DYNAMIC OF PHYSICO-CHEMICAL PARAMETERS DURING RIPENING OF PECORINO CHEESE MADE FROM GOAT MILK

Sonja Srbinovska, Dushica Santa

Faculty of Agricultural Sciences and Food - Skopje, University Ss. "Cyril and Methodius" in Skopje, Republic of Macedonia

Corresponding author: ssrbinovska@fznh.ukim.edu.mk

Abstract

In this study, technological process and dynamic of the main characteristics of Pecroino cheese from goat milk are presented. Analyses were performed on 5th, 10th, 20th , 40th and 90th day of ripening. Pecorino on 90th day of the ripening contained 39.8±0.57% dry matter, 60.20±0,57% fat, 26.48±0.44% proteins (1,44±0.056% Soluble N, 0,94±0.068% Peptides N, 0,54±0.064 Amino Acid N), 4.60±0.20% salt, 1.76±0.09 lactic acid and pH 5.36 ±0.20%. The most dominant Free Amino Acid (FAA) in cheese was proline (Pro) with 159.61±0,55 mg $100g^{-1}$, then leucine (Leu) 143.71± 0,44 mg $100g^{-1}$ phenylalanine (Phe) 137.21± 0.54 mg $100g^{-1}$ and isoleucine (Ile) 131,22 ±0,32 mg $100g^{-1}$. Regarding the Free Fatty Acid, capric acid (C10:0) was most dominant (1.3241 mg $100g^{-1}$) and caprylic acid (C8:0) with 1.1210 mg $100g^{-1}$. Compared with other hard cheeses from cow or sheep milk, higher concentration of FAA and FFA in goat pecorino cheese was noticed. Intensive lypolitic and proteolytic process in this cheese is due to the specific content and enzymatic activity of the goat milk especially because of the higher content of capric acid and other short-chain fatty acids (SCFA).

Keywords: quality, composition, free amino acid, free fatty acid.

Introduction

Goat milk cheeses have distinctive flavor, mostly due to particular compounds, such as medium-chain Free Fatty Acids (McSweeney, 2017). Its composition varies according to milk origin (e.g., species and breed), rearing conditions (e.g., feeding and management), and cheese-making technology (e.g., coagulation process, addition of salt, ripening period) (Manuelian et al., 2017). The quality characteristics of goat milk give us a base to consider that goat cheese is closer to the composition on the cheese made from ewe's milk (Baltadzieva, 1985). Goats are highly suitable for milk production because they can yield up to 10 % of their weight in milk (400−1500 L per lactation) (Grille et al., 2013). In the last few years in Republic of Macedonia, there is an increasing popularity of the goat's milk and its products. The increased interest on the marketplace and the scientific community is consistent with the general trend and efforts for production of healthy food, since the goat's milk has been well known for its beneficial effects on human health (Srbinovska et al., 2001). Having in mind that in the last years there is a permanent tendency to increase the number of goats in our country, as well as the increased interest for production of goat cheeses, there is a necessity to find possibilities for its processing into the characteristic dairy products. There is an increase of popularity and consumption of cheeses produced from goat's milk. The flavor and aroma are the main properties that influence the selection of cheeses by the consumers. Cheese provides essential nutrients for human nutrition and health, such as minerals and fatty acids (FA). The process of ripening of various types of cheeses has the specific path, characterized mainly by changes of protein and milk fat. These changes determine the typical quality of the product. This has resulted in more interest in research on chemical composition and fatty and amino acids profile. In this direction, it also important to research the production of pecorino's cheese from goat milk.

Pecorino's cheese is made from ewe's milk. During the ripening process of Pecorino, in the same time proteolysis and lipolysis occurred resulting to specific aroma and taste. The aim of this study is to describe the technological process and dynamic of the main characteristics during ripening of Pecorino cheese made from goat milk. The Free Amino Acid (FAA) and Free Fatty Acid profile is also presented in this paper.

