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SOME CARBONYL COMPOUNDS, FREE FATTY ACID COMPOSITIONS AND TOCOPHEROL CONTENTS OF KAYMAK (CLOTTED CREAM) PRODUCED FROM COW, SHEEP AND GOAT MILK

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Keywords

Carbonyl Compounds, Free Fatty Acids, Tocopherol, Clotted Cream.

Abstract

The aim of this study is to determine the effect of cow, goat and sheep milk used in traditional clotted cream production on some properties of clotted cream. The produced clotted cream was stored during 7 days. Some chemical analyses of the clotted cream, free fatty acid composition and tocopherol contents using gas chromatography (GC) and high-performance liquid cromatography (HPLC) were determined. Saturated fatty acids were found to be the highest in sheep's clotted cream and the lowest in goat's clotted cream. Monounsaturated fatty acids were found to be higher in clotted cream produced from goat's milk. Eicosapentaenoic Acid (EPA) and docosanhexaenoic acid (DHA) and δ-tocopherol were determined only in clotted cream produced from sheep milk. The content of α-tocopherol in sheep's clotted cream and β-tocopherol in cow's clotted cream is higher than in the other clotted cream. 2-Methylbutyraldehyde was identified as the most important carbonyl component in all samples. Although all three clotted creams were quite similar in appearance and some chemical properties, it was determined that they contain significant differences in terms of carbonyl compounds, fatty acid profiles and tocopherol contents.

İNEK, KOYUN VE KEÇİ SÜTÜNDEN ÜRETİLEN KAYMAKLARIN BAZI KARBONİL BİLEŞİKLERİ, SERBEST YAĞ ASİDİ BİLEŞİMLERİ VE TOKOFEROL İÇERİKLERİ

Anahtar Kelimeler

Karbonil Bileşikler, Serbest Yağ Asitleri, Tokoferol, Kaymak.

Öz

Bu çalışmanın amacı, geleneksel kaymak üretiminde kullanılan inek, keçi ve koyun sütlerinin kaymakların bazı özellikleri üzerine etkisini belirlemektir. Üretilen kaymak 7 gün boyunca depolamaya tabi tutulmuştur. Kaymakların, gaz kromatografisi (GC) kullanılarak serbest yağ asidi bileşimi ve yüksek performanslı sıvı kromatografisi (HPLC) kullanılarak tokoferol içeriği belirlenmiş ve bazı kimyasal analizleri yapılmıştır. Doymuş yağ asitleri en yüksek koyun kaymağında, en düşük ise keçi kaymağında bulunmuştur. Keçi sütünden üretilen kaymakta tekli doymamış yağ asitlerinin daha yüksek olduğu tespit edilmiştir. Eikosapentaenoik asit (EPA) ve dokosanhekzaenoik asit (DHA) ve δ-tokoferol sadece koyun sütünden üretilen kaymaklarda belirlenmiştir. Koyun kaymağındaki α-tokoferol ve inek kaymağındaki β-tokoferol içeriği diğer kaymaklara göre daha yüksektir. 2-Metilbütiraldehit, tüm numunelerde en önemli karbonil bileşeni olarak tanımlanmıştır. Her üç kaymakta, görünüm ve bazı kimyasal özellikler açısından oldukça benzer olmasına rağmen, karbonil bileşikleri, yağ asidi profilleri ve tokoferol içerikleri açısından önemli farklılıklar içerdikleri belirlenmiştir.

Cite

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SOME CARBONYL COMPOUNDS, FREE FATTY ACID COMPOSITIONS AND TOCOPHEROL CONTENTS OF KAYMAK (CLOTTED CREAM) PRODUCED FROM COW, SHEEP AND GOAT MILK

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Highlights

- Three types of clotted cream were produced from cow, goat and sheep milk and stored for 7 days.
- Carbonyl compounds, free fatty acid compositions and tocopherol contents of clotted cream were determined and some chemical analyzes were made.
- The carbonyl compounds, fatty acid profiles, tocopherol contents of the creams showed differences.

Purpose and Scope

In this study, it was aimed to investigate the effects of cow, sheep and goat milk on some carbonyl compounds, free fatty acid compositions and tocopherol contents of clotted cream.

Design/methodology/approach

The free fatty acid compositions of the clotted creams were determined using gas chromatography (GC) and the tocopherol content was determined using high performance liquid chromatography (HPLC), and some chemical analyzes (pH, dry matter and fat) of the samples were made.

Findings

It has been determined that clotted cream produced from goat milk contains much more flavoring substance than other clotted creams and is very different in fatty acid composition. It has been determined that sheep clotted cream contains some fatty acids (monounsaturated fatty acids, EPA, DHA, etc.) that are important for health and its α-tocopherol content is higher.

Research limitations/implications

As an alternative to clotted cream produced from cow's milk, sheep or goat clotted cream is believed to have many important components.

Social Implications

It is thought that the production of these clotted creams should be expanded and that these products will make an important contribution to dairy technology in terms of economy and health.

Originality

The originality of the study is stated in the similarity report.

