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Effects of added caper on some physicochemical properties of White Cheese

*Oktay Yerlikaya, Cem Karagozlu**

Ege University Faculty of Agriculture Department of Dairy Technology, 35100 Bornova/İzmir, Turkey

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Abstract

In this study, the effects of caper berries addition on some physicochemical and functional properties of White Cheese were investigated. Three batches of White Cheese were produced: a control group with no caper addition (C), a group with whole grain caper addition (W) and a group with minced caper addition (M). Caper berries were added to the cheese vat after cutting at a level of 8 g per 100 g of curd weight. Changes in chemical compositions, proteolysis (ripening index), lipolysis (acid degree value), free amino acids, free fatty acids (FFAs), and some mineral substances of White Cheese samples were analysed during the ripening period for 90 days at + 4 °C. According to the results obtained from statistical analyses, when compared to control sample, there was a significant difference by adding caper to White Cheese for salt %, lactic acid %, and mineral contents ($p<0.05$). Generally, the data obtained from this study showed that adding caper to White Cheese reduced some quality characteristics, while some properties such as physicochemical were improved.

Key words: cheese, ripening, caper, proteolysis, lipolysis

Introduction

Capparies is called capers (C*apparis L.*) of the Capparaceae family are the fruit of a shrub, a perennial plant having medicinal and aromatic properties, and grown wildly at various regions of the world were profited for several purposes since ancient times (Ozcan et al., 2004). The roots, fruits, flower buds and leaves of caper are used in medical action. Also it is used in cosmetic and food industry. The processed flowers (or capers) and fruits (or caper berries) of the shrub C*apparis* spp. (Capparidaceae) are very popular in the Mediterranean countries for their flavour and digestive properties. Approximately 10.000 tonnes are produced annually, while the main producer and exporter countries are Spain, Morocco, Turkey and Italy. The caper fruits and plant are regarded as an important source of protein. Caper plays an important role in the human diet, since caper fruits contain approximately 67 mg calcium, 65 mg phosphorus, 9 mg iron and 24.01 mg protein in 100 g of edible dried substance (Sessiz et al., 2007). Capers and caper berries have gained importance in the food industry and the international trade, but manufacturing processes are expensive due to the lack of extensive farming of C*apparis* spp. (production often relies on wild growing plants), the seasonal availability of the raw materials and the absence of processing industries with adequate production capacities (Pérez - Pulido et al., 2007).

In many countries, young shoots, flower buds, fruits and seeds of C. *spinosa* are used as nutritional additive. Also, C*apparis* species were used in the traditional medicine as a poultice and for their diuretic, antihypertensive and tonic properties as well as in certain pathological conditions related to an uncontrolled lipid peroxidation. The fresh aerial parts, including the fruit and the flower buds, are usually stored in salt and vinegar, or brined and used as an appetizer with olives, cheese and nuts or as a complement to meat, salads or pasta. Additionally, fruits with small, soft seeds are preferred for the production pickles (Trombetta et al., 2005; Tlili et al., 2009).

*Corresponding author/Dopisni autor: E-mail: cem.karagolu@ege.edu.tr

Cheese evolved in the "Fertile Crescent" region between the Tigris and Euphrates rivers, about 8000-9000 years ago. This area now forms part of Turkey, Iraq and Iran. More than 1000 varieties of cheese are produced around the world. In Turkey, nearly 40 different cheeses are known, but only few of them have national and economic value (Hayaloglu et al., 2002). White Cheese is one of the most commercially significant types of cheese. Turkish White Cheese has a soft texture when fresh, while after ripening for 3 months in brine, it can be classified as "semi - hard" or "semi - soft" (Oner et al., 2006). White Cheese is made in different ways according to the area of production: using cow's, water buffalo's, ewes' or goat's milk, or a combination of these with varying proportions of fat and salt. Also a variety of packaging materials are used to store White Cheese, and it may be packaged dry or in brine, with or without ripening (Kamber, 2008).

In cheese production, various kinds of herbs are added to cheese curd produced from raw or pasteurized milk. After production, the cheese is usually ripened for 3 months. The herbs commonly used in dairy products are as follows: *Allium* sp., *Prangos* sp., *Silene vulgaris*, *Tymus* sp., and *Mentha* sp., and these herbs are added to cheese in different ratios. In the herb added dairy products these herbs have odour, flavour and bio-preservative characteristics (Tarakci and Kucukoner, 2008).

Cheese ripening is a complex microbiological and enzymatic process characterized by the production of compounds that contribute to certain aroma and texture characteristics of cheese. From the technological point of view it is important to determine the changes occurring during the course of ripening in order to standardize and control the manufacturing process. Also, in some cases, this might help to prevent the alteration of sensory properties of cheese (Temiz et al., 2009).

In this study, caper was used in order to create White Cheese with different flavours and to offer new products with improved nutritional features to the consumers. The aim of this study was also to develop a new cheese making process through additions of whole grain caper and minced caper as well as to create a new food product with improved functional properties.

Materials and methods

For cheese production raw cow's milk supplied from Ege University, Menemen Practise and Research Farm in Faculty of Agriculture (Izmir, Turkey) was used. The average composition characteristics of raw cow's milk used in making cheese with caper were, 12.70 ± 0.69 % total solids , 4.5±0.42 % fat, 3.65±0.35 % lactose, 0.68±0.02 % total nitrogen and 0.18±0.01 % acidity as lactic acid.

Rennet was obtained from Mayasan Gida Sanayi ve Ticaret A.S. (Yenibosna, Istanbul, Turkey) and used to coagulate milk in liquid form (coagulating power 1:8000). Calcium chloride was obtained commercially from Horasan Kimya (Ankara). Cheese starter cultures *Lactococcus lactis* subsp. *lactis* and *Lactococcus lactis* subsp. *cremoris* (1:1) were obtained from Maysa Gida Sanayi ve Ticaret A.S. (Kozyatagi, Istanbul, Turkey). Freeze-dried concentrated cultures were activated by incubating at 37 °C overnight in de Mann, Ragosa, Sharpe (MRS) broth (Fluka Chemie GmbH, Buchs, Switzerland) and this procedure was repeated twice (Halkman, 2005). Activated cultures were incubated overnight at 37 °C in heat-treated (110 °C for 15 min) 12 g per 100 mL reconstituted skim milk before the addition into the cheese vats.

Canned caper berries were obtained from Susitas A.S. (Cigli, Izmir) and added to the cheese vat after cutting the curd. The added amount of caper in pickled form was 8 % of curd weight, acidity 1 %, pH=3.5, salt 10 % while the control cheese contained no caper. The experiment was repeated three times and the analyses were carried out in duplicate.