Material and methods

Cheese was produced from bulk goat milk in the "Milk Way" Dairy Plant in the Republic of Bulgaria. Chemical composition of cheese from 5 batches were analyzed on the 5th, 10th, 20th, 40th and 90th days of ripening. The cheese composition was analyzed by standard methods: dry matter (AOAC, 1995), fat ((Van Gulik (Inihov, 1971)), protein (Inihov, 1971), salt (Moor (Inihov,1971)), pH meter (Mettler Toledo, Spain) Free Amino Acids were analysed on Hd-1200E, method Martini Seideim, (Inihov, 1971) and Free Fatty Acid according the Demurov (cit in Dimitrov 1976) with gas chromatograph. FFA and FAA were analyzed in cheese on 30th, 60th and 90th days from the production. Analysis were performed on the Faculty of Agricultural Sciences and Food in Skopje and Food Institute in Plovdiv, Bulgaria. The production of Pecorino cheese was followed in cheese plant in Nova Zagora, Bulgaria.

Results and discussion

Technological procedure for manufacturing of Pecorino cheese is defined on Scheme 1. Goat milk is pasteurized on 65-68° C about 30 min. Than starter culture *St. lactis* is inoculated and the ripening of the milk starts in order to give the culture time to begin acid production before the rennet is added. After that, starter culture (0.15 % *St. termophilus, Lb helveticus, Lb. delbrueckii ssp bulgaricus),* $CaCl_2$ (0.015 %) and rennet are added. Coagulation takes 5 min on 34-35 ^{o}C and after the coagulation, the coagulum is cut into small granules with wheat grain size. The curd is cooked on 45-46 °C about 45-50 min. Then, the curd is moved to a draining vat and pressed. The titratable acidity of drained whey was 14-15^{0} T (0.126-0.135 g lactic acid). The cheese is salted with brine (21 $\pm$ 1 % NaCl, 48 hours). Duration of the ripening process takes 90 days on 12-14 °C, moisture 80-85 %, with dry salting till the 30th day.

Physicochemical characteristics

The results of the changes of the main parameters in Pecorino cheese during a ripening period of 90 days are given in Table 1.From the results, it can be seen that in the ripening process the moisture from 47.7 $\pm$ 0,61 % on the 5th day decreased to 39.8 $\pm$ 0.57 % on the 90th day. More intensive decreasing of moisture was noticed in the period from the 10th to the 20th day. The results of the acidity changes show a comparatively higher acidity at that time, thus the intensive reduction of the moisture in the same period.

The active acidity (pH) in the cheese increased during the period of cheese ripening and ranged from 5.14$\pm$0.04 at the beginning to 5.36$\pm$0.02 on the 90th day. The higher result on pH was reported by Marrone et al. (2014) on pecorino made from sheep's milk.

These changes in acidity are influenced by the fermentation of lactose and the depth of the proteolysis. In this type of cheese pH is increasing gradually, which shows that the proteolysis is moderate.

Similar findings that confirm our results are also presented by several authors who examined ripening process of hard cheeses (Litopoulou-Tsantaki et al., 1985; Terner and Tomas, 1980). The total fat in the cheese did not show significant changes during the ripening period, and at the end of the period it was 26.84$\pm$0.21, and the fat in dry matter was 44.58%. Results for the fat in dry matter are in accordance with the findings by Addis at al. (2015) on Pecorino Romano cheese. The content of the total proteins in the Pecorino cheese is comparatively high due to the low moisture content in the cheese on 90th days of ripening (26.48$\pm$0.44%). The soluble nitrogen is one of the indicators for proteolysis intensity in cheese. The content of water soluble nitrogen increased during the ripening

of the pecorino cheese and on the 5th day was 0.63±0.031%, on the 20th was 0.92± 0.054 and the 90th day reached to 1.44±0.056 (Table 2.) Peptides nitrogen gradually increased during ripening and at the end of ripening the concentration was 0.94±0.068.