1. Introduction

Cream is a dairy product with a high fat content. The density difference between the fat in milk/cream (0.93 g/cm^3) and serum (~1.036 g/cm^3) phases is one of the main reasons for the accumulation of fat globules on the surface, that is, creaming (Atamer et al., 2016). Milk fat globules are collected on the surface by moving upwards at a certain temperature. The cream layer, which contains about 60% of the fat formed by these fat globules, is called clotted cream (Akarca et al., 2014). Clotted cream, which is unique to Türkiye, is consumed for breakfast with honey and jam, and for decoration and flavoring in some desserts (kadayıf, baklava) (Kocatürk et al., 2019). Apart from Turkey, clotted cream is widely produced in the Balkans, Asia, the Middle East, India, Iran, Afghanistan. Kaymak is expressed in these countries with names such as kaimak, geymar, gemagh and kajmak (Jokovic et al., 2008; Cakmakcı and Hayaloglu, 2011). In the production of clotted cream, milk of different kinds of animals such as buffalo, cow, sheep and goat is used. For the production of clotted cream, buffalo milk with a high fat and dry matter content or cow's milk with an increased fat content with the addition of clotted cream is usually used (Akarca et al., 2014; Kocatürk et al., 2019). However, in recent years, clotted cream can also be made from different types of milk such as sheep and goat milk by applying a physical separation method due to the inadequacy of buffalo milk production and the laboriousness of the traditional production method (Pamuk, 2017). For traditional clotted

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cream production, raw milk is heated and left for 30 minutes when its temperature reaches 90°C. The milk is then left to cool at room temperature overnight. After the following morning's milking, milk is added to the heat treated cream obtained from the previous evening's milk. The mixture (morning and evening milks) is slowly heated again to 90°C for 45 minutes. After slowly cooling to room temperature, it is kept in the refrigerator (Şenel, 2011). The shelf life of the clotted cream produced by the traditional method is 4-7 days on average (Akarca et al., 2014; Akalin et al., 2006). Clotted cream is of great nutritional importance due to the high fat content of milk. Milk fat is of great nutritional importance due to the essential unsaturated fatty acids it contains, the fat-soluble vitamins A, D, E, K and conjugated linoleic acid (Dewhurst et al., 2006; Akarca et al., 2014). In addition, the fatty acid composition of dairy products varies according to the fatty acid composition of the milk used in its production, and the fatty acid composition of milk fat varies according to the type, diet and lactation period of the animal from which it is obtained, and season (Kocatürk et al., 2019).

The fatty acid composition of milk has an effect on the organoleptic quality, oxidative stability and physical properties of dairy products. Milk fat is one of the most complex fats found in nature due to the wide variety of fatty acids (chain length -short, medium, long-, degree of unsaturation and branching, etc.) contained in it (Kahyaoğlu, 2014). α-tocopherol is the primary antioxidant that works by ending free radical chain reactions, giving hydrogen or electrons to free radicals, and converting them into more stable products (Karabulut, 2010). As a result of chemical and biochemical transformations of milk components, aroma and flavor compounds are formed. These compounds; carbonyl compounds (diacetyl, acetone, acetaldehyde, etc.), volatile acids (butyric, acetic and formic, etc.), non-volatile acids (such as lactic and pyruvic) and various compounds (lactose, fat or protein components, which are formed by the thermal decomposition of specific amino acids). Among the aroma and flavor compounds, free fatty acids, carbonyl and lactic acid have a significant impact on the shelf life of dairy products and the formation of their characteristic aroma and flavor. Aldehydes are especially associated with taste changes and lead to a reduced shelf life, unpleasant odors, texture disorders and reduced nutritional value (Panseri et al., 2011).

In clotted cream, some chemical and microbiological properties (Tosun, 2016), the content of some carbonyl components and free fatty acids and their effect on aroma (Şenel, 2011), volatile aroma properties (Cakmakcı and Hayaloglu, 2011), microbiological properties (Yılsay and Bayizit, 2002), active isomers of conjugated linoleic acid (Akalin et al., 2005) were investigated. But, there is no research on the comparison of fatty acid, carbonyl compound and tocopherol content in clotted creams produced from different types of milk, such as goat and sheep cream. In this study, the fatty acid composition, carbonyl compounds and tocopherol content of cow, goat and sheep clotted cream, which have a significant effect on their quality and nutritional value, were examined. The free fatty acid composition by gas chromatography (GC), carbonyl components by solid phase microextraction system and tocopherol contents by HPLC were determined in clotted cream samples on the first and 7th days.

2. Material and Method

2.1. Material

In this study, raw sheep, goat and cow milk provided from Isparta Keçiborlu center-Türkiye and Isparta Unsut plant –Türkiye were used. Clotted cream production was carried out in Isparta Unsut plant.

2.2. Method

2.2.1. Clotted Cream Production

The raw milks for the production of clotted cream were standardized with cream of its own species to a ratio of 55-60% (sheep, goat and cow). Then, the first heat treatment was applied for 20 minutes at 95±1°C. Pasteurized milk was poured into trays with a depth of 15±2 cm from a height of one meter to foam the milk which has high fat content (so that the cream could acquire a porous appearance). The milk which has high fat content in the trays was cooled to 42±1°C. Afterwards, the second heat treatment was applied at 72±1°C for 10 minutes without much movement. The milk which has high fat content was cooled to 4±1°C in a short time and left for 12 hours to form a layer of clotted cream on the surface. The resulting clotted cream is cut and separated from the milky part (Pamuk, 2017). The samples were packed in airtight plastic packages and stored for 7 days at 4±1°C (Fig 1). The clotted cream production was carried out three times. The appearance of clotted cream produced from goat, sheep and cow milk is given in Fig 2.

