

## COMPARATIVE STUDY OF BULGARIAN WHITE BRINED CHEESE FROM COW AND BUFFALO MILK

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### Abstract

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Changes in the physicochemical and fatty acid composition in samples of white brined cheese from cow and buffalo milk were examined with a focus on their dynamics during ripening. Significant differences in the physicochemical composition of the samples tested were found, owing to the specific chemical composition of the raw materials. The chromatographic analysis revealed that the amount of saturated fatty acids in both varieties of white cheese accounted for approximately  $70 \text{ g} \cdot 100 \text{ g}^{-1}$  of the fatty matter, while the proportion of unsaturated fatty acids was about  $30 \text{ g} \cdot 100 \text{ g}^{-1}$ . The acid and peroxide values in both experimental cheese variants remained relatively stable throughout the study period, which is evidence of the low degree of hydrolysis and oxidation of the milk fat.

**Key words:** white brined cheese from cow and buffalo milk; physicochemical and fatty acid composition

**Abbreviations:** Bulgarian National Standard (BNS); white brined cheese (WBC)

### Introduction

In recent years, there has been a rapid increase in global cheese production. The reason is the better understanding and scientific evidence of the valuable nutritional and biological properties of cheese. The production and consumption of high quality dairy products with high protein and fat content are important prerequisites to balanced human nutrition (Borghese, 2005, 2004).

White brined cheese (WBC) is an original and traditional product for Bulgarian consumers, constituting the largest share of the total cheese production.

The main ingredients of milk – milk fat and protein content – are major components influencing the composition and characteristics in the manufacture of different types of cheese (Barron et al., 2001; Guinee et al., 2000; Lindmark-Manson et al., 2000, 2003).

Milk fat content in milk is an essential factor affecting the formation of flavour and aroma in ripening cheeses. Fat-

ty acids are closely involved in flavour formation in different types of cheeses and are important precursors for other volatile aromatic compounds in cheese (Khalid and Marth, 1996). Proteolysis of protein during ripening leads to formation of amino acids - precursors for catabolic reactions with formation of important volatile aromatics (Belitz et al., 2013; Fox et al., 2004; Katsiari et al., 2000a, 2000b; Mallou et al., 2005, 2004).

The aim of this study is to examine the changes in the major physicochemical parameters and in the fatty acid composition during ripening of white brined cheese made from cow and buffalo milk.

### Materials and Methods

The WBC samples tested were prepared using the traditional manufacturing technology under industrial conditions, following the requirements of the Bulgarian National Standard (BNS) 15-2010. For the purposes of the experiment,

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the ripening process was carried out at  $12 \pm 1^\circ\text{C}$  for 45 and 60 days for cow and buffalo cheese, respectively. The WBC samples were evaluated in terms of the following physicochemical parameters:

- acidity, according to BNS 1111-80;
- potentiometric pH;
- moisture content and dry matter, according to BNS 1109-80;
- total protein, according to BNS EN ISO 8968-1:2002;
- fatty content, according to BNS 1671-89;
- salt content, according to BNS 8274-82.

Fatty acid composition: determined by the method of Bligh and Dyer (1959). Methylation of fats was performed according to BNS ISO 5508:2000. The analysis of methyl esters was conducted on a SHIMADZU GC - 17A gas chromatograph (Shimadzu Corp., Kyoto, Japan).

Peroxide value of fat: determined by the method of Bligh and Dyer (1959). The iodometric method according to EN ISO 3960:2008 was used.

Acid value of fat: determined by the method of Bligh and Dyer (1959). The titrimetric method according to EN ISO 660:2009 was applied.

#### **Statistical analysis**

Computer processing of the results is performed using the program Microsoft Excel 2010 (ANOVA). Multiple comparisons are made by LSD method. The results are presented as mean value  $\pm$  SD ( $n=4$ ).

## **Results and Discussion**

The physicochemical composition of samples of white brined cheese from cow and buffalo milk after 45 and 60 days of ripening are presented in Table 1.

The results obtained indicated that on the first day of the ripening period the titratable acidity of cheese samples was

1.64 and 1.56 g.100g<sup>-1</sup> lactic acid, while the active acidity was 4.7 and 4.6 for the cow and buffalo milk cheese, respectively. During ripening, there was a constant upward trend in the above indicators, and at the end of the ripening period (day 45 and 60) the indicators reached acidity values of 2.39 and 2.45 g.100g<sup>-1</sup> lactic acid, and active acidity of 4.2 and 4.1, for cow and buffalo milk cheese, respectively. The change in the indicators correlated directly with the intensive fermentation processes during ripening.