Methods

Cheese-making and sampling

The production of White Cheese with caper addition was carried out in the pilot plant of Dairy Technology Department of Ege University, Izmir, Turkey. Raw milk was first filtered, pasteurized at 72 °C for 2 min and cooled down to 32 °C. Starter cultures were added in amount of 0.5 mL per 100 mL of milk and $CaCl_2$ in amount of 0.2 g per 1000 mL of milk. The milk was then coagulated by using calf rennet. After coagulation, the curd was cut into 1 cm^3 cubes. After the removal of whey, curd was divided into 3 equal groups. One of them was used as control group without caper. After draining of brined capers and keeping them in water for 12 h, capers were drained again and added to curds (in % 8 ratio) in two different ways, as whole and minced, and mixed well. The curd was weighed and cut into blocks of 7 x 7 x 7 cm^3. Fresh cheeses were soaked in brine of 16 % salt for 3 h. Afterwards, the brined blocks were dry salted, taken out and left for 12 h uncovered on a cheese table at room temperature. Cheeses were put into cans with 12 % brine and transferred to cold rooms (4-5 °C), and ripened for 90 days at this temperature (Figure 1).

In the study, the experimental cheese sample without caper addition (control) was labelled as "C"; the sample with addition of whole grain as "W" and the one with minced caper as "M". From each batch, samples were taken out on the 1^{st}, 30^{th}, 60^{th}, 90^{th} days of ripening. In each sample chemical composition, degrees of proteolysis and lipolysis, and mineral elements were analysed.

Caper analysis

Caper samples were analysed for curd weight, acidity, pH and salt content according to Ozcan et al. (2004) and Ozcan and Aydin (2004).

Cheese analysis

Chemical analysis

Grated cheese samples were analysed for total solids by oven drying at 102 °C (Anonymous, 2006), fat by the method of Gerber-Van Gulik (Anonymous, 2006), salt by the Mohr method (Oysun,

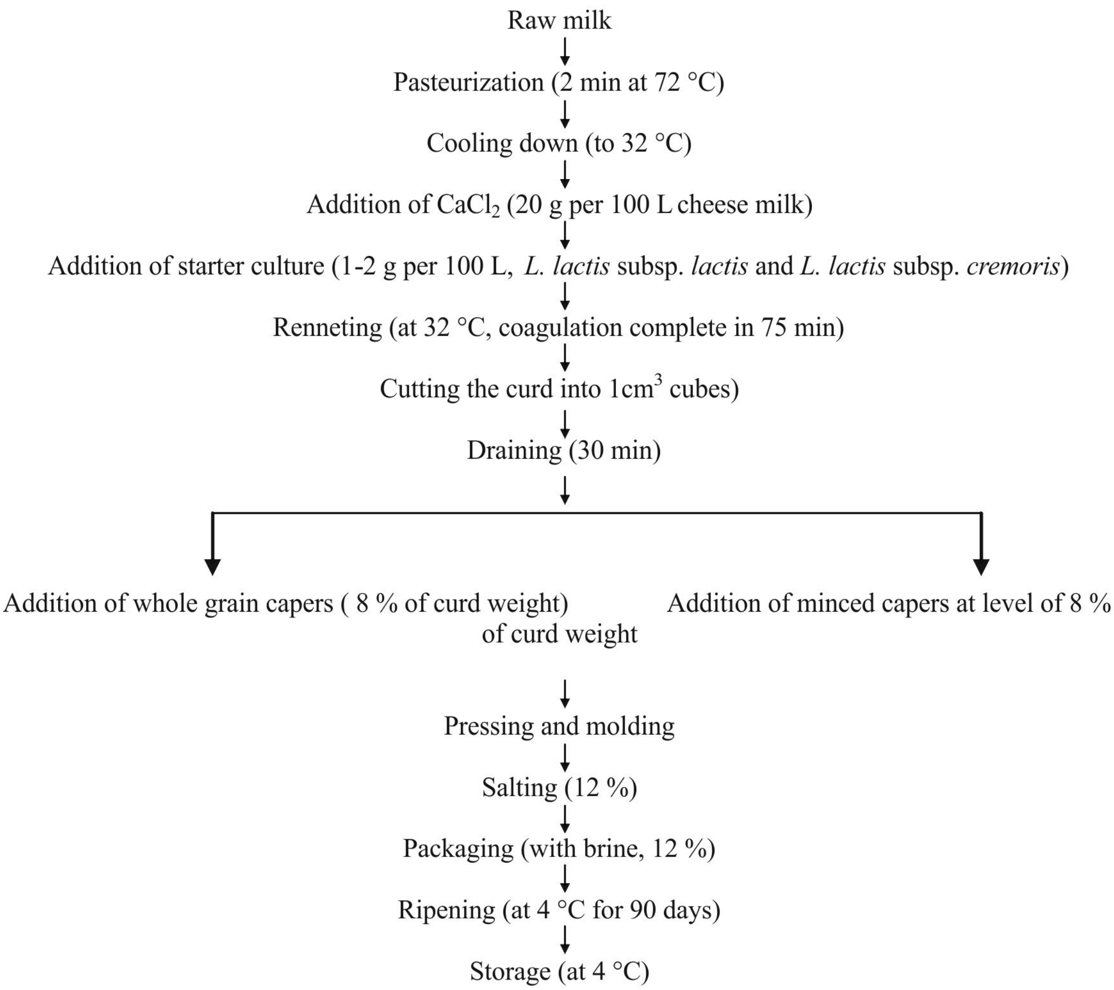

Figure 1. Manufacture of White Cheese with caper

2001), pH by the combined electrode Hanna 211 pH meter (Hanna Instruments Inc., Portugal), titratable acidity according to Anonymous (Anonymous, 2006). The total nitrogen (TN) was measured by the Kjeldahl method according to Gripon et al. (1975). Water soluble nitrogen (WSN) and non-protein nitrogen (NPN) were determined by the Kjeldahl method according to Anonymous (1980). Proteose-peptone nitrogen (PPN) was calculated by subtracting WSN from TN. The ripening index was estimated using the formula of WSN / TN x 100 (Venema et al., 1987).

Acid degree value (ADV)

The acid degree value (ADV) is an indicator of fat hydrolysis and was determined according to the method described by Renner (1993).

Free fatty acid analysis

Free fatty acid analyses of cheese samples were determined according to Paquot (1979) in TUBITAK Marmara Research Centre Food Institute Laboratory.

Tyrosine

Tyrosine was determined by using a spectrophotometer (722 Grating Spectrophotometer Analytical Instrument Factory, Shanghai) at a 650 nm wavelength according to the method described by Citti (1963).

Free amino acid analysis

Free amino acid analyses of cheese samples were determined according to Ozcan and Senyuva (2006) in TUBİTAK Marmara Research Centre Food Institute Laboratory.