Standardized raw cow- ewe- goat milk (≤ 60% fat)
↓
Heat treatment at 95±1°C for 20 minutes
↓
Transfer of milk to trays with a thickness of 15±2 mm by frothing
↓
Cool down to 42±1°C
↓
Second heating to 72±1°C (10 minutes)
↓
Cutting of the clotted cream into strips and taking it onto perforated grids
↓
Packaging and 7 days storage at 4°C

Figure 1. Clotted cream production flow chart

a b c

Figure 2. The appearance of clotted cream samples (a) sheep cream, (b) goat clotted cream, (c)cow clotted cream

2.2.2. Chemical Analysis

In clotted cream samples, the dry matter (gravimetric method) and the fat (gerber method) was determined (AOAC, 2000). The pH value was detected using the digital pH meter WTW pH 315 (Weilhelm, Germany).

2.2.3. Analysis of Fatty Acids

Sample preparation: Clotted cream samples were kept in chloroform:methanol mixture (2:1) and the fat layers were extracted for 12 hours. Then, samples derived with 0.5 ml sodium methoxide were prepared by taking the organic phase and giving them to the system.

The analysis of fatty acid methyl esters was carried out according to AOAC 996.06 (AOAC, 2005) method. In the determination of fatty acids, Perkin Elmer Autosystem XLGC and GC-FID detector were used. The study was conducted at 240°C. The detector temperature is 240°C, the flow rate is 15ps. Helium gas was used in the study a column with dimensions of 100 m * 0.25 mm and 0.25 m (Cp SIL 88 FOR FAME) was studied. After waiting for 4 minutes at a temperature of 60°C, 175°C was reached with an increase of 13°C per minute. After waiting at 175°C for 27 minutes, the samples waiting at this temperature for 5 minutes were delivered to 240°C with an increase of 4°C per minute, reaching 215°C with an increase of 4°C per minute, and the analyzes were performed by waiting at this temperature for 15 minutes.

2.2.4. Analysis of Volatile Aroma Compounds

Analysis of volatile aroma compounds was performed according to the method by Yang and Peppard (1994). For solid phase microextraction (SPME) analysis, 15 ml of silicone septal viale (Supelco 27159 ml clear PTFE/Silicone septa Cap) 3.0 g was taken from frozen (-20°C) clotted cream samples. The samples were first placed in a heating block at 45°C and left for 15 minutes without fiber. The extraction process was carried out using CAR/PDMS fiber (75-µm Fused Silica, Supelco Ltd., Bellefonte, PA, USA) by using a vial injection. It was left for 30 minutes at 45°C to absorb volatile compounds from the fiber. The desorption of volatile compounds to be extracted was carried out in the GC-MS system and kept at 250°C for 5 minutes. Shimadzu GC–2010 gas chromatography system and Shimadzu MS-QP2010 mass spectrometry system (Shimadzu Corporation, Kyoto, Japan) were used to determine the volatile aroma compounds of samples. The analysis conditions are as follows: column Rx-5sil MS (30 m x 0.25

mm, i=0.25 um film thickness; Restek, Bellefonte, catalog No:13623, PA, USA); the temperature program was kept at 40°C for 2 minutes. It was raised to 250°C at a speed of 4°C / min and kept at 250°C for 5 minutes; injector and detector temperatures were 250°C (detector voltage, 70 eV; carrier gas, is He; at a flow rate of 1.61 ml / min). The data processing was done with GCMS solution. GC / MS analysis was performed in the scanning mode in the december range of 40-300 amu. Volatile compounds were identified by comparing their retention time (RT) and mass spectra with analytical standards. The volatile compounds determined in the slider samples were verified by Wiley-NIST, Tutor, FFNSC (Flavor and Fragrance Natural and Synthetic) mass spectra libraries and RI values. The RI was calculated using an alkane series for each compound.

2.2.5. Analysis of Tocopherols

In the tocopherol analysis of clotted cream samples, the method given by Lampi et al. (1999) was modified and used. Detection and quantification were carried out with a Shimadzu LC-20AT prominence System controller (Kyoto, Japan), SIL-20AC prominence Autosampler, LC-20AT prominence pump and RF-10AXL Fluorescence Detector (Ex 295 nm, Em 330 nm). The Luna Silica (250*4.6 mm) 5 l (Supelco, Inc., Bellefonte, PA) column was used for tocopherols (α -, β-, γ-, δ-) analyse. The mobile phase consists of heptane/THF (95/5) (v/v), flow rate 1.2 ml/min and injection volume 10 µl.

2.2.6. Statistical analysis

The statistical evaluation of the study was determined by using the SPSS 22.0 program and by examining the significance level of the differences between the groups ($p<0.01$) with the Duncan multiple comparison test.

3. Experimental Results and Discussion

3.1 Chemical Analysis

The pH values of the clotted cream produced from sheep, goat and cow's milk were determined as 6.32±0.04, 6.23±0.03 and 6.44±0.02, respectively. The fat ratios were found to be 56.5±0.05%, 54.5±0.02% and 53.5±0.04%. The dry matter contents were detected as 65.57±0.12%, 63.18±0.34% and 61.47±0.54%. Tosun (2016) was reported that the dry matter values of clotted cream were between 64.06-67.51%, and the fat content was between 61.00-65.00%. Albay and Şimşek (2019) found the lactic acid values of clotted cream samples to be 0.25-0.51% and the pH values to be 6.44-6.51. The results in this study are similar to the findings of these researchers.