The results obtained for acidity and pH are consistent with the results of Kestenova and Chomakov (1984). The moisture content values decreased during ripening by about 5.7 g.100 g<sup>-1</sup> for cow milk cheese and by 7 g.100 g<sup>-1</sup> for buffalo milk cheese. The lower moisture content (higher dry matter) found in the buffalo milk cheese, as compared to the cow milk cheese, is due to the different physicochemical composition of either type of milk. A similar trend of change in the moisture content and dry matter was reported by Peichevski et al., 1998. The changes in the diffusion processes occurring in the cheese matrix are directly dependent on the process of acid formation. At the beginning of ripening, the salt content was 3.5 for cow milk cheese, and 3.2 g.100 g<sup>-1</sup> for buffalo milk cheese, while at the end of the study period the amount of salt reached 3.7 g.100 g<sup>-1</sup> for both samples analysed.

The milk fat content in both white brined cheeses differed significantly ( $p < 0.05$ ). The fat content in the total mass and the fat content in the dry matter in cow white brined cheese were 24.5 g.100 g<sup>-1</sup> and 53.8 g.100 g<sup>-1</sup>, and for buffalo cheese they were 30.5 g.100 g<sup>-1</sup> and 62.8 g.100 g<sup>-1</sup>. The protein content in the cow and buffalo cheese at the end of the ripening period was found to be 14.4 g.100 g<sup>-1</sup> and 12.5 g.100 g<sup>-1</sup>, respectively. The data obtained on the chemical composition show that white brined cheese is a source of high amounts of protein and fat to the body.

The fatty acid composition of samples of white brined cheese from cow and buffalo milk during ripening is given in Table 2.

**Table 1**

**Physicochemical composition of samples of white brined cheese from cow and buffalo milk**

Properties	WBC from cow milk		WBC from buffalo milk	
	1 day	45 day	1 day	60 day
Acidity, g.100g <sup>-1</sup> lactic acid	1.64 $\pm$ 0.12 <sup>a</sup>	2.39 $\pm$ 0.22 <sup>b</sup>	1.56 $\pm$ 0.13 <sup>a</sup>	2.45 $\pm$ 0.15 <sup>b</sup>
pH	4.7 $\pm$ 0.1 <sup>a</sup>	4.2 $\pm$ 0.1 <sup>b</sup>	4.6 $\pm$ 0.1 <sup>a</sup>	4.1 $\pm$ 0.1 <sup>b</sup>
Moisture content, g.100g <sup>-1</sup>	60.2 $\pm$ 0.1 <sup>a</sup>	54.5 $\pm$ 0.2 <sup>b</sup>	59.2 $\pm$ 0.1 <sup>c</sup>	52.2 $\pm$ 0.2 <sup>d</sup>
Dry matter, g.100g <sup>-1</sup>	39.8 $\pm$ 0.2 <sup>a</sup>	45.5 $\pm$ 0.2 <sup>b</sup>	40.8 $\pm$ 0.3 <sup>c</sup>	47.8 $\pm$ 0.3 <sup>d</sup>
Proteins, g.100g <sup>-1</sup>	15.3 $\pm$ 0.3 <sup>a</sup>	14.4 $\pm$ 0.4 <sup>b</sup>	12.3 $\pm$ 0.2 <sup>c</sup>	12.5 $\pm$ 0.3 <sup>c</sup>
Fat content in the total mass, g.100g <sup>-1</sup>	21.0 $\pm$ 0.4 <sup>a</sup>	24.5 $\pm$ 0.3 <sup>b</sup>	26.0 $\pm$ 0.2 <sup>c</sup>	30.5 $\pm$ 0.4 <sup>d</sup>
Fat content in dry matter, g.100g <sup>-1</sup>	53.2 $\pm$ 0.3 <sup>a</sup>	53.8 $\pm$ 0.3 <sup>a</sup>	63.7 $\pm$ 0.3 <sup>b</sup>	63.8 $\pm$ 0.3 <sup>b</sup>
Salt content, g.100g <sup>-1</sup>	3.5 $\pm$ 0.1 <sup>a</sup>	3.7 $\pm$ 0.1 <sup>b</sup>	3.2 $\pm$ 0.2 <sup>c</sup>	3.7 $\pm$ 0.2 <sup>d</sup>

a, b, c, d – means with different letters within a row are significantly different ( $p < 0.05$ )

