Potravinarstvo, vol. 7, Special Issue, March 2013

Available online: 20 March 2013 at www.potravinarstvo.com
ISSN 1337-0960 (online)

THE EFFECT OF COLD STORAGE OF RAW EWE'S MILK AND ŻENTYCA ON THEIR SELECTED CHEMICAL INDICATORS

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Abstract: The effect of cold storage on stability of raw ewe's milk and żentyca by various chemical methods was examined. In ewe's milk putrescine, cadaverine, tryptamine and agmatine were deteced, while in żentyca instead of agmatine, tyramine and histamine were found. In most cases cold storage caused increase in amine concentrations; however, their amounts have no adverse health effects. During the storage of both products, oxidation of fat and hydrolysis of protein occurred, which was proved by TBA and HPLC methods.
Key words: ewe's milk, żentyca, cold storage, biogenic amines

INTRODUCTION

In order to try unique and healthy traditional products from Malopolska region, such as ewe's milk and żentyca (a kind of whey of ewe's milk), enthusiasts of such delicacies must arrive in the vicinity of Tatra Mountains. In Poland these products are not available in supermarkets, but only in traditional shepherd's huts. Hopefully, tourism in this region will continue to grow, so a wider range of customers will be able to enjoy the taste and nutritional values of those products.

Admittedly, ewe's milk due to its chemical composition is used mostly in cheese manufacturing; however, because of its flavour and biological value can be perceived as a good alternative to cattle milk. A traditional by-product, żentyca, is produced from ewe's milk mostly in shepherd's huts. Its production was endangered by the variety flow of industrially manufactured dairy products widely available for consumers. Luckily, knowledge of its production was passed on from father to son, and due to its positive influence on human organism żentyca is recommended for consumption (**Bonczar, 2006**).

Due to the labile constituents of milk and dairy products, and the presence of microorganisms, it is essential to provide cold storage; however, sometimes in shepherd's huts a refrigeration conditions can cause a significant problem. Therefore, the aim of present study was to measure the effect of two storage temperatures on stability of ewe's milk and żentyca by using selected chemical indicators.

MATERIAL AND METHODS

Raw ewe's milk and żentyca were obtained at the beginning of June and September from the shepherd's hut located near Nowy Targ, Poland. Ewe's milk was kept at 2 °C for 10 days and at 10°C for 6 days, while żentyca for 35 and 14 days, respectively.

Moisture, protein, lipids and ash content were determined according to the Polish Standard PN-73/A-86232. **pH** was measured directly in a product using pH-meter combined with glass electrode. **Titration acidity** (°SH) was analysed according to PN-73/A-86232. **TBARS** were determined using the method described by **Krełowska-Kułas (1993),** while the **sensory evaluation** was conducted by assessing colour, taste, odour and consistency on a 5-point classical scale (**Baryłko-Pikielna, Matuszewska, 2009**). **Low molecular weight proteinaceous substances** were analyzed with a Merck-Hitachi LaChrom HPLC System

according to procedure described by **Michalczyk, Surówka (2007). Biogenic amines** (BA) analysis was carried out using the HPLC method according to Ozogul et al. (2002) modified by **Rzepka, Surówka (2012).**

RESULTS AND DISCUSSION

Ewe's milk, intended for analyses and collected both in June and September, was characterized by typical chemical composition (Table 1) **(Pijanowski, 1980; Danków & Pikul, 2011**). It should, however, be emphasized that the raw material collected in June contained less water but more fat than those from September. A similar tendency was observed with respect to żentyca, although determined contents of water and fat were higher than those reported by **Danków, Pikul (2011).**

Table 1. Proximate composition of fresh ewe's milk and żentyca.