3.2. Fatty Acid Composition

The amounts of fatty acids determined in cow, goat and sheep clotted cream is given in Table 1. In this study, it was determined that the saturated fatty acid (SFA) content of sheep's clotted cream samples was 65.39% and the total unsaturated fatty acid (TUFA) content was 30.03% on the first day. The saturated fatty acid (SFA) and total unsaturated fatty acid (TUFA) contents at the end of storage were 64.82% and 28.59%, respectively. Carta et al. (2008) found that the ratio of monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) was approximately 28% and 6%, respectively, in sheep's milk, and the saturated fatty acid (SFA) level in milk fat was also quite high (more than 60%) was shown. Accordingly, the monounsaturated fatty acid (MUFA) content (26.55%) and polyunsaturated fatty acid (PUFA) content (3.48%) of this study were lower than the values determined in sheep's milk by Carta et al. (2008).

The saturated fatty acid (SFA) content of cow's clotted cream (first day) the content of monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA) was found to be 61.66%, 32.29% and 2.66%, respectively. It was determined that the saturated fatty acid (SFA) content (61.66%) in cow clotted cream of this study was lower than the fatty acid results of the cow cream samples analyzed by Tosun (2016). PUFA and SFA contents of sheep cream and cow cream samples in this study were observed to be lower than the values given by Sbihi et al. (2015).

The lowest SFA value (50.24%) was determined in goat's milk compared to other milks. During storage, it was found that this value (47.56) decreased gradually in clotted cream. Polyunsaturated fatty acid (PUFA) content of 6.16% and saturated fatty acid (SFA) content of 67.04% were determined in goat milk by Sbihi et al. (2015).

Şenel (2011) determined that there was a decrease in the total value of short-chain fatty acids (SCFA) and medium-chain fatty acids (MCFA) in Afyon clotted cream at the end of storage (7 day), but there was an increase in the total value of unsaturated free fatty acids. Tosun (2016) stated that in stored cream samples, the content of polyunsaturated fatty acids (PUFA) decreased by oxidation, while the content of saturated fatty acids (SFA)

increased during storage. In the study, it is stated that this is an indicator of oxidation of linolenic (C18:3) acid and decreases in all clotted cream samples during storage.

Table 1. Fatty acid content of cow, goat and sheep clotted cream (%)

Fatty acid	C		G		E	
Days	1	7	1	7	1	7
SFA	**61.66**	**60.72**	**50.24**	**47.56**	**65.39**	**64.82**
C4:0	1.22±0.47	1.20±0.00	2.32±0.38	2.34±0.13	1.21±0.11	1.25±0.10
C6:0	0.85±0.28	0.86±0.00	2.76±0.11	3.60±0.55	1.12±0.22	1.14±0.02
C8:0	0.60±0.15^{b}	0.59±0.00^{b}	4.85±1.06	5.18±0.10	1.14±0.21^{a}	1.17±0.06^{a}
C10:0	1.54±0.17^{b}	1.46±0.03^{b}	17.88±2.97	12.16±2.06	3.75±0.56^{a}	3.92±0.44^{a}
C11:0	0.16±0.02^{a}	0.14±0.01^{a}	14.97±2.85	16.56±1.31	-	-
C12:0	2.79±0.00	2.39±0.07	0.22±0.04	0.24±0.01	2.53±0.10	2.58±0.29
C 13:0	-	-	5.20±0.73	5.89±0.41	-	-
C14:0	10.14±0.38	9.52±0.17	-	-	9.77±0.06	9.71±0.51
C15:0	0.94±0.04^{b}	0.92±0.01^{b}	0.29±0.06	0.27±0.00	1.25±0.03^{a}	1.23±0.06^{a}
C16:0	30.88±0.07^{a}	30.69±0.47^{a}	-	-	28.92±0.07^{b}	28.43±0.40^{b}
C17:0	0.76±0.05b	0.77±0.04^{b}	0.48±0.05	0.45±0.01	0.91±0.01a	0.93±0.03^{a}
C18:0	11.57±0.01^{c}	11.96±0.07^{b}	-	-	14.18±0.13^{a}	13.89±0.19^{a}
C20:0	-	-	0.88±0.37	0.59±0.05	-	-
C21:0	-	-	0.39±0.07	0.28±0.03	-	-
C22:0	0.21±0.00^{b}	0.22±0.00^{b}	-	-	0.44±0.02^{a}	0.43±0.02^{a}
C23:0	-	-	-	-	0.03±0.04	-
C24:0	-	-	-	-	0.14±0.16	0.14±0.16
TUFA	**34.95**	**36.31**	**43.00**	**46.07**	**30.03**	**28.59**
MUFA	**32.29**	**33.22**	**32.32**	**35.36**	**26.55**	**25.24**
C14:1	0.68±0.08^{a}	0.75±0.02^{a}	8.91±0.63	10.08±0.42	-	-
C15:1	-	-	0.88±0.02	0.99±0.02	-	-
C16:1	2.15±0.07^{a}	2.03±0.02^{a}	17.25±0.26	19.03±0.30	1.35±0.04^{b}	1.35±0.06^{b}
C17:1	0.31±0.09^{a}	0.29±0.09^{a}	0.39±0.01	0.36±0.01	-	-
C18:1n9t	2.46±0.25^{a}	2.14±0.10^{a}	3.91±0.39	4.17±0.29	1.14±1.32^{a,b}	-
C18:1n9c	26.35±1.47^{a}	27.76±0.10^{a}	0.98±0.39	0.73±0.05	22.06±1.60^{b}	22.07±1.03^{b}
C20:1	0.22±0.03^{b}	0.20±0.03^{b}	-	-	1.83±0.03^{a}	1.82±0.02^{a}
C22:1n9	-	-	-	-	0.17±0.00^{a}	-
C24:1	0.12±0.18	0.05±0.00	-	-	-	-
PUFA	**2.66**	**3.09**	**10.68**	**10.71**	**3.48**	**3.35**
C18:2n6t	0.20±0.00a	0.20±0.00^{a}	9.16±1.67	8.90±0.55	-	-
C18:2n6c	2.23±0.00^{b,c}	2.62±0.01^{a}	-	-	2.01±0.22^{c}	2.34±0.06^{a,b}
C18:3n3	-	-	0.6±0.2	0.48±0.03	1.01±0.04^{a}	1.01±0.03^{a}
C20:3n3	0.23±0.02^{a}	0.27±0.00^{a}	-	-	0.10±0.11	-
C20:5n3	-	-	-	-	0.21±0.24	-
C22:2	-	-	0.92±0.52	1.33±0.67	0.10±0.02^{a}	-
C22:6n3	-	-	-	-	0.05±0.05	-

