Table 2. The average dry matter content of CM and MM Izmir Tulum Cheese are 56.528% and 60.157%, respectively. Total solid content of cheese is largely determined by the length of syneresis (Üçüncü, 2004). Therefore, the difference in total solid contents is mostly related to

syneresis. Dry matter contents of both cheese samples were in agreement with TS 3001 Tulum cheese standard and but were not agreement with Turkish Food Codex-Cheese Bulletin, 2015. MM Izmir Tulum Cheeses had high levels of dry matter than those of CM due to the higher solid content of sheep's milk compared to that of cow milk.

Cheese is a dairy product which is rich in milk fat and casein constituents of milk. Especially solid contents of sheep's milk are higher in sheep's milk than those of cow's milk. Salt plays a major role in the texture, flavor and microbial quality of cheese. Izmir Tulum Cheeses were analyzed for salt content and it was found that average salt contents of CM and MM Izmir Tulum Cheeses were 6.31% and 5.97%, respectively. The maximum salt content of CM Izmir Tulum Cheeses was 8.66% and the minimum salt content was 3.75%. The maximum salt content of MM Izmir Tulum Cheeses was 9.65% and the minimum salt content was 3.02%. Anonymous (2006) stated that salt content in dry matter of Tulum cheese should not exceed 6%. Although the salt -in- dry matter levels of all Izmir Tulum Cheeses varied within a large margin, most of the cheeses did not exceed the upper limit given in TS 3001.

Table 2. Dry matter, fat, and salt content of Izmir Tulum Cheeses (n=37)

Izmir Tulum Cheese samples made from cow's milk (CM) (%)						Izmir Tulum Cheese samples made from mix milk type (MM) (%)					
Sample No	Dry Matter	Fat	Fat in Dry Matter	Salt	Salt in Dry Matter	Sample No	Dry Matter	Fat	Fat in Dry Matter	Salt	Salt in Dry Matter
1	57.139	27.5	48.12	2.340	4.10	2	62.038	30.5	48.84	1.872	3.02
6	60.016	27.5	45.82	3.627	6.04	3	58.022	28.0	48.25	3.042	5.24
11	52.086	19.0	36.48	3.627	6.96	4	56.076	27.0	48.15	4.680	8.35
13	68.381	25.0	36.56	4.212	6.16	5	71.854	27.0	37.58	4.456	6.20
19	51.401	21.0	40.86	3.978	7.74	7	55.448	28.0	50.5	3.276	5.91
21	54.534	24.5	44.93	3.510	6.44	8	55.469	25.0	45.07	3.978	7.17
22	51.038	22.5	44.08	3.276	6.42	9	71.456	24.0	33.59	3.51	4.91
23	57.115	26.0	45.52	3.159	5.53	10	57.647	30.0	52.04	3.627	6.29
24	55.573	20.0	35.99	3.627	6.53	12	56.043	27.0	48.18	4.095	7.31
25	63.326	23.0	36.32	3.393	5.36	14	61.465	25.0	40.67	3.276	5.33
26	49.920	17.5	35.06	3.861	7.73	15	54.587	27.0	49.46	5.265	9.65
27	58.678	30.5	51.98	3.393	5.78	16	59.777	28.0	46.84	2.925	4.89
29	52.666	24.0	45.57	4.563	8.66	17	62.638	32.0	51.09	2.925	4.67
30	50.048	21.0	41.96	3.393	6.78	18	55.021	29.0	52.71	3.627	6.59
31	56.462	27.0	47.82	3.159	5.59	20	68.798	28.0	40.7	2.691	3.91
32	57.278	27.0	47.14	4.563	7.97	28	56.165	26.0	46.29	3.393	6.04
33	53.338	26.0	48.74	2.808	5.26						
34	56.464	25.0	44.28	4.446	7.87						
35	68.648	25.0	36.42	2.574	3.75						
36	56.951	26	45.65	2.925	5.13						
37	56.022	27	48.19	3.744	6.68						
Average	56.528	24.38	43.21	3.532	6.31	Average	60.157	27.0	46.248	3.540	5.97
Maximum	68.648	30.50	51.98	4.563	8.66	Maximum	71.854	32.0	52.710	5.265	9.65
Minimum	49.920	17.50	35.06	2.340	3.75	Minimum	54.587	24.0	33.590	1.872	3.02