**Table 2****Fatty acid composition of samples of white brined cheese from cow and buffalo milk**

Type of fatty acids	Fatty acids in WBC from cow milk, g. 100 g <sup>-1</sup>		Fatty acids in WBC from buffalo milk, g. 100 g <sup>-1</sup>	
	1 day	45 day	1 day	60 day
C4 : 0	2.4 ± 0.3 <sup>a</sup>	2.7 ± 0.1 <sup>a</sup>	3.0 ± 0.2 <sup>b</sup>	3.4 ± 0.2 <sup>b</sup>
C6 : 0	2.0 ± 0.1 <sup>a</sup>	2.2 ± 0.1 <sup>a</sup>	1.2 ± 0.2 <sup>b</sup>	1.4 ± 0.1 <sup>b</sup>
C8 : 0	1.2 ± 0.1 <sup>a</sup>	1.3 ± 0.1 <sup>a</sup>	1.0 ± 0.2 <sup>a</sup>	1.4 ± 0.2 <sup>a</sup>
C10 : 0	2.8 ± 0.2 <sup>a</sup>	2.6 ± 0.3 <sup>a</sup>	1.8 ± 0.2 <sup>b</sup>	2.0 ± 0.2 <sup>b</sup>
C12 : 0	2.9 ± 0.1 <sup>a</sup>	2.9 ± 0.1 <sup>a</sup>	2.7 ± 0.1 <sup>a</sup>	2.9 ± 0.1 <sup>a</sup>
C14 : 0	11.1 ± 0.2 <sup>a</sup>	11.2 ± 0.1 <sup>a</sup>	11.0 ± 0.3 <sup>a</sup>	11.6 ± 0.3 <sup>a</sup>
C16 : 0	32.0 ± 0.2 <sup>a</sup>	32.7 ± 0.3 <sup>b</sup>	36.2 ± 0.2 <sup>c</sup>	35.1 ± 0.3 <sup>d</sup>
C16 : 1	1.9 ± 0.2 <sup>a</sup>	1.4 ± 0.3 <sup>a</sup>	1.9 ± 0.2 <sup>a</sup>	1.8 ± 0.3 <sup>a</sup>
C17 : 0	0.6 ± 0.2 <sup>a</sup>	0.4 ± 0.1 <sup>a</sup>	0.9 ± 0.2 <sup>a</sup>	0.8 ± 0.2 <sup>a</sup>
C18: 0	13.4 ± 0.2 <sup>a</sup>	13.2 ± 0.1 <sup>a</sup>	11.5 ± 0.2 <sup>b</sup>	11.6 ± 0.1 <sup>b</sup>
C18: 1	27.8 ± 0.4 <sup>a</sup>	27.4 ± 0.4 <sup>a</sup>	27.1 ± 0.3 <sup>a</sup>	26.3 ± 0.4 <sup>b</sup>
C18: 2	1.3 ± 0.2 <sup>a</sup>	1.3 ± 0.2 <sup>a</sup>	0.9 ± 0.1 <sup>b</sup>	0.9 ± 0.2 <sup>a</sup>
C18 : 3	0.6 ± 0.1 <sup>a</sup>	0.6 ± 0.1 <sup>a</sup>	0.6 ± 0.1 <sup>a</sup>	0.6 ± 0.1 <sup>a</sup>
C20 : 0	0.1 ± 0 <sup>a</sup>	0.1 ± 0 <sup>a</sup>	0.2 ± 0.1 <sup>a</sup>	0.2 ± 0.1 <sup>a</sup>

a, b, c, d – means with different letters within a row are significantly different ( $p < 0.05$ )