Mineral analysis

Contents of calcium, manganese and potassium in cheese samples were determined according to the AOAC 985.35.2005a method. The content of Phosphorus analyses was determined according to the AOAC 986.24.2005b method. Zinc content of cheese samples was determined according to AOAC 999.10.2005c. All minerals analyses were performed in TUBİTAK Marmara Research Centre Food Institute Laboratory.

Statistical analysis

Statistical analysis of the data was performed using the analysis of variance in SPSS© v.9.05 (SPSS Inc., Chicago, USA). Means with significant differences were compared by the Duncan's multiple range tests. All analyses were performed in duplicate.

Results and discussion

Chemical properties

Mean values for pH, lactic acid, fat, dry matter, salt, salt in dry matter, and fat in dry matter throughout the ripening of cheese samples are presented in Table 1-2.

As presented in Table 1, there was a significant effect of storage on dry matter contents in cheese samples ($p<0.05$). Also, when compared to the control group, caper addition as whole grain had a significant effect on the dry matter contents ($p<0.05$). While an increase was observed in the dry matter content of the control sample after 30 and 90 days of ripening, a decrease was observed in the sample with whole grain caper. During the ripening process, peptide ties in the αS1- casein are being destructed and new ionic groups are formed. These ionic groups play an important role in binding the water in the brine and influence the increase in the water absorption capabilities of proteins during the storage at low temperatures which causes a decrease in the dry matter contents of cheeses (Tzanetakis et al., 2002; Sarantinopoulos et al., 2002; Gursoy and Kinik, 2010). Dry matter contents and changes in the cheese samples during ripening are in agreement with results of other researchers (Sarantinopoulos et al., 2002; Hayaloglu (2003), Gursoy and Kinik (2010), Karaman (2005), Kesenkas and Akbulut (2008).

While the fat content of the control sample increased during ripening, the fat contents of samples with caper addition decreased. Since dry matter contents change during ripening in brine, the composition of cheese might also change (Kesenkas and Akbulut, 2008). Therefore, components such as fat and salt were evaluated based on their ratios within the dry matter (Anonymous, 2006). The effect of storage was statistically significant ($p<0.05$) in relation to fat contents in the dry matter hence the fat ratio in the dry matter with minced caper decreased,

Table 1. Changes in chemical composition of cheeses during storage

Cheese	Ripening (Days)	pH	Lactic acid (%)	Fat (%)	Dry Matter (%)	Salt (%)	Salt (Dry Matter Basis) (%)	Fat (Dry Matter Basis) (%)
C	1	5.23 ± 0.04^{dX}	0.67 ± 0.05^{aY}	23.00 ± 1.41^{aY}	45.55 ± 0.07^{aY}	3.52 ± 0.06^{aZ}	7.74 ± 0.06^{aZ}	51.50 ± 0.00^{aZ}
	30	5.13 ± 0.04^{bZ}	0.88 ± 0.04^{bX}	24.00 ± 0.00^{bX}	45.80 ± 0.07^{aX}	3.84 ± 0.05^{bZ}	8.39 ± 0.05^{bZ}	52.34 ± 0.00^{bY}
	60	4.93 ± 0.04^{cZ}	1.00 ± 0.01^{cX}	24.00 ± 0.00^{bX}	43.33 ± 0.04^{cY}	4.42 ± 0.04^{cZ}	10.22 ± 0.10^{cZ}	55.43 ± 0.00^{dY}
	90	4.78 ± 0.04^{aY}	1.09 ± 0.01^{dX}	24.00 ± 1.41^{bX}	43.87 ± 0.04^{bY}	4.50 ± 0.03^{dZ}	10.27 ± 0.04^{dZ}	54.74 ± 0.00^{cY}
W	1	5.13 ± 0.39^{bZ}	0.81 ± 0.13^{aX}	23.00 ± 0.02^{cY}	43.84 ± 2.39^{aZ}	4.62 ± 0.05^{aX}	10.58 ± 1.51^{aY}	53.28 ± 8.53^{cY}
	30	5.63 ± 0.39^{aX}	0.85 ± 0.18^{aY}	22.00 ± 0.04^{bY}	39.72 ± 0.66^{Bz}	4.67 ± 0.02^{bY}	11.78 ± 1.05^{bY}	55.34 ± 6.21^{bX}
	60	5.13 ± 0.11^{bY}	0.88 ± 0.22^{aY}	21.00 ± 0.00^{aZ}	38.51 ± 3.71^{cZ}	5.17 ± 0.00^{cY}	13.43 ± 1.29^{cX}	56.00 ± 3.55^{aX}
	90	5.18 ± 0.11^{bX}	0.86 ± 0.26^{aY}	21.00 ± 0.00^{aZ}	38.39 ± 3.08^{cZ}	5.48 ± 0.04^{dY}	14.29 ± 0.24^{dX}	55.80 ± 3.11^{aX}
M	1	5.20 ± 0.28^{bY}	0.69 ± 0.07^{aY}	26.00 ± 0.06^{dX}	46.64 ± 1.89^{aZ}	4.46 ± 1.51^{aX}	9.57 ± 0.77^{aX}	55.56 ± 9.89^{aX}
	30	5.43 ± 0.25^{aY}	0.70 ± 0.09^{aZ}	24.00 ± 0.05^{cX}	44.17 ± 0.61^{bY}	5.58 ± 0.05^{bX}	13.25 ± 1.31^{bX}	55.52 ± 8.77^{aX}
	60	5.20 ± 0.07^{bX}	0.72 ± 0.13^{aZ}	22.00 ± 0.02^{aY}	44.11 ± 2.79^{bX}	5.86 ± 0.04^{cX}	13.29 ± 0.59^{bY}	49.75 ± 3.30^{bZ}
	90	5.15 ± 0.21^{bX}	0.75 ± 0.24^{aZ}	23.00 ± 0.00^{bY}	45.13 ± 0.61^{cX}	5.78 ± 0.02^{dX}	12.81 ± 1.48^{cY}	50.12 ± 3.63^{bZ}

C: control, W: whole grain caper, M: minced caper
X,Y,Z,T: Values with the same capital letters in the same column for each analysis differ significantly (P<0.05)
a,b,c,d: Values with the same lower-case letters in the same row differ significantly (P<0.05)

while it slightly increased in the control sample and the sample with whole grain caper.