Fat content plays several important functions in cheese; it affects cheese firmness, adhesiveness, mouth-feel and flavor (Fox, et al. 2000). The average

fat-in-dry matter of CM Izmir Tulum Cheese was 43.21%. Maximum fat content was 51.98% and minimum fat content was 35.06%. The average fat-in-

dry matter level of MM Izmir Tulum Cheese was 46.24%. Maximum fat content was 52.71% and minimum fat content was 33.59%. Turkish Tulum Cheese Standard (Anonymous, 2006) suggested that whole fat tulum cheese samples should have minimum 45% fat in dry matter. Most of Izmir Tulum Cheeses were in full fat cheese class. Bayar (2008) compared tulum cheese produced with traditional methods by using different packaging materials and reported that the fat –in-dry matter content of tulum cheeses produced with traditional methods were 49.09% for plastic packaging and 44.83% for skin bag packaging at the end of the ripening. Hayaloglu et al. (2007) stated that tulum cheese had maximum 58.81% and minimum 52.79% dry matter contents.

Proteolysis

Proteolysis is an essential biochemical process in the ripening of most cheese varieties (Fox et al. 2000; Pappa et al. 2006). Proteolysis, which contributes to the development of cheese texture and flavor, is due to the action of enzymes from coagulant, milk (general plasmin), starter bacteria, the adventitious nonstarter microflora and secondary starter (in some cheese varieties). The extent of proteolysis varies from very limited to very extensive. The pH 4.6 soluble fractions contain all proteins except casein, all

peptides, amino acids and amine. These peptides and amino acids are contributed by action of microorganisms on the caseins and their peptides (Tarakçı and Kuçukoner, 2006). Trichloroacetic acid-soluble nitrogen fraction is also known to be an indication of the amount of small peptides and amino acids present in cheese. Therefore, their levels are related to the ripening index.

Izmir Tulum Cheese samples were analyzed in order to determine protein contents and ripening indices. Table 3 shows the protein and nitrogen fraction values of CM Izmir Tulum Cheese and MM Izmir Tulum cheese. The average protein content of CM Izmir Tulum Cheese was 24.48% while the maximum value was 27.37% and the minimum content was 20.99%. The average protein content of MM Izmir Tulum Cheese was 24.65% while the maximum value was 27.50% and minimum content was 21.50%. These protein content values were higher than those of Erzurum Şavak type cheese (Hayaloglu et al., 2007). Hayaloglu et al. (2007) reported that Erzurum Şavak type cheese had protein content between 17.10-19.46% at the end of the ripening period. Bayar et al. (2008) found that at the end of the ripening time protein content of tulum cheese samples which produced from pasteurized milk and raw milk changed between 28.05-30.87% for skin bag packaging and 23.85-26.66% for plastic packaging.

Table 3. Protein, Total Nitrogen (TN), Water-Soluble Nitrogen (WSN), Soluble Nitrogen in Trichloroaceticacid (TCA-N), (Proteos-Peptone Nitrogen (PPN), values of Izmir Tulum Cheeses (n=37)