The results obtained revealed that the proportion of the fatty acids did not alter significantly during the ripening period in both experimental samples. This is due to the low lipolytic activity occurring during ripening. A similar conclusion was made by Michailova et al., 1995, and Khalid and Marth, 1996, according to whom milk fat undergoes an insignificant change during ripening of white brined cheese, owing to the low activity of the intracellular lipases and esterases produced by the lactobacilli in the starter culture. The essential fatty acids identified in the samples of both types of cheese were palmitic, oleic, stearic and myristic. In both cheese samples the predominant fatty acid was palmitic. The short-chain fatty acids were represented by butyric and capric acids, while the percentage of caprylic fatty acid was the lowest. It should be noted that the content of butyric acid was higher in the buffalo cheese sample than in the cow milk cheese sample. The amounts of caproic and caprylic acid were lower in the buffalo cheese. The medium-chain fatty acids were predominantly represented by myristic, lauric and capric acids. The contents of capric and lauric acids were higher in the cow milk cheese, while the percentage of myristic fatty acid was higher in the buffalo white cheese. Of the long-chain fatty acids, palmitic acid content was found to be

the highest, followed by oleic and stearic acids.

The results in Table 2 show that the amount of saturated fatty acids predominates in the experimental samples, amounting to 69.2 g.100 g<sup>-1</sup> in the cow white cheese, and 70.1 g.100 g<sup>-1</sup> in the buffalo white cheese. The amount of saturated fatty acids changed during the ripening period by about 1.3 g.100 g<sup>-1</sup> in the cow, and by 0.7 g.100 g<sup>-1</sup> in the buffalo white cheese. The unsaturated fatty acid content was 30.8 g.100 g<sup>-1</sup> in the cow, and 29.9 g.100 g<sup>-1</sup> in the buffalo cheese.

Table 3 shows the results obtained from the analysis of peroxide and acid values of cow and buffalo white cheese after ripening at  $t = 12 \pm 1^\circ\text{C}$ .

By measuring the peroxide value it is possible to determine the degree of milk fat oxidation in the experimental cheese samples. The acid values observed indicate that there is a correlation between milk fat hydrolysis and the ripening period. The upward change in these two indicators leads to deterioration of the organoleptic properties and loss of nutritional and biological value of the cheese samples.

The data in Table 3 show that the peroxide and acid values of the cheese samples remain unchanged for the entire study period.

**Table 3****Change in peroxide value and acid value of white brined cheese from cow and buffalo milk**

Properties	WBC from cow milk		WBC from buffalo milk	
	1 day	45 day	1 day	45 day
Peroxide values, meqO <sub>2</sub> .kg <sup>-1</sup>	0.24 ± 0.10 <sup>a</sup>	0.25 ± 0.09 <sup>a</sup>	0.24 ± 0.08 <sup>a</sup>	0.24 ± 0.10 <sup>a</sup>
Acid values, mgKOH.g <sup>-1</sup> fat	2.70 ± 0.11 <sup>a</sup>	2.70 ± 0.19 <sup>a</sup>	2.64 ± 0.15 <sup>a</sup>	2.64 ± 0.16 <sup>a</sup>

In both cheese variants, the acid value and the peroxide value remained relatively constant on day 45 and day 60 of the ripening period, compared to the values established on the first day of the ripening period. This trend can be explained with the low lipolytic activities during ripening.

## Conclusions

The more intense physical and chemical processes occurring during ripening in the white brined cheese from cow milk than in the cheese from buffalo milk are directly dependent on the structure, moisture and fat content of the cheese. The low lipolytic activity during the ripening period correlates with the minimum change in the peroxide and acid values. The amount of saturated fatty acids in both types of white brined cheese accounts for approximately 70 g.100 g<sup>-1</sup> of the fatty matter, while the proportion of unsaturated fatty acids is approximately 30 g.100 g<sup>-1</sup>.