Salt content in a dry matter of samples increased during storage and it was higher in samples with caper than in the control sample (p<0.05). It is obvious that this difference relays on the use of pickled capers. The effect of storage on the salt content in the dry matter was statistically significant (p<0.05) in all of the tested cheese samples. Since salt is water soluble, it's content is highly affected by the amount of water in the cheese or in other words, by the dry matter ratio. Differences between the dry matter contents most probably also affected the penetration of salt into cheese. Thus, the salt content in cheese can be defined as "salt in dry matter". Therefore, differences among the cheeses and the changes during storage were found significant (p<0.05). The high ratios of salt contents measured in this study were observed in other studies on white pickled cheeses as well (Gonc and Gahun, 1982; Kinik, 1987). Such findings were probably influenced by factors like the cheese brining, the temperature during brining process; the salt ratio of packaging brine; the acidity of cheese and brine; the composition of cheese and the size of molds (Kinik, 1987; Gursoy et al., 2001; Kesenkas and Akbulut, 2008; Gursoy and Kinik, 2010).

While the effect of storage period on pH change in the control sample was significant (p<0.05), it was insignificant in cheeses with caper addition (p>0.05). In comparative examinations among cheese samples, average pH values of cheeses with whole grain caper and minced caper were found close but that of control sample was lower (p<0.05). The pH levels of cheeses with caper addition were lower probably due to the acidity originating from caper brine. Studies on pickled cheeses have reported that pH value of cheeses changed depending on the type and amount of the starter culture, the ripening duration, the temperature and garnishes added during the cheese making process (Gardiner et al., 1998; Corbo, 2001; Hannon et al., 2003; Hayaloglu, 2003).

There was a statistically significant (p<0.05) effect of storage on lactic acid percentages in the control sample whereas it was insignificant for the samples with capers (p>0.05). Addition of whole grain caper and minced caper showed a statistically significant influence (p<0.05) on acidity development in cheese samples In ripening period of cheese, lactic acid metabolism; formation of base by-products such as ammonia and carbonyl and final products of amino acid catabolism were found interrelated (Gursoy et al., 2000). While acidity development of the control sample showed similarities to those of other studies, it was slower in samples with caper which led us to consider probability of a suppressing capacity of caper on acid bacteria.

Changes in total nitrogen amounts of control samples during storage was found statistically insignificant ($p>0.05$), but it was significant in samples with caper ($p<0.05$). While total nitrogen decreased in the control sample and in sample with whole grain caper during storage, it slightly increased in the sample with minced caper until 60th day and decreased from then on.

Total nitrogen and protein contents of sample cheeses probably increased due to additions of caper ($p<0.05$). The highest total nitrogen and protein content was measured in the sample with minced caper and it was followed by the sample with whole grain caper and finally the control sample. According to the literature, fruit of caper contains 24 % protein (Sessiz et al., 2007). This high ratio resulted in increase in total nitrogen and protein contents of cheeses. Protein ratio of the control sample remained almost unchanged during the storage period, while it increased and reached the maximum on the 60th day of storage in the sample with minced caper. Proteolysis is the most complex and perhaps the most important primary biochemical process during ripening of most cheese varieties (Barać et al., 2013). Decrease in protein contents depending on the decrease in total nitrogen can occur due to tendencies of peptides and amino acids with low molecular weights to be infused in the brine which emerges from the enzymatic proteolysis of casein (Gursoy and Kinik, 2010). Tyrosine content belongs to one of the indicators which is often used for identifying proteolysis degree in cheese. In this study there was a statistically significant ($p<0.05$) effect of storage on the amount of tyrosine in the control sample. However, it was insignificant in samples with caper addition ($p>0.05$). The increase in proteolysis, especially in the control group, most probably resulted from the autolysis of starter culture at final phases of the ripening period (Gursoy and Kinik, 2010; Collins et al., 2003).

Table 2. Proteolysis parameters of cheeses during ripening

Cheese	Ripening (Days)	TN (%)	Protein (%)	WSN (%)	NPN (%)	PPN (%)	RI (%)	ADV (%)	Tyrosin (mg per g)
C	1	1.97 ± 0.01^{aZ}	12.57 ± 0.01^{aZ}	0.15 ± 0.02^{aX}	0.13 ± 0.07^{dZ}	0.02 ± 0.00^{cZ}	7.56 ± 0.08^{aZ}	1.33 ± 0.10^{aX}	1.38 ± 0.01^{dZ}
	30	1.97 ± 0.01^{aZ}	12.57 ± 0.00^{aZ}	0.30 ± 0.02^{bY}	0.22 ± 0.01^{cY}	0.08 ± 0.00^{aY}	15.22 ± 0.02^{bY}	1.38 ± 0.03^{abX}	3.16 ± 0.03^{aY}
	60	1.96 ± 0.00^{aY}	12.50 ± 0.00^{aY}	0.41 ± 0.02^{cY}	0.33 ± 0.07^{bX}	0.08 ± 0.00^{aZ}	20.91 ± 0.02^{cX}	1.51 ± 0.05^{bX}	2.66 ± 0.03^{bZ}
	90	1.96 ± 0.00^{aY}	12.50 ± 0.00^{aY}	0.52 ± 0.06^{dY}	0.47 ± 0.01^{aY}	0.05 ± 0.00^{bZ}	26.52 ± 0.02^{dX}	1.54 ± 0.00^{bX}	1.94 ± 0.02^{cZ}
W	1	2.87 ± 0.10^{aY}	18.31 ± 0.01^{aY}	0.29 ± 0.06^{bY}	0.16 ± 0.01^{cY}	0.13 ± 0.00^{bY}	9.76 ± 0.08^{aY}	1.22 ± 0.00^{aY}	3.16 ± 0.91^{bY}
	30	2.17 ± 0.69^{bY}	13.84 ± 0.69^{bY}	0.34 ± 0.05^{cY}	0.21 ± 0.01^{bY}	0.14 ± 0.01^{bX}	15.67 ± 0.03^{bY}	1.33 ± 0.00^{bY}	2.90 ± 1.89^{cZ}
	60	1.96 ± 0.40^{cY}	12.50 ± 0.40^{cY}	0.40 ± 0.05^{aY}	0.25 ± 0.02^{aY}	0.16 ± 0.01^{bX}	20.41 ± 0.04^{cY}	1.40 ± 0.00^{cY}	4.37 ± 3.42^{aY}
	90	1.81 ± 0.58^{dZ}	11.55 ± 0.58^{dZ}	0.52 ± 0.32^{dY}	0.28 ± 0.00^{aZ}	0.24 ± 0.00^{aX}	28.73 ± 0.04^{dX}	1.54 ± 0.00^{dX}	4.43 ± 2.38^{aX}
M	1	$2.66\pm0.20_{cX}$	16.97 ± 1.26^{dX}	0.56 ± 0.01^{aZ}	0.33 ± 0.01^{cX}	0.24 ± 0.01^{aX}	21.05 ± 0.01^{aX}	1.28 ± 0.07^{aZ}	4.04 ± 2.31^{bX}
	30	$3.07\pm1.20_{bX}$	19.59 ± 7.97^{cX}	0.56 ± 0.01^{aX}	0.41 ± 0.01^{bX}	0.15 ± 0.00^{bX}	18.24 ± 0.03^{cX}	1.33 ± 0.10^{abZ}	4.19 ± 1.17^{bZ}
	60	$3.50\pm0.00_{aX}$	22.33 ± 0.00^{aX}	0.58 ± 0.10^{aX}	0.37 ± 0.01^{bX}	0.12 ± 0.01^{cY}	16.57 ± 0.00^{dZ}	1.47 ± 0.10^{abZ}	6.18 ± 0.85^{aX}
	90	3.43 ± 0.10^{aX}	21.89 ± 0.63^{bX}	0.60 ± 0.00^{aX}	0.53 ± 0.01^{aX}	0.08 ± 0.01^{dY}	17.55 ± 0.06^{bZ}	1.54 ± 0.00^{bX}	3.64 ± 3.30^{cY}