Izmir Tulum Cheese samples made from cow's milk (CM) (%)						Izmir Tulum Cheese samples made from mix milk type (MM) (%)					
Sample No	Protein	TN	WSN	TCA-N	PRN	Sample No	Protein	TN	WSN	TCA-N	PRN
1	23.48	3.68	0.62	0.32	0.30	2	27.50	4.31	0.83	0.68	0.15
6	24.44	3.83	0.81	0.49	0.32	3	24.95	3.91	1.05	0.76	0.29
11	24.31	3.81	1.15	0.82	0.33	4	23.03	3.61	0.75	0.51	0.24
13	21.69	3.40	0.66	0.48	0.18	5	25.20	3.95	0.92	0.66	0.26
19	26.09	4.09	0.87	0.55	0.32	7	22.90	3.59	0.65	0.36	0.29
21	26.80	4.20	1.08	0.91	0.17	8	25.33	3.97	1.29	1.03	0.26
22	21.82	3.42	0.75	0.40	0.35	9	24.50	3.84	0.59	0.46	0.13
23	23.48	3.68	0.93	0.72	0.21	10	26.73	4.19	0.81	0.60	0.21
24	24.18	3.79	0.69	0.39	0.30	12	25.71	4.03	1.05	0.70	0.35
25	25.07	3.93	0.64	0.38	0.26	14	23.54	3.69	0.9	0.78	0.12
26	24.50	3.84	0.68	0.34	0.34	15	21.50	3.37	0.66	0.53	0.13
27	23.48	3.68	0.93	0.67	0.26	16	23.61	3.70	1.25	0.65	0.60
29	24.82	3.89	0.47	0.35	0.12	17	24.63	3.86	0.56	0.44	0.12
30	23.29	3.65	0.57	0.36	0.21	18	23.22	3.64	0.9	0.55	0.35
31	26.54	4.16	0.92	0.50	0.42	20	25.84	4.05	0.64	0.34	0.3
32	27.05	4.24	0.63	0.43	0.20	28	26.22	4.11	0.68	0.52	0.16
33	20.99	3.29	0.64	0.34	0.30						
34	27.37	4.29	1.21	0.88	0.33						
35	23.67	3.71	0.67	0.43	0.24						
36	27.05	4.24	0.95	0.64	0.31						
37	23.99	3.76	1.13	0.67	0.46						
Average	24.48	3.84	0.81	0.53	0.28	Average	24.65	3.86	0.85	0.60	0.25
Maximum	27.37	4.29	1.21	0.91	0.46	Maximum	27.50	4.31	1.29	1.03	0.60
Minimum	20.99	3.29	0.47	0.32	0.12	Minimum	21.50	3.37	0.56	0.34	0.12

Aslaner (2008) determined some quality properties of Erzincan tulum cheese made from different milks by using traditional method and applying heat treatment and ripened in assorted packaging materials and found that the average protein content of tulum cheese samples were 29.92% at the end of the ripening.

Average TN, WSN, TCA-N and PPN contents of CM Izmir Tulum Cheese samples were 3.84%, 0.81%, 0.53%, 0.28%, respectively. Maximum values for stated parameters were found as 4.29%, 1.21%, 0.91% and 0.46% while the minimum values were determined as 3.39%, 0.47%, 0.32% and 0.12%, respectively. Average

TN, WSN, TCA-N and PPN contents of MM Izmir Tulum Cheese samples were 3.86%, 0.85%, 0.60% and 0.25%, respectively. Maximum TN contents were 4.31%, 1.29%, 1.03% and 0.6%, respectively. Minimum total nitrogen contents were 3.37%, 0.56%, 0.34% and 0.12%, respectively.

Aroma Compounds

Analysis of the volatile compounds of ripened Tulum Cheeses points out several marker compounds of maturation such as free fatty acids, ketones, aldehydes, esters and others (Table 4). There are limited data on volatile flavor compounds in Tulum cheese (Hayaloglu et al. 2007).

Table 4. Aroma compounds detected in Izmir Tulum Cheese samples produced from Cow's Milk (CM) and Mix Milk Type (MM) (n=37)