## References

- Barron, L., E. Labastida, S. Perea, F. Chavarri, C. Vega, M. Vicente, M. Torres, A. Najera, M. Virto, A. Santisteban, F. Perez-Elortonto, M. Albisu, J. Salmeron, C. Mendia, P. Torre, C. Ibanez and M. Renobales,** 2001. Seasonal changes in the composition of bulk raw ewe's milk used for Idiazabal cheese manufacture. *International Dairy Journal*, **11**: 771–778.
- Belitz, H., W. Grosch, S. Schieberle-Delgado, C. Caio Rachid, E. Fernández, T. Rychlik, Á. Alegria, S. Peixoto and B. Mayo,** 2013. Diversity of thermophilic bacteria in raw, pasteurized and selectively-cultured milk, as assessed by culturing, PCR-DGGE and pyrosequencing. *Elsevier Food Microbiology*, **36**: 103–111.
- Bligh, E. and W. Dyer,** 1959. A rapid method for total lipid extraction and purification. *Canadian Journal of Biochemistry and Physiology*, **37**: 911–917.
- BNS 1109-89,** 1989. Milk and milk products. Methods for determination of moisture and dry matter (Bg).
- BNS 1111-80,** 1980. Milk and milk products. Determination of acidity (Bg).
- BNS 15-2010,** 2010. Bulgarian white cheese in brine (Bg).
- BNS 8274-82,** 1982. Milk and milk products. Methods for determination of NaCl (Bg).
- BNS EN ISO 5508:2000,** 2000. Animal and vegetable fats and oils - Analysis by gas chromatography of methyl esters of fatty acids (Bg).
- BNS EN ISO 8968-1,** 2001. Milk – Determination of nitrogen content - Part 1: Kjeldahl method (Bg).
- BNS ISO 3433/IDF 222,** 2010. Cheese-Determination of fat content- Van Gulik method (Bg).
- Borghese, A.,** 2004. Recent developments of buffaloes in Europe and Near East. Proceedings of the Seventh World Buffalo Congress, Manila, Philippines 20–23 October, 2004. pp. 10–16.
- Borghese, A.,** 2005. Buffalo production and research. *FAO Ed. REU Technical Series*, **67**: 1–315.
- Fox, P. and P. McSweeney,** 2004. *Cheese: Chemistry, Physics and Microbiology*, 1: 617 pp.
- Guinee, T., M. Auty, C. Mullins, M. Corcoran and E. MulHolland,** 2000. Preliminary observation on effects of fat content and degree of fat emulsification on the structure-functional relationship of Cheddar-type cheese. *Journal of Texture Studies*, **31** (6): 645–663.
- ISO EN 3960:2008,** 2008. Animal and vegetable fats and oils. Determination of peroxisid value. Iodometric (visual) end point determination.
- ISO EN 660:2009,** 2009. Animal and vegetable fats and oils. Determination of acid value matter content.
- Katsiari, M., E. Alichanidis, L. Voutsinas and I. Roussis,** 2000a. Proteolysis in reduced sodium Feta cheese made by partial substitution of NaCl by KCl. *International Dairy Journal*, **10**: 635–646.
- Katsiari, M., L. Voutsinas, E. Alichanidis and I. Roussis,** 2000b. Lipolysis in reduced sodium Feta cheese made by partial substitution of NaCl by KCl. *International Dairy Journal*, **10**: 369–373.
- Kestenova, M. and C. Chomakov,** 1984. Effect of starter amount and salting degree on cow white brine cheese quality. *Animal Science*, **21** (5): 17–22 (Bg).
- Khalid, N. and E. Marth,** 1996. Lactobacilli- their enzymes and role in ripening and spoilage of cheese: a review. *Journal of Dairy Scence*, **73**: 2669–2684.
- Lindmark-Mansson, H., R. Fonde'n and H. Pettersson,** 2003. Composition of Swedish dairy milk. *International Dairy Journal*, **13** (6): 409–425.
- Lindmark-Mansson, H., U. Svensson, M. Paulsson, G. Alden, B. Frank and G. Johnson,** 2000. Influence of milk components, somatic cells and supplemental zinc on milk process ability. *International Dairy Journal*, **109**: 423–433.
- Mallatou, H. and E. Pappa,** 2005. Comparison of the characteristics of Teleme cheese made from ewes, goats, cows or a mixture of ewes and goats milk. *International Journal of Dairy Technology*, **58** (3): 158–163.
- Mallatou, H., E. Pappa and V. Boumba,** 2004. Proteolysis in Teleme cheese made from sheep's, goat's or a mixture of sheep's and goat's milk. *International Dairy Journal*, **14**: 977–987.
- Mihailova, G., I. Peichevski, T. Dimitrov and T. Iliev,** 1995. Fatty acid composition of white brine cheese during production, ripening and storage. *Analytical Laboratory*, **3**: 207–210 (Bg).
- Peichevski, I. and T. Iliev,** 1986. Effect of sheep milk standardization on the quantity and composition of the white brine cheese. *Scientific Works of Zootechnical Faculty VIZVM*, **34**: 423–435 (Bg).