C: control, W: whole grain caper, M: minced caper, TN: total nitrogen, WSN: water-soluble nitrogen,
NPN: non-protein nitrogen, PPN: proteose-peptone nitrogen, RI: ripening index, ADV: acid degree value
X,Y,Z,T: Values with the same capital letters in the same column for each analysis differ significantly ($P<0.05$)
a,b,c,d: Values with the same lower-case letters in the same row differ significantly ($P<0.05$)

Table 3. Mean free fatty acid composition (%) of cheese samples during 90 days of ripening

Fatty acids	C					W					M				
	1	30	60	90	Av	1	30	60	90	Av	1	30	60	90	Av
C4:0	2.638	2.584	2.489	2.417	2.532	2.421	2.306	2.421	2.340	2.372	2.507	2.408	2.200	2.414	2.382
C6:0	1.945	1.899	1.853	1.797	1.873	1.708	1.801	1.877	1.839	1.806	1.930	1.897	1.770	1.868	1.866
C8:0	1.220	1.202	1.183	1.154	1.189	1.258	1.199	1.254	1.238	1.237	1.268	1.258	1.195	1.244	1.241
C10:0	2.614	2.595	2.583	2.524	2.579	2.851	2.795	2.839	2.833	2.830	2.866	2.853	2.774	2.843	2.834
C11:0	0.167	0.140	0.267	0.258	0.208	0.164	0.155	0.070	0.101	0.123	0.165	0.162	0.156	0.165	0.162
C12:0	2.885	2.569	2.870	2.85	2.793	3.219	3.220	3.254	3.254	3.237	3.230	3.231	3.200	3.248	3.227
C13:0	0.116	0.106	0.139	0.107	0.177	0.119	0.118	0.117	0.116	0.119	0.116	0.115	0.126	0.116	0.118
C14:0	10.138	11.182	10.194	10.330	10.461	10.784	10.902	10.931	10.961	10.895	10.812	10.849	10.880	10.939	10.870
C14:1	1.496	1.487	1.487	2.225	1.674	1.529	1.505	1.498	1.493	1.506	1.522	1.504	1.483	1.505	1.504
C15:0	1.157	1.158	1.181	1.181	1.169	1.160	1.170	1.176	1.187	1.173	1.159	1.173	1.182	1.164	1.170
C15:1	0.355	0.368	0.379	0.375	0.369	0.349	0.349	0.377	0.360	0.359	0.359	0.347	0.355	0.352	0.353
C16:0	29.168	29.462	29.507	30.109	29.561	30.497	31.085	30.905	31.164	30.913	30.585	30.827	31.108	31.021	30.885
C16:1	2.007	1.998	1.989	1.951	1.986	1.943	1.906	1.897	1.904	1.913	1.926	1.918	1.910	1.905	1.915
C17:0	0.723	0.734	0.736	0.750	0.736	0.706	0.719	0.713	0.718	0.714	0.711	0.716	0.723	0.7145	0.716
C17:1	0.523	0.522	0.482	0.508	0.509	0.532	0.479	0.487	0.472	0.493	0.492	0.481	0.480	0.471	0.481
C18:0	9.950	10.144	10.177	10.642	10.230	9.712	10.050	9.861	9.993	9.904	9.756	9.877	10.105	9.912	9.913
C18:1n9t	0.867	0.866	0.842	0.863	0.859	0.822	0.886	0.916	0.893	0.879	0.842	0.870	0.863	0.895	0.868
C18:1n9c	24.849	24.696	24.675	23.923	24.536	22.444	22.339	22.024	22.081	22.222	22.600	22.428	22.424	22.169	22.405
C18:2n6t	0.420	0.417	0.415	0.319	0.393	0.410	0.417	0.427	0.391	0.411	0.417	0.393	0.418	0.389	0.404
C18:2n6c	2.181	2.155	2.150	11.086	4.393	2.167	2.079	2.085	2.080	2.103	2.125	2.101	2.092	2.076	2.099
C20:0	0.142	0.142	0.137	0.154	0.144	0.141	0.148	0.177	0.146	0.153	0.143	0.145	0.146	0.148	0.146
C18:3n3	0.203	0.199	0.194	0.193	0.197	0.200	0.189	0.213	0.191	0.198	0.206	0.202	0.198	0.198	0.201
C20:1n9	0.492	0.491	0.488	0.468	0.485	0.474	0.458	0.518	0.459	0.477	0.468	0.468	0.462	0.462	0.465
C20:3n3	0.109	0.106	0.101	0.102	0.104	0.105	0.106	0.111	0.107	0.107	0.111	0.106	0.104	0.103	0.106
C21:0	0.033	0.000	0.052	0.030	0.029	0.030	0.031	0.048	0.015	0.031	0.031	0.027	0.030	0.000	0.022
C22:0	0.069	0.027	0.053	0.068	0.054	0.031	0.049	0.050	0.032	0.041	0.0328	0.047	0.032	0.033	0.036
C22:2	0.211	0.198	0.199	0.198	0.201	0.193	0.186	0.191	0.189	0.190	0.191	0.191	0.186	0.185	0.188

Av: average values
C: control. W: whole grain caper. M: minced caper

Findings in terms of the increase in the amount of tyrosine depending on proteolysis in different cheese types are confirmed by other studies such as Dinkci and Gonc (2000), Güven and Karaca (2001), Ozer et al. (2002), Gursel et al. (2003), Kesenkas and Akbulut (2008).