* a,b,c: Small letters indicate that the difference is statistically significant ($p<0.01$).
SFA: Saturated fatty acids; TUFA:Total unsaturated fatty acids; MUFA: Monounsaturated fatty acids, PUFA: Polyunsaturated fatty acids.
C: Cow clotted cream, G: Goat clotted cream, E: Sheep clotted cream

The butyric acid (C4:0) produced by bacterial fermentation was found to be 1.21 and 1.22 in sheep's clotted cream and cow's clotted cream, respectively. It was determined that the butyric acid (2.32-2.34) was higher in the clotted cream produced from goat's milk. Accordingly, the butyric acid in cow clotted cream was determined to be lower than the butyric acid value (2.70 ± 0.27) of cow cream samples determined by Tosun (2016). Myristic acid (C14:0) is one of the most determined medium chain fatty acids in clotted cream samples (C8:0-C15:1). On the first and seventh days, myristic acid levels were determined as 10.14 and 9.52 in cow clotted cream and 9.77 and 9.71 in sheep clotted cream, respectively. However, myristic acid was not determined in goat clotted cream during storage. It was observed that the caprylic acid (C8:0) level was highest in sheep clotted cream (1.14-1.17) and lowest in goat clotted cream (4.85-5.18) during storage. It was determined that the capric acid (C10:0) level (17.88-12.16) of goat clotted cream during storage was considerably higher than the other clotted creams (between 1.46 and 3.92). On the 7th day of storage, lauric acid (C12:0) levels of cow, goat and sheep clotted cream were found to be 2.39, 0.24 and 2.58, respectively, and the lowest value was found in goat clotted cream. In addition, at the end of storage, the level of pentadecanoic acid (C15:0) was lower in goat clotted cream (0.27). The highest level of pentadecanoic acid was found in sheep clotted cream (1.23). It has been reported that the mean

values of caprylic acid, capric acid and myristic acid in Afyon clotted cream are 8.21, 17.41 and 198 mg/kg, respectively (Şenel, 2011).

It was determined that palmitic acid (C16:0) and linolenic acid (C18:3) are the longest chain fatty acids (C16:0-C18:3) in both clotted cream varieties (sheep and cow). In addition, palmitic acid levels were determined to be 28.92±0.07% in sheep's clotted cream and 30.88±0.07% in cow's clotted cream. Palmitic acid level was found to be similar to the values reported by Akyıldız (2008) and Atasoy and Türkoğlu (2010).

The ratio of palmitoleic (C16:1), linoleic acid (C18:2 n6t) and elaidic (C18:1 n9t) acid level in goat's clotted cream is much higher than in other clotted cream. The elaidic (C18:1 n9t) acid was detected at least in sheep's clotted cream. According to these fatty acid values, it can be said that sheep clotted cream may be more advantageous for heart patients. In a study, it was stated that this ratio was lower in goat milk than in cow milk (Haenlein, 2004). It is thought that the stages of clotted cream production may have changed the ratio of this fatty acid.

3.3. Volatile Aroma Compounds

Carbonyl components of the sheep, cow and goat clotted cream produced in this study are given in Tables 2, 3, 4 during storage. When the tables are examined, it is seen that the volatile components are less in both variety and amount in cow clotted cream, but more in goat clotted cream. In addition, at the end of storage, it was determined that there was a decrease in the carbonyl compounds of cow clotted cream, but an increase in sheep and goat clotted cream.

Aldehydes which have a significant effect on taste are the first oxidation products of primary alcohols. Alcohols are formed by the reduction of aldehydes, and acids are formed by oxidation of aldehydes. The smell of low-molecular aldehydes is pungent, and as the number of carbon atoms in the molecule increases, odors that affect taste are formed. Since aldehydes are transitional compounds, they do not accumulate in the product and immediately turn into alcohols or suitable acids (Kahyaoğlu, 2014). Aldehydes can be formed by Strecker degradation of amino acids, and linear aldehydes can be formed by β-oxidation of unsaturated fatty acids (Kesenkaş and Akbulut, 2006). Azine aldehyde (5.67%) was determined on the first day of cow clotted cream, but no aldehyde was detected on the seventh day. However, it was determined that the dominant carbonyl component in sheep (71.47-64.55%) and goat (76.18-50.79%) clotted creams during storage was 2-methylbutyraldehyde. In addition, pentanal, pelargonaldehyde and enanthaldehyde were detected in goat clotted cream.