Scheme 1. Technology process of Pecorino cheese made from goat milk

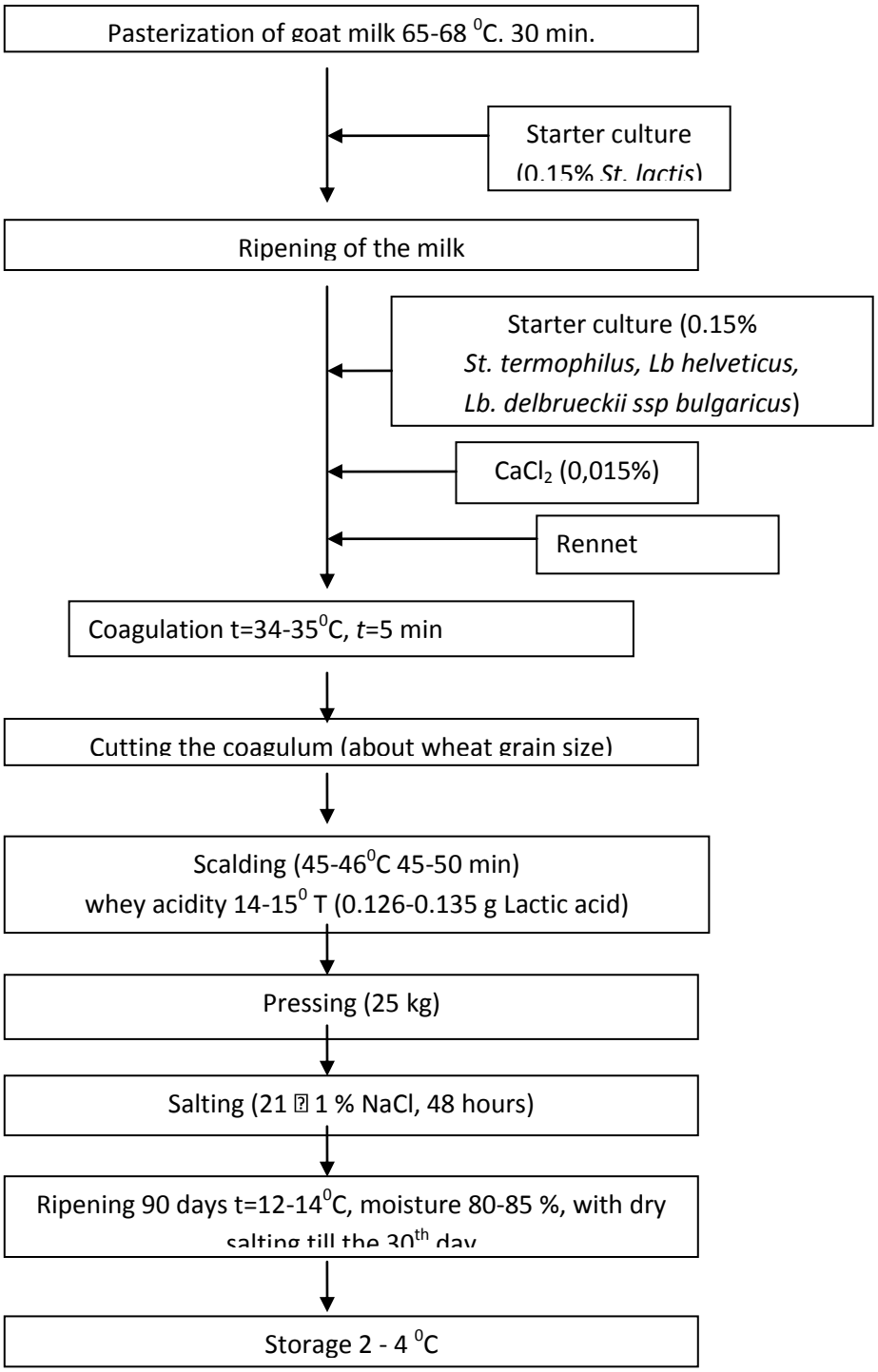

Table 1. Physicochemical characteristics of Pecorino cheese during ripening

Parameters	Ripening period (days)				
	5	10	20	40	90
Moisture %	47.68±0.61	45.34±0.49	42.48±0.72	41.15±0.88	39.80±0.57
Total solid %	52.32±0.61	54.66±0.49	57.52±0.72	58.85±0.88	60.20±0.57
Titratable acidity ^{o}T	206 ± 0.91	225 ± 0.94	220 ± 0.92	213 ± 1.10	196 ± 1.03
Lactic acid %	1.85±0.07	2.02±0.08	1.98±0.07	1.92±0.09	1.76±0.09
pH	5.14±0.04	5.17±0.05	5.19±0.04	5.25±0.01	5.36±0.02
Fat	26.85±0.60	26.40±0.71	27.10±0.31	27.20±0.53	26.84±0.21
Fat in dry matter %	51.30±1.32	48.29±1.41	47.11±0.97	46.22±1.01	44.58±0.95
Protein %	26.60±0.65	26.34±0.58	26.09±0.84	25.84±0.38	26.48±0.44
Protein in dry matter %	50.84±1.41	48.19±1.39	45.36±1.56	43.91±0.97	43.99±1.24
Salt %	3.06 ± 0.31	3.64 ± 0.16	3.65 ± 0.06	3.70 ± 0.07	4.60±0.20
Salt in dry matter	6.42±0.58	8.03±0.39	8.59±0.20	8.99±0.22	11.56±0.41

Table 2. Nitrogen fractions in goat Pecorino cheese

Parameters	Ripening period (days)				
	5	10	20	40	90
Total N, %	4.17 ± 0.36	4.13 ± 0.25	4.09 ± 0.32	4.05 ± 0.51	4.15 ± 0.17
Soluble N, %	0.63±0,031	0.81±0.042	0.92± 0.054	1.20±0.047	1.44±0.056
Peptides N, %	0.54±0.040	0.58± 0.053	0.62±0.048	0.86±0.053	0.94±0.068
Amino acid N, %	0.15±0.020	0.24±0.180	0.36±0.084	0.48±0.076	0.54±0.064

The content of Amino acid nitrogen also increased in the ripening process and the 5th day was 0.15±0,020, at 20th day increased for 2.4 times in the 90th day for 3.6 times. The participation of PN and AAN in soluble N can be significant parameters of proteolytic processes