The content of water soluble nitrogen (WSN) during ripening was statistically significant ($p<0.05$) in the control sample and in the sample with minced capers, while it was insignificant in the sample with whole grain caper ($p>0.05$). No significant changes were observed in WSN values of the control sample. In samples with whole grain caper and minced caper WSN values decreased until 60^{th} day of ripening, while the highest values were obtained for both cheeses on the 90^{th} day. Comparative examinations showed that the sample with minced caper had the highest WSN value on the 90^{th} day of ripening. The WSN value for both, the control sample and the sample with whole grain caper, were the same.

The protease-peptone nitrogen (PPN) that constitutes the coagulated part of WSN together with 12 % trichloroacetic acid (TCA) is used for evaluation of ripeness in cheese. PPN changes in cheese samples were statistically significant ($p<0.05$).

In defining ripeness levels of cheese samples, a correlation factor obtained from the ratio of WSN to total nitrogen (TN) was used. Changes in ripening indexes of all cheese samples during ripening were statistically significant ($p<0.05$). The amount of WSN, which is accepted as an indicator of ripening, might differ depending on the TN and humidity of cheeses (Gursoy and Kinik, 2010). Results obtained in this study showed similarities to those of Ozer et al. (2002), Gursel et al. (2003), Karaman (2005), Oner et al., 2006, Kesenkas and Akbulut (2008), Gursoy and Kinik (2010).

During the ripening of cheese, a certain amount of present fat undergoes the hydrolysis. Among the hydrolytic products, volatile fatty acids like butyric, caproic, caprylic and capric acids, belong to the most important ones. Considerable amounts of acetic and propionic acids are fromed during hydrolysis of fat and fermentation of lactate. Free fatty acids, with 4-16 carbon atoms have considerable effect on aroma of the cheese (Ayar and Akyuz, 2003). There was a statistically significant ($p<0.05$) effect of storage on the percentage of free fatty acids in this study. Total free fatty acids content expressed as ADV increased during ripening in all cheese samples, which occurred probably due to lipolysis originating from microbiological activity. Also, in all cheese samples similar values of free fatty acid contents, or ADV, were detected at the early stages of storage. However on the final day of storage, the total free fatty acid values of all cheese samples were equal (1.54 %). The increase in total free fatty acid content through the ripening period in different cheese types was also reported by Georgala et al. (1999), Dinkci and Gonc (2000), Katsiari et al. (2000), Mallatou et al. (2003), Georgala et al. (2005), Kesenkas and Akbulut (2008).

Free fatty acid composition

Free fatty acid compositions of all samples are presented in Table 2. Among the saturated fatty acids (SFA), the most abundant was palmitic acid (C16:0), followed by myristic acid (C14:0) and stearic acid (C18:0). Oleic acid (C18:1) content predominated and was the highest among the total unsaturated fatty acids (TUFA). These results were not significantly different among the samples.

From results presented in Table 3 it can be observed that fatty acid contents were very similar between samples produced without and with capers. In addition, the ratio of fatty acids to the total amount did not change significantly during ripening. Butyric acid (C4:0) is known as a fatty acid with capabilities that have effect on rancid taste formation in cheese types ripened in brine (Georgola et al., 1999). When compared to the control sample, cheese samples with caper had lower butyric acid contents. In lots of cheese types similar to White Cheese, acids such as, butyric, caproic (C6:0) and caprilic (C8:0) are reported to be indicators of lipolytic activities caused by the starter (Akalin et al., 1998). The results concerning ADV contents in this study also support such findings.

As shown in Table 3, ratios of capric (C:10), lauric (C:12) and miristic (C14:0) acids of cheese samples with caper addition were higher in comparison to the control sample. The above quoted results mentioned related to fatty acids content are relatively higher than those obtained by Kesenkas (2005). Also, as presented in Table 2, among the long chained fatty acids (C:16-C:20) palmitic acid (C16:0) had the highest proportion within the

Table 4. Mean free amino acid composition (%) of cheese samples ripened for 90 days (average values)

Amino acids	C					W					M				
	1	30	60	90	Av	1	30	60	90	Av	1	3	60	90	Av
Ala	5.29	5.88	8.66	11.93	7.94	3.85	3.76	6.36	8.90	5.72	5.47	5.59	4.19	8.63	5.97
Arg	1.06	0.55	0.49	0.44	0.64	1.33	1.10	1.36	1.02	1.20	1.01	1.28	1.12	2.34	1.44
Asn	2.62	9.60	4.03	3.63	5.05	3.68	5.61	11.38	15.57	9.06	5.16	8.87	7.20	8.03	7.32
Asp	3.21	3.26	2.29	2.63	2.85	3.02	3.54	4.99	6.10	4.41	3.13	3.47	4.54	3.85	3.75
Cys	2.28	7.38	9.22	6.91	6.45	2.27	4.10	8.55	6.43	5.34	3.07	5.58	3.17	10.85	5.67
C-c	4.19	4.80	5.29	3.88	4.54	3.90	4.73	2.43	1.65	3.18	2.68	4.22	2.39	3.89	3.30
Gln	1.37	0.02	0.02	0.02	0.34	0.02	0.02	0.02	0.02	0.02	0.17	0.02	0.02	0.02	0.06
Glu	1.09	1.28	1.26	1.58	1.30	0.95	1.07	1.22	1.50	1.19	0.64	1.25	0.50	1.26	0.91
Gly	0.86	1.98	2.46	3.45	2.19	0.77	1.15	2.32	3.38	1.91	0.95	1.50	1.22	3.34	1.75
His	1.28	2.01	2.08	2.27	1.91	1.13	1.29	2.43	3.25	2.03	0.83	1.90	1.42	3.10	1.81
Hyp	0.89	0.51	0.68	0.79	0.72	0.76	0.50	0.50	0.51	0.57	1.06	0.72	0.35	0.44	0.64
Leu-ile	2.87	14.96	19.86	27.98	16.42	5.52	8.90	21.21	31.08	16.68	6.82	12.08	11.15	28.74	14.70
Lys	4.15	24.23	16.85	22.45	16.92	12.62	18.77	32.69	52.86	29.24	17.77	23.31	25.41	51.52	20.50
Met	1.22	5.64	7.06	9.70	5.91	1.79	3.46	7.67	10.71	5.91	2.69	4.88	5.21	10.16	5.75
Phe	4.72	19.69	28.06	34.46	21.73	7.35	11.94	25.15	28.99	18.36	9.72	17.10	15.43	27.73	17.50
Pro	2.80	7.67	7.85	10.63	7.24	3.84	5.89	12.37	17.81	9.98	4.71	6.64	7.14	14.28	8.19
Ser	1.21	4.18	3.77	3.01	3.04	1.22	2.34	3.19	3.85	2.65	1.81	3.06	2.93	3.98	2.95
Thr	1.00	3.21	3.69	5.71	3.40	0.87	1.60	3.88	6.09	3.11	1.45	2.41	2.40	5.17	2.86
Trp	0.21	2.04	2.49	2.87	1.90	0.36	1.13	2.47	2.94	1.73	0.72	0.61	1.20	3.41	1.49
Val	2.30	10.89	16.03	22.68	12.98	4.34	6.69	14.54	22.83	12.10	5.57	8.73	7.53	19.50	10.33