	Aroma Components	CM	MM
Free Fatty Acids	Acetic Acid	0.24±0.16	-
	Butyric Acid	5.35±0.26	3.68±0.71
	Hexanoic Acid	25.74±2.59	28.12±2.34
	Heptanoic Acid	2.04±0.09	0.55±0.12
	Octanoic Acid	18.42±0.58	27.24±2.17
	4 Metil octanoic Acid	1.05±0.06	0.62±0.18
	Decanoic Acid	26.42±0.48	16.51±0.40
	Dodecanoic Acid	1.52±0.40	0.83±0.19
Ketones	Acetone	-	1.23±0.12
	Diacetyl	-	-
	Acetoine	0.91±0.03	2.64±0.34
	2 Nonanone	1.65±0.17	1.59±0.41
	2 tri Decanone	0.34±0.08	1.68±0.38
Aldehydes	Hexanal	-	-
	Octanal	0.10±0.02	0.15±0.04
	Nonanal	-	1.05±0.44
	Decanal	0.32±0.06	0.32±0.06
	E-2-nonenal	0.20±0.01	-
	(E,Z)-2,6-nonadienal	0.05±0.01	-
	2-3 butanediale	1.02±0.12	6.89±1.33
e-2-decenale	0.42±0.16	1.18±0.17	
Esters	Etil butyrate	-	-
	Etil hexanoate	0.85±0.15	1.05±0.06
	Acetyl acetate	1.53±0.85	1.16±0.18
	Ethyl octanoate	1.67±0.30	0.66±0.18
	Ethyl decaoate	1.62±0.39	0.75±0.07
Others	Ethanol	0.85±0.05	2.35±0.15
	Isoamilalcohol	-	0.15±0.01
	D Limonen	0.06±0.01	1.49±0.07
	δ Decalactone	0.75±0.21	2.52±0.08
	γ Dodecalactone	2.32±0.14	3.27±0.52
	4-Amino aceto heptane	0.76±0.46	1.33±0.09

The highest free fatty acids which were determined aroma compound in Izmir tulum cheese were Hexanoic Acid, Octanoic Acid and Decanoic Acid. On the other hand, in Izmir tulum cheese which produced with mix milk type, acetic acid was the highest level. Ketone

content of cheeses showed difference. While 2 Nonanone (1.65±0.17) was the highest level in produced with cow milk cheese, Acetoine (2.64±0.34) was the highest level in produced with mix milk type cheese. The diacetyl was not determined in both

cheese type. The acetone (1.23 ± 0.12) was detected only in mix milk type cheese. Aldehydes were higher level in mix milk type cheese than cow milk cheese. Especially, while content of 2-3 butanedial was 6.89 ± 1.33 in mix milk cheese, it was below to 1.02 ± 0.12 in cow milk. Ethyl butyrate which is included of ester groups was not detected in both cheeses. γ Dodecalactone, Ethanol, δ Decalactone and 4-Amino aceto heptane was the determined aroma compounds in cheeses. Results show that milk type and manufacture methods in producing Izmir tulum cheese is significantly effective on the formation of aroma compounds.

Hayaloglu et al. (2007) has showed that the main components were short-chain fatty acids, 2-butanone, diacetyl, and primary alcohols in Tulum Cheeses. The principal acids in Tulum cheeses were ethanoic and butanoic acids. Several report show that ethyl esters are very important in Tulum cheese aroma. Researcher emphasized that ethyl ester is very important in 16 esters such as propyl, and butyl esters. The concentrations of ethyl acetate, ethyl butanoate, ethyl lactate, propyl acetate, and 3-methylbutyl acetate were high and were the principal volatile compounds in the cheeses (Durlu-Özkaya & Gün, 2014). The aroma profile analysis of Izmir Tulum cheese showed that, the major volatile compounds of this cheese were 2,2,4,6,6-pentamethylheptane, ethylhexanoate, p-cresol, γ -dodecalactone, ethyltetradecanoate. Furthermore, according to aroma extract dilution analysis (AEDA) results, diacetyl, 3-hydroxy butanone, ethylbutanoate, 1-octen-ol, acetic acid, propanoic acid, butanoic acid, pentanoic acid and hexanoic acid play an important role on aroma (Durlu-Özkaya & Gün, 2014; Avşar et al., 2009).

The origin of these volatile compounds could be chemical and biological degradation of proteins and lipids (Collins et al., 2003). Free fatty acids (FFAs), (even numbered C2-C16, decanoic acid) saturated and unsaturated aldehydes and ethyl esters are fat derived flavor volatiles that play an important role in the overall flavor of cheese (Alewjini et al., 2005). FFAs are formed by oxidation and decarboxylation of fatty acids (Marilley and Casey, 2004; Leuven et al., 2008). Hexanoic, octanoic and decanoic acids are the most abundant free acids present in ripened tulum cheeses. A more intense lipolysis is produced in traditional Turkish cheese varieties as in Tulum Cheese because of using raw or thermized milk in the production and longer ripening period. Hexanoic, octanoic, decanoic and butyric acids were perceived as a mild to strong goat-like, waxy and cheesy odor.