Hydrocarbons can be produced directly from feed or during maturation as a result of lipid autooxidation (Albay, 2022). The dominant carbonyl component in cow clotted cream was found to be n-hexane hydrocarbon. At the end of storage, n-hexane level increased, but toluene level decreased and total hydrocarbon level and variety decreased. In addition, at the end of the storage, no hydrocarbon was formed in goat clotted cream, but toluene component was determined from sheep clotted cream.

There was a decrease in terpene levels with storage in sheep and cow clotted cream. In goat clotted cream, it was observed that terpenes were formed more than other clotted creams, and the variety and level of terpenes increased with storage. Furthermore, on the seventh day of storage in goat clotted cream, limonene (9.09%) was the third dominant carbonyl component. Terpenes are compounds related to animal feed or pasture, meadow and green fodder. Ketones have typical odors and low detection thresholds (Albay, 2022). Ketone formation occurred in goat clotted cream more than others. On the first day of storage, the second dominant carbonyl component of goat clotted cream was 2-propanone acetone (11.74%) ketone component and total ketone level decreased with storage.

Alcohols can be formed by different metabolic pathways such as amino acid metabolism, lactose metabolism, reduction of methyl ketones and breakdown of linolenic or linoleic acid (Collins et al., 2003; Kesenkaş and Akbulut, 2006). Alcohol was formed on the seventh day (0.23%) of sheep's clotted cream, on the first day of cow's clotted cream (0.08%), and on the first (0.37%) and seventh (1.02%) days of goat's clotted cream. Acids formed by proteolysis, lipolysis and glycolysis reactions or produced by microorganisms are important for the aroma of food (Kahyaoğlu, 2014). At the end of storage, propiolic acid (1.42%) was formed in cow clotted cream and propionic acid (0.44%) in goat clotted cream. In particular, various esters, such as ethyl esters of fatty acids C4-C10, can be found in raw cow, goat, sheep and buffalo milk. Although esters have a positive effect on taste at low concentrations, they can cause fruity taste disorders at high concentrations (Ertekin and Seydim, 2009). On the seventh day of sheep (28.67%) and goat (18.42%) clotted creams, the second dominant carbonyl component was acetate isopropyl- ester component. On the seventh day of cow clotted cream, only pyridine and ethyl acetate esters were formed, while in goat clotted cream, esters were formed during storage and ester variety was more.

Tosun (2016) reported that 40 aroma components consisting of 12 hydrocarbons, 9 terpenes, 5 acids, 4 ketones, 4 alcohols, 3 aldehydes, and 3 esters were formed in cream samples during storage. It was also stated that aldehydes, esters, acids, terpenes and ketones increased due to oxidation during storage.

Şenel (2011) determined the amount of some carbonyl compounds (acetaldehyde, acetone, butanone-2 and diacetyl) in Afyon clotted cream. It was determined that the acetone level (7.73 mg/kg) on the first day had the highest level compared to other carbonyl compounds. Acetaldehyde, butanone-2, and diacetyl were reported to be 4.50 mg/kg, 2.18 mg/kg, and 4.11 mg/kg, respectively.

Examining the volatile aroma properties of Ispir dry clotted cream, Cakmakcı and Hayaloglu (2011) determined that there are 73 volatile substances (such as chloroform, toluene, hexane, heptane) in these samples consisting of 26 esters, 9 alcohols, 9 ketones, 8 terpenes, 5 aldehydes, 3 acids and 13 other various compounds. It was determined that Ispir clotted cream is characterized by high levels of esters.

Kahyaoğlu (2014), who examined the butters obtained from cow, sheep and goat milk stored for 90 days, found 126 volatile aroma compounds in total. As a result of the research, heptanal, octanal, 2,3-butanedione, butanoic acid 2-methylpropyl ester, carbonic acid diethyl ester, azulene, butane 2-3, dimethyl were found in cow butter, while 2-decanal, 5-methyl-2-hexanol, 1-heptanol-6-methyl, 2-butanol-3-methyl, alpha-terpinen, gamma-terpinen, 1,3-oktadien were determined in sheep butter. It was determined that 2,4-hexadienal, 2-octanone, formic acid pentyl ester, 6-octen-1-ol 3,7-dimethyl, heptanol, 1-nonanol in goat butter. Most of the aldehyde and ketone compounds are in cow butter; Acid, terpene and hydrocarbon compounds are mostly in sheep butter; It has been reported that ester, alcohol, sulfur and other compounds are mostly found in goat butter.

During the storage of milk fat as a result of lipid oxidation, volatile bad taste-aroma compounds such as hydroxyl acids are formed. These components negatively affect taste and quality (Kocaoğlu, 2009).