C: control. W: whole grain caper. M: minced caper. Av: avarage values
Ala: alanine. Arg: arginine. Asn: asparagine. Asp: aspartic acid. Cys; cycteine. C-c: Gln: glutamine. Glu: glutamic acid. Gly: glycine. His: histidine. Hyp: Hydroxyproline. Leu-ile: leucine-isoleucin. Lys: lysine. Met: methionine. Phe: phenylalanine. Pro: proline. Ser: serine. Thr: threonine. Trp: tryptophan. Val: valine

total fatty acid content and varied between 29.561-30.913 %. When samples were compared in terms of palmitic acid contents, samples with caper addition had higher values than control samples while the highest value was measured in the sample with whole grain caper addition (30.913 %). No significant difference was detected between the samples with minced and whole grain caper addition. Following palmitic acid, the second highest fatty acid content was detected for oleic (C18:1n9c) and stearic acid (C18:0). The average ratio of palmitoleic acid (C16:1), which is reported to indicate the level of lipolysis and to even cause defects in taste and aroma, within the composition of fatty acids varies between 1.913 and 1.986 %. Another important fatty acid in the total fatty acids composition is linoleic acid (C18:2 cis-9.12) and it varied from 2.099 % to 4.393 %. When compared to the control samples, caper added samples had lower linoleic acid contents.

The composition of fatty acids in cheese samples with caper addition also showed some similarities to of the control sample. The amount of fatty acids such as butyric (C4:0), caprolic (C6:0), caprilic (C8:0), which are the indicators of the starter-dependant lipolytic activity, were almost identical in samples with and without caper addition. This is may indicate that caper addition does not encourage lipolytic activity. Palmitoleic fatty acid, which indicates the level of lipolysis in cheese and causes defects in cheese taste and aroma, was also found in similar amounts in samples with and without caper addition. The content of palmitic acid (C16:0) was higher in samples with caper than in the control sample. Contrary to that, oleic (C18:1 cis-9.12) and stearic (C18:0) acid contents were higher in the control sample.

Free amino acid composition

The content and ratio of FAAs significantly influenced the texture and sensory characteristics of cheese. The relationship between the release of amino acids and the flavour formation in cheese has been assumed by many researchers. Amino acids may contribute to flavour either directly or indirectly by serving as precursors for volatile aroma compounds such as aldehydes, acids, alcohols, esters and sulphur compounds (Eren-Vapur and Ozcan, 2012).

Free amino acid contents in cheese samples with caper and the control sample and changes during storage are presented in Table 4. The contents of free amino acids such as alanine, cysteine, glycine, threonine and valine were high in the control sample, while the contents of arginine, asparagine, aspartic acid, lysine and proline levels were high in samples with caper addition. In general, tryptophane contents in all cheese samples increased during storage. Threonine and tryptophan content ratios were the highest in the control sample (Table 4). The contents of leucine and isoleucine were the highest in the sample with grain caper addition, and were followed by the sample with minced caper and the control sample respectively. Valine is mostly found in food products of animal origin. The highest content was detected in the control sample and showed an increasing trend during storage. Lysine, limited in vegetative nutriments but abundant in animal based food (meat, milk, egg), is an important amino acid for human health. While it was detected in quite high amounts in samples with whole grain capers, the content was quite low in the control sample. Similarly to other analysed free amino acids, lysine content also increased during storage.

The highest content of histidine, which exists together with arginine and lysine within globulin structure, was detected in the sample with grain capers and was followed by the control sample and the one with minced caper respectively. The highest amount of arginine, which constitutes 87 % of protamines, was detected in the sample with whole grain capers. While a decrease of arginine was observed in the control sample and the sample with whole grain capers, an increase was observed in the sample with minced capers. Alanine is present in almost all proteins. There is a number of aliphatic and aromatic amino acids are substitution products of alanine. As presented in Table 4, the highest average level of alanine content was detected in the control sample and showed an increase during storage. Asparagine content in the control sample decreased during storage, while it increased in samples with caper addition. According to the average values, the highest asparagine content was detected in the sample with grain caper and was followed by the sample with chopped/minced caper and the control sample. Cystine was found in highest amounts in the control sample and was followed by the sample with minced caper and the one with whole grain caper respectively. Proteins containing cysteine are not destructed easily. Glycine is very important amino acid since it is not available in most proteins and is taking part in disposal of toxic substances out of the body. The contents of glycine increased in all samples during storage and were the highest in the control sample. The highest proline content was measured in the sample with grain capers. Proline contents of samples with caper addition were higher than in the control sample. Serine contents of experimental cheeses varied between 2.65 g / kg and 3.04 g / kg, while the highest content was detected in the control sample. Similar results were obtained by Eren-Vapur and Ozcan (2012).

Mineral substances

Variations in the calcium, potassium, zing, manganese and phosphorus contents of cheese samples are presented in Table 5.

There was a statistically significant ($p<0.05$) effect of storage on the calcium content in the tested cheese samples. Referring to the obtained average values, calcium content of the control sample was higher in comparison to the samples with caper addition. While calcium contents decreased in the samples with whole grain and minced caper during storage, it increased in the control sample (Table 5). Changes in calcium contents are most probably caused by transfers of minerals from/to brine and cheese (Kesenkas, 2005). Results obtained in this study were higher than those of Mendil (2006) and Karagozlu et al. (2008), but similar to those of Kilic et al. (2002). Thereby, it should be taken into consideration that calcium amounts in raw milk and cheese depend on the season, lactation, feeding and also on the use of $CaCl_2$ in different proportions in cheese making process and their origins as well.