during cheese ripening. Also, they can describe «width», and especially «depth» of ripening. The participation of PN in soluble N was 65.28±3.02%, and AAN 37.50±2.21%, respectively, which give us a base to conclude that the protein degradation is more intensive in «width» than «depth» during the Pecorino cheese ripening.

Free amino acids

The profile of the Free Amino Acid (FAA) in Pecorino cheese made from goat milk is presented in Table 3. The most dominant FAA in cheese was proline (Pro) with 159.61±0.55 mg 100g^{-1}, then leucine (Leu) 143.71± 0.44 mg 100g-1, phenylalanine (Phe) 137.21± 0.54 mg 100g^{-1} and isoleucine (Ile) 131.22 ±0.32 mg 100g^{-1}. The total quantity of the essential amino acids at the end of the ripening was 652,82±0.98 mg 100g^{-1}, and on the non-essential amino acids 540.44±0.74 mg 100g^{-1}.Some of the amino acids were not detected, probably due to their transformation in the ripening process thus the occurrence of some amino acids later during ripening is explained by the selective action of the enzymes (Requena et al., 1992). Our results were slightly higher than the free amino acids determined in sheep's Pecorino analyzed by Gallistu, 1995, which is confirmed also by other authors who examined the amino acid profiles on cheeses produced from different animals than goats (Baltadzieva, 1985). Litopoulou-Tsanataki and Manolkidis (1985), comparing the content of the free amino acids in hard cheeses made from sheep, goat and cow's milk, determined the higher concentration of FAA in the goat's cheese, than sheep and cows cheese, which is explained by the increased enzymatic activity of goat milk.