McSweeney and Sousa (2000) observed that linear FFAs are generally produced from lipolysis of milk fat. The source of FFAs can also be related to metabolism of deamination of amino acids and lipid oxidation. Similarities were found between FFA of Tulum Cheese, Maltese goat milk, Minas, Jack, Blue cheeses containing goat and sheep milk. Ketones such as acetoin, 2 nonanone, 2 tridecanone were found in volatile fractions of Tulum Cheeses. The formation of methyl ketones is a result of enzymatic oxidation of FFAs to β -ketoacids and decarboxylation to alkan-2-ones with one less carbon atom (McSweeney and Sousa, 2000; Ercan et al., 2014). The odor intensities of tri-decanone and 2-nonanone were significantly related to lipolysis. The aroma intensities values of ketones changed between medium to weak in cheese samples. Frank et al. (2004) also stated that 2-nonanone was significant aroma components in blue cheese. Gonzales De Llano et al. (1990) reported that the odd carbon numbered ketones especially 2-heptanone and 2-nonanone were the most intensive volatile substances of artisanal Gambero blue cheeses. Similarly ketones were also found in the volatile fraction of Tulum, Sepet and Gouda cheeses (Hayaloglu et al., 2007; Leuven et al. 2008; Ercan et al., 2014).

Weak flavor intensities of ethanol, isoamylalcohol, δ -decalactone, γ -dodecalactone and 4 aminoaceto heptane were also determined in Tulum cheese produced from cow milk and cow/goat/sheep milk blends and its flavor intensities were recorded as weak (Chiofalo et al. 2004; Frank et al. 2004; Nogueira et al., 2005; Attai, 2009; Ercan et al., 2014).

The esters in the volatile fraction of Tulum cheeses were ethyl hexanoate, ethyl octanoate, ethyl dodecanoate and acetylacetate. The flavor intensities of esters appeared to be responsible for the characteristic fruity and green odor. Esters are occurred by esterification of alcohols, carboxylic acids or alcoholysis of alcohols and acylglycerols and from alcohols and fatty acyl coenzyme A derived from the metabolism of fatty acids, amino acids and carbohydrates (Liu et al., 2004; Ercan et al. 2014). Similar esters were determined in Parmesan-Reggiano, Minas, Gouda and Domiati cheeses (Collins et al. 2003; Qian and Reineccius, 2002; Nogueira et al. 2005; Leuven et al. 2008). Octanal, (E,Z)-2,6-nonadienal, 2-3 butanedial, 2-decenal, and nonanal were aldehydes found in Tulum cheese. Since their levels were too low, they affected the aroma of Tulum cheeses with green and fatty odor. Carunchia Whetstine et al. (2003) and Leuven et al. (2008) stated that aldehydes affect the overall aroma of cheese

especially containing goat milk. On the other hand, aldehydes can be produced from transamination or by Strecker degradation (Ercan et al., 2014). As a result, the revealing aroma compounds of Izmir Tulum Cheese are needed further investigate.

CONCLUSIONS

The present study represents knowledge about some physicochemical properties and aroma compounds of Izmir Tulum Cheeses produced from cow's milk and mix milk type in Turkey. A total of 37 samples; 21 produced from cow's milk, 16 produced from the mixture of cow's, sheep's and goat's milks were analyzed and the examined physicochemical parameters varied depending on the milk type especially in the mixed milk type. Free fatty acid,

esters, aldehydes and ketones in tulum cheese samples became prominent as aroma fractions and also it was determined that the properties of composition were effected by type of milk and production methods. Izmir Tulum Cheese obtained from different markets had some differences in terms of chemical compositions and patterns of aroma compounds.

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