Average phosphorous contents of cheese samples varied between 58.00 and 85.98 mg/kg and the highest phosphorous contents were measured on the 30th day of the storage. The effect of storage on phosphorous contents of cheese samples was statistically significant ($p<0.05$). Similar to calcium content

Table 5. Changes in mineral composition of cheeses during ripening (mg/1000 g)

Mineral elements	Ripening, days	C	W	M
Calcium	1	7530 ± 21.75^{bX}	6274 ± 513.71^{aZ}	7214 ± 605.28^{aY}
	30	6762 ± 21.76^{cX}	5523 ± 851.00^{bZ}	6265 ± 279.66^{bY}
	90	7893 ± 21.75^{aX}	5081 ± 1170.62^{cZ}	5716 ± 865.15^{cY}
	x±sd	**7062 21.75^{X}**	**5626 ± 873.35^{Z}**	**6398 ± 835.77^{Y}**
Phosphorus	1	34.71 ± 1.81^{aZ}	38.93 ± 36.37^{cY}	57.67 ± 26.45^{cX}
	30	123.05 ± 1.81^{cX}	83.73 ± 22.09^{aZ}	92.44 ± 3.92^{aY}
	90	100.19 ± 1.81^{bX}	51.35 ± 1.17^{bZ}	78.53 ± 5.09^{bY}
	x±sd	**85.98 ± 1.81^{X}**	**58.00 ± 28.11^{Z}**	**76.21 ± 19.82^{Y}**
Potassium	1	2148 ± 67.88^{bY}	1949 ± 346.48^{aZ}	2663 ± 387.14^{aX}
	30	1779 ± 0.00^{aZ}	1944 ± 368.40^{aY}	2530 ± 424.97^{bX}
	90	2273 ± 4.24^{cY}	2024 ± 20.15^{aZ}	2625 ± 223.45^{aX}
	x±sd	**2067 ± 231.73^{Y}**	**1972 ± 229.85^{Z}**	**2606 ± 282.52^{X}**
Zinc	1	30.44 ± 0.62^{aY}	29.78 ± 1.97^{aZ}	31.41 ± 12.76^{aX}
	30	30.98 ± 0.03^{aY}	27.65 ± 3.85^{aY}	28.28 ± 12.94^{aY}
	90	28.18 ± 025^{bY}	25.66 ± 2.40^{aY}	24.83 ± 21.00^{aY}
	x±sd	**29.87 ± 1.36^{X}**	**27.70 ± 2.88^{Z}**	**28.17 ± 64.51^{Y}**
Mangan	1	140.80 ± 1.13^{aZ}	283.63 ± 6.26^{aX}	206.58 ± 9.37^{aY}
	30	133.95 ± 1.34^{bY}	184.25 ± 21.07^{bX}	184.95 ± 12.94^{bX}
	90	99.99 ± 0.35^{cY}	164.33 ± 61.62^{cX}	162.40 ± 21.00^{cX}
	x±sd	**124.91 ± 19.69^{X}**	**210.74 ± 64.21^{Y}**	**184.64 ± 23.01^{Z}**

C: control. W: whole grain caper. M: minced caper
X,Y,Z,T: Values with the same capital letters in the same column for each analysis differ significantly ($P<0.05$)
a,b,c,d: Values with the same lower-case letters in the same row differ significantly ($P<0.05$)

results, phosphorus content was also the highest in the control sample and was followed by the samples with whole grain caper and the one with minced caper respectively. Such results probably origin from the lower phosphorus and salt content of the added capers in comparison to the phosphorus content of cheese. In the literature, phosphorus contents of white pickled cheeses varied between 314 and 519 mg per 100 g cheese (Ozdemir, 1990; Diraman and Demirci, 1998; Demirci, 1998; Kilic et al., 2002; Karagozlu et al. 2008). Also, Greek and Danish Feta cheeses, which have similar properties to Turkish White Cheese, had phosphorus contents varying between 377 and 392.06 mg per 100 g cheese (Vafopoulou-Mastroyannaki, 1977). Phosphorus values obtained in this study were lower than those of the above mentioned studies.

Average potassium contents of the cheese samples varied between 1972 mg per kg and 2606 mg per kg and the highest potassium content was detected in the sample with minced caper. The effect of storage on potassium contents was statistically significant ($p<0.05$) for all samples Kilic et al. (2002) reported potassium contents of their cheese samples between 1160-2859 mg/kg, which is almost identical to results obtained in this study. However, these were considerably different from the results obtained by Mendil (2006) and Karagozlu et al. (2008).

The effect of storage on zinc contents was also statistically significant ($p<0.05$) for all cheese samples. Zinc content of the control sample was higher than in the samples with caper addition. Mendil (2006) reported the zinc content of White Cheeses as; 12.0 ± 1.1 μg per g. Compared to the above presented values, zinc amounts detected in this study were higher.

Capers contain a certain amount of manganese which most probably caused the higher manganese contents in samples with caper addition when compared to the control sample. According to the results of the variance analysis and Duncan test, the effect of storage on manganese contents of cheeses was statistically significant ($p<0.05$).

Conclusion

In this study, effect of capper addition on some physical and chemical properties of White Cheese was investigated. In the overall composition, parameters of the tested cheeses were in compliance with the characteristics of white pickled cheese. Capper addition to cheese showed some negative effects to certain properties, while the chemical properties were improved, particularly the mineral content and the amino acid composition. In cheese making it is possible to make cheese with low salt content by using brine with low salt concentration. In samples with caper addition salt contents were higher than the values recommended by Standards for Turkish White Cheese. To decrease this high salt content, either brine with lower salt concentration or producing, pickled capers in brine with lower salt concentration could be considered. At the time this study was carried out, no publication on making cheese with capers was available. Evaluating the data that this study presents, making cheese with caper using different milks (sheep, goat) or with their mixtures could be suggested. In conclusion, we suggest conducting further research on improvement of making cheese with caper, considering the growing demand on flavoured cheese types in constantly growing functional food market.

Učinci dodanog kapara na neka fizikalno-kemijska svojstva bijelog sira

Sažetak

U ovom radu je istraživan učinak dodatka bobica kapara na neka fizikalno-kemijska i funkcionalna svojstva bijelog sira. Proizvedene su tri serije bijelog sira: kontrolna skupina bez dodatka kapara (C), skupina s dodatkom cijelog zrna (W) te skupina s dodatkom mljevenih kapara (M). Bobice kapara dodane su u sirnu kadu nakon rezanja u količini od 8 g na 100 g gruša. Tijekom zrenja u trajanju od 90 dana +4 °C izuzimani su uzorci bijelog sira te su praćene promjene kemijskog sastava, proteoliza (indeks zrenja), lipoliza (vrijednost kiselinskog stupnja), a određivan je udjel slobodnih aminokiselina, slobodnih masnih kiselina (FFAs) i nekih mineralnih tvari.

Prema rezultatima dobivenim statističkom analizom, u odnosu na kontrolni uzorak, značajna razlika dobivena je dodavanjem kapara u bijeli sir za udjel soli, mliječne kiseline i mineralnih tvari (p<0,05). Općenito, podaci iz istraživanja pokazali su da je dodavanje kapara u bijeli sir smanjilo neka svojstva vezana uz kvalitetu, ali su poboljšana određena fizikalno-kemijska svojstva.

Ključne riječi: sir, dozrijevanje, kapara, proteoliza, lipoliza

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