Table 2. Carbonyl compounds of sheep clotted cream during storage

Storage Time (Days)	**1**			**7**	
Components	**RT(min)**	**%**	**Components**	**RT(min)**	**%**
Aldehydes			**Aldehydes**		
2-Methylbutiraldehid	1.829	71.47±4.14[a]	2-Methylbutiraldehid	1.826	64.55±3.56[a]
Acid			**Esters**		
Isopropylsulfonyl chloride	1.934	14.93±0.23	Acetate isopropyl-	2.642	28.67±2.78
Alkane			**Terpenes**		
Pentane	2.550	3.95±0.18	(1S)-α-Pinene	8.570	1.78±0.45
Heptane	2.699	1.65±0.14	**Ketones**		
1-Bromopropane	1.719	0.34±0.07	Acetoin	2.825	0.92±0.33
Hydrocarbone			**Alcohol**		
2,2,4-trimethyl-Toluene	3.788	3.75±0.08	Ethanol	1.375	0.23±0.12
Terpene			**Alkane**		
(1S)-α-Pinene	8.576	3.73±0.12	Pentane, 2,2,4-trimethyl-	2.537	1.78±0.23
Ketones			n-Butane	1.446	0.11±0.03
4-Methyl-2-thiapentane	3.942	0.02±0.01	Butane, 2,3-dimethyl-	1.663	0.08±0.01
Others			1,6-Heptadiene	2.642	0.07±0.01
3-Pentanethiol	1.681	0.16±0.01	n-Heptane	2.688	0.43±0.04
			Hydrocarbones		
			Toluene	3.802	0.53±0.11
			Others		
			Nitrous oxide	1.231	0.49±0.09
			Isobutyl nitrite	1.739	0.35±0.17

RT: Retention Time

Table 3. Carbonyl compounds of cow clotted cream during storage

Storage Time (Days)	1			7	
Components	**RT (min)**	**%**	**Components**	**RT (min)**	**%**
Hydrocarbones			**Hydrocarbones**		
n-Hexane	1826	79.60±2.11	n-Hexane	1826	84.71±3.12
Pentane, 2,2,4-trimethyl-	2550	1.16±0.11	Toluene	8570	0.35±0.08
Toluene	3809	1.52±0.15	2-Bromopropane	1756	0.33±0.03
1,3,6-0ctatriene, 3,7 -dimethyl-, (Z)-	11407	2.94±0.52	**Terpenes**		
Propane, 2-nitro-	1752	0.24±0.05	Bicyclo[3.1.1]hept-2-ene, 2,6,6,trimethyl-, (.+/-.)-	2699	5.16±0.62
Aldehydes					
Azine	3369	5.67±0.31	n-Heptane	3809	0.49±0.07
Terpenes			**Esters**		
Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (.+/-.)-	8570	5.62±0.45	Pyridine	2785	3.19±0.42
			Ethyl acetate	1929	2.81±0.21
n-Heptane	2699	0.69±0.09	**Hydrocarbones**		
Carboxilic acides			Pentane, 2,2,4-trimethyl-	2550	1.54±0.17
Ethyl acetate	1929	2.46±0.24	**Fatty Acid**		
Alcohols			Propiolic acid	2620	1.42±0.12
2-Furanol, tetrahydro-2,3-dimethyl	1675	0.08±0.01			

RT: Retention Time

Table 4. Carbonyl compounds of goat clotted cream during storage

Storage Time (Days)	1			7	
Components	**RT(min)**	**%**	**Components**	**RT(min)**	**%**
Aldehydes			**Aldehydes**		
2-Methylbutyraldehyde	1.829	76.18±1.05[a]	2-Methylbutyraldehyde	1.802	50.79±4.02[b]
Pentanal	1.790	0.12±0.03	Pelargonaldehyde	7.684	0.22±0.12
Ketones			Enanthaldehyde	7.684	0.14±0.05
2-Propanone Acetone	1.427	11.74±1.68	**Esters**		
2-Heptanone Heptan-2-one	7.263	0.38±0.11	Acetate isopropyl-	1.430	18.42±1.12
2-Pentanone Methyl propyl ketone	2.550	0.24±0.05	Butyrate ethyl-	4.637	2.90±1.11
Terpenes			Formate isobutyl-	7.585	1.64±0.41
Limonene	12.384	4.13±0.71	Capronate ethyl-	11.305	0.71±0.21
2-.Beta.-Pinene	10.363	0.43±0.19	Acetate butyl-	4.993	0.57±0.23
m-Cymene	12.205	0.42±0.18	Ethanoate hexyl-	11.830	0.46±0.16
Alpha.-Pinene, (-)-	8.731	0.23±0.15	Formate butyl-	2.316	0.42±0.14
Sabinene	10.210	0.21±0.11	Propionate isobutyl-	5.991	0.28±0.09
Gamma.-Terpinene	13.530	0.15±0.05	Formate isoamyl-	3.910	0.25±0.08
Hydrocarbons			Isobutyrate methyl-	1.655	0.22±0.03
Propane, 1-bromo- 1-Bromopropane	1.726	4.08±0.13	Acetate amyl-	6.931	0.19±0.02
Ester			Capronate butyl-	4.050	0.12±0.03
Butanoic acid, ethyl ester	4.637	0.74±0.21	Isobutyrate isobutyl-	7.585	0.11±0.01
Capronate ethyl-	11.302	0.24±0.16	**Terpenes**		
Acetic acid, butyl ester n-Butyl acetate	4.992	0.16±0.09	Limonene	12.389	9.09±0.87
Ethanoate hexyl-	11.827	0.15±0.04	Pinene beta-	8.736	0.85±0.15
Propanoate ethyl-	2.877	0.05±0.01	Cymene para-	12.220	0.63±0.18
Alcohols			Eucalyptol	12.525	0.50±0.14
1-Pentanol Amylol	1.653	0.16±0.01	Sabinene	10.218	0.47±0.21
1-Butanol, 3-methyl-	3.291	0.12±0.02	Pinene alpha-	8.731	0.46±0.09
2-Methyl-1-butanol	3.356	0.09±0.01	Terpinene gamma-	13.530	0.45±0.11
			Carene delta-3-	11.584	0.20±0.08
			Ketones		
			Propyl methyl ketone	2.195	3.41±0.72
			Methyl isobutyl ketone	2.395	1.50±0.51
			Amyl methyl ketone	6.520	1.30±0.62
			Pimelic ketone	6.651	0.78±0.18
			Heptyl methyl ketone	14.875	0.34±0.15
			Acetylpropionyl	2.640	0.24±0.10
			Hept-5-en-2-one 6-methyl-	10.759	0.18±0.08
			Alcohols		
			Pent-2(Z)-enol	3.354	1.02±0.06
			Sulphur Compound		
			Mercaptan sec-amyl-	3.289	0.68±0.07
			Fatty Acid		
			Propionic acid	2.880	0.44±0.13