Table 3. FAA profile of Pecorino cheese made from goat milk during ripening

FAA mg 100 g^{-1}	Ripening period (days)			
	15	30	60	90
Lysine	44.50 ± 0.23	57.6 ± 0.45	81.72 ± 0.13	89.21 ± 0.62
Histidine	9.40 ± 0.31	19.4 ± 0.32	32.1 ± 0.14	38.41 ± 0.32
Arginine	/	/	4.5 ± 0.12	7.42 ± 0.71
Threonine	/	/	/	18.41 ± 0.71
Valine	25.32 ± 0.41	/	42.71 ± 0.42	63.12 ± 0.37
Methionine	/	/	13.22 ± 0.54	24.11 ± 0.67
Isoleucine	31.12 ± 0.43	41.77 ± 0.23	83.73 ± 0.42	131.22± 0.32
Leucine	43.71 ± 0.36	58.45 ± 0.61	101.61 ± 0.12	143.71 ± 0.44
Phenylalanine	23.71 ± 0.27	31.66 ± 0.78	86.37 ± 0.19	137.21± 0.54
Total essential FAA	177.76±0.44	208.88±0.38	445.96±0.40	652.82±0.98
Aspartic acid	8.3 ± 0.23	12.2 ± 0.52	48.1 ± 0.33	68.21 ± 0.25
Serine	/	/	/	21.71 ± 0.21
Glutamic acid	39.6 ± 0.61	43.5 ± 0.62	101.21 ± 0.15	118.3 ± 0.41
Proline	32.17 ± 0.21	39.6 ± 0.31	143.12± 0.16	159.61± 0.55
Glycine	13.18±0.36	22.36±0.44	50.52±0.23	83.42 ± 0.71
Alanine	11.43± 0.21	19.44± 0.16	54.16± 0.71	89.19 ± 0.62
Cysteine	/	/	/	/
Tyrosine	/	/	/	/
Total non-essential FAA	104.68±0.29	137.10±0.52	397.11±0.39	540.44±0.74
Total	283.23± 0.31	350.4 ±0.62	853.21± 0.42	1201.2± 1.12

Free Fatty acids

From the results on 90th days of ripening, it can be seen that the highest concentration was determined on caprylic acid (1.3241 mg 100 g^{-1} and capric acid (1.1210 mg 100g^{-1}, followed by the butyric acid (0.8173 mg 100g^{-1}). Similar findings on dynamic and concentration of free fatty acids in semi-hard and hard goat cheese are also determined by other authors (Attaie and Richter, 1996; Ha and Landsay, 1991). It can be noticed from the results that lipolysis in this type of cheese occur with higher activity than other cheeses. It is assumed that micrococcus that are present in milk at the pasteurization regime of 65-68 °C which is applied in the production of this cheese, are also involved in the degradation of milk fat. In the Pecorino cheese milk, compared with other literature data, a higher amount of free fatty acids was found in relation to other hard cheeses obtained from cow's and sheep's milk (Baltadzieva 1985, Litopoulou-Tsanataki and Manolkidis, 1985). This is explained by the specific composition and properties of the fat in goat milk, which are characterized by the higher content of capric acid. Moreover, the fats are morebetter dispersed in the cheese, which allows a more active lipolytic process and a more active lipoprotein lipase in goat milk (Chilliard et al., 1984; Le Jaoven, 1990).

Table 4. FFA profile of Pecorino cheese made from goat milk during ripening

FFA mg 100 g^{-1}	Ripening period (days)		
	30	60	90
Acetic acid	0.0518	0.1628	0.1843
Propionic acid	0.0421	0.0073	0.0107
Isobutyric acid	0.0823	0.1623	0.2343
Butyric acid	0.4191	0.7300	0.8173
Isovaleric acid	0.5821	0.7321	0.8132
Pentanoic acid	0.0921	0.1362	0.1832
Caprylic	0.6731	1.2831	1.3241
Capric	0.5342	1.1831	1.1210

Conclusions

In this paper the technological process, dynamic of the main characteristics, FFA and FAA during ripening of Pecorino cheese made from goat milk are presented. The most dominant Free Amino Acid (FAA) in cheese was proline (Pro), then leucine (Leu), phenylalanine (Phe) and isoleucine (Ile). Regarding the Free Fatty Acid, capric acid and caprylic acid (C8:0) were most dominant. Compared with other hard cheeses from cow or sheep milk, higher concentration of FAA and FFA in goat pecorino cheese was noticed. Intensive lypolitic and proteolytic process in this cheese is due to the specific content and enzymatic activity of the goat milk especially because of the higher content of capric acid and other short-chain fatty acids (SCFA).

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