RT: Retention Time

* a,b: Small letters indicate that the difference is statistically significant ($p<0.01$).

3.4. Tocopherol content

The amounts of tocopherol determined in sheep, goat and cow clotted cream stored for 7 days are shown in Table 5 . The most α-tocopherol was detected in all clotted cream samples. The amount of α-tocopherol was found to be 24.14 ppm in sheep's clotted cream, 19.18 ppm in cow's clotted cream, and 18.23 ppm in goat's clotted cream. It was determined that the amounts of β-tocopherol, γ-tocopherol and δ-tocopherol in sheep clotted cream were 0.05 ± 0.00, 0.24 ± 0.01 and 0.02 ± 0.00 ppm, respectively, and in cow clotted cream, the amounts of β-tocopherol and γ-tocopherol were 0.40 ± 0.12 and 0.98 ± 0.01 ppm, respectively. γ -tocopherol wasn't determined in clotted cream produced from goat and cow's milk. It was observed that the tocopherol amounts of all three clotted creams decreased in general during storage.

In a study, it was found that the amount of vitamin E in dairy products was 21.7 μg/g (Hewavitharana et al., 1996). In a study on goat milk, it was reported that 70.9% of α-tocopherol and 22.02% of β-tocopherol were found (Sbihi et al., 2015). Gornas et al. (2014) found the α-tocopherol contents of butter samples sold in local markets in Poland and Latvia to be 2.00-16.92 mg/100 g and 2.61-2.98 mg/100 g, respectively. Derewiaka et al. (2011) determined 1-4 mg/100g tocopherol in milk fat. Karabulut (2010), examined the effects of α-tocopherol on the oxidative stability of butter fat triacylglycerols, determined that α-tocopherol provided the most effective antioxidant protection at a concentration of 50 μg/g. The amount of α-tocopherol was determined approximately half of this value in cow, goat and sheep clotted cream samples. It is thought that this situation is caused by the milk fat ratio in clotted cream and butter. In this study, the fat ratios of cow, sheep and goat clotted creams varied between 53.5% and 56.5%, while the fat ratios of cow, sheep and goat butters varied between 81.64% and 81.78% in the study by Kahyaoğlu (2014).

Table 5. Amounts of tocopherols in cow's, goat's and sheep's clotted cream (ppm)

Tocopherol	**C**		**G**		**E**	
Days	**1**	**7**	**1**	**7**	**1**	**7**
α-tocopherol	19.18 ± 1.50^{b}	6.35 ± 1.20^{c}	18.23 ± 2.75^{b}	15.18 ± 0.18^{b}	24.14 ± 0.25^{a}	21.48 ± 0.90^{a,b}
β-tocopherol	0.40 ± 0.12^{a}	0.14 ± 0.03^{b}	0.04 ± 0.00^{c}	0.03 ± 0.00^{c}	0.06 ± 0.00^{c}	0.05 ± 0.00^{c}
γ-tocopherol	0.98 ± 0.01^{a}	0.35 ± 0.07^{b}	0.45 ± 0.03^{b}	0.58 ±0.21^{b}	0.27 ± 0.01^{c}	0.24 ± 0.02^{c}
δ-tocopherol	-	-	-	-	0.02 ± 0.00^{a}	0.02 ± 0.00^{a}

*a,b,c: Small letters indicate that the difference is statistically significant ($p<0.01$).
C: Cow clotted cream, G: Goat clotted cream, E: Sheep clotted cream

4. Conclusion

In this study, some chemical properties, free fatty acids, carbonyl compounds and tocopherol contents of sheep, goat and cow clotted cream which are generally produced for breakfast were determined. It is seen that clotted cream produced from goat milk contains much more flavoring substance than other clotted creams and is very different in fatty acid composition. It has been determined that sheep clotted cream contains some fatty acids (monounsaturated fatty acids, EPA, DHA, etc.), which are important for health, with higher α-tocopherol content. It has been observed that sheep or goat clotted creams to be produced as an alternative to clotted cream produced from cow's milk have many important components. It is thought that the production of these clotted creams should be expanded and that these products will make an important contribution to dairy technology in terms of economy and health.

Conflict of Interest

No conflict of interest was declared by the authors.

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