	Water (%)	Lipid (%)	Protein (%)	Ash (%)
		Ewe's milk		
June	80.74 ± 0.18	8.95 ± 0.01	5.48 ± 0.06	0.89 ± 0.07
September	82.35 ± 0.03	7.50 ± 0.01	6.34 ± 0.11	0.92 ± 0.14
		Żentyca		
June	87.40 ± 0.38	6.30 ± 0.40	3.25 ± 0.0	0.52 ± 0.01
September	89.20 ± 0.46	5.31 ± 0.16	2.41 ± 0.03	0.55 ± 0.03

Fresh raw milk, collected both in June and September, had similar pH and acidity (Fig. 1). In milk from both periods, changes in above mentioned parameters showed a similar tendency over the storage period; however, they were far more dynamic at higher temperature (10ºC). The presumable reason for rather high differences in pH and acidity between żentyca manufactured in June and September, were different time-temperature conditions of fermentation conducted in shepherd's huts in various periods of the year (Fig. 2). Żentyca, milk alike, was souring during storage; however, the extent of the process was generally significantly lower.

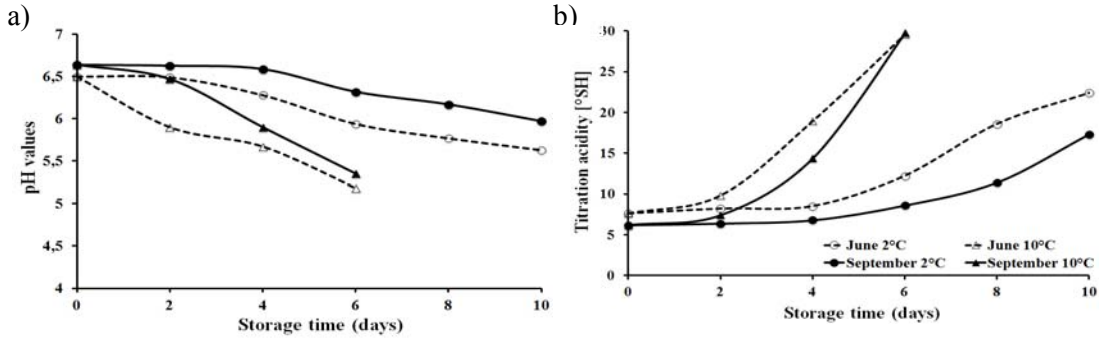

Fig. 1. The effect of storage temperature on pH (a) and titration acidity (b) of raw ewe's milk collected in June and September

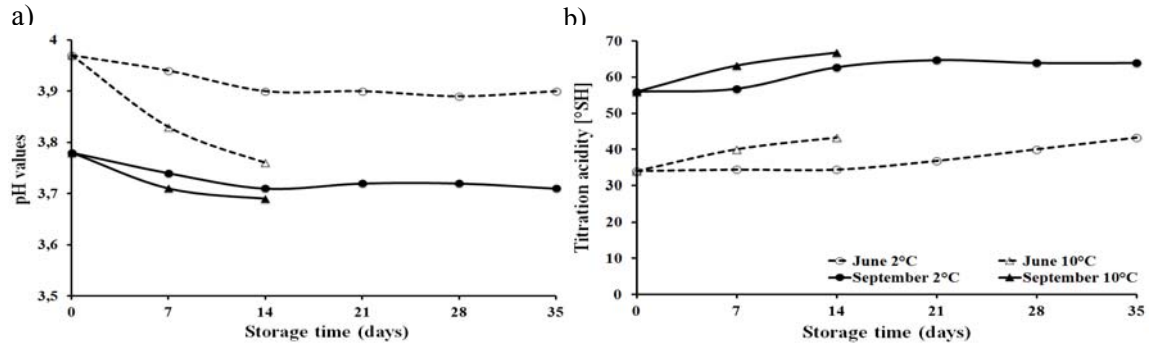

Fig. 2. The effect of storage temperature on pH (a) and titration acidity (b) of żentyca obtained from milk collected in June and September

During storage of ewe's milk, moderate oxidative changes occurred. An initial TBA value was about 0.5 mg MDA/kg**;** after 6-day storage at 10ºC or 10-day storage at 2ºC, a 2-fold increase was found. Oxidative changes were also observed in żentyca with a maximal effect expressed by the TBA value of 2.4 mg MDA/kg after 2 weeks of storage at 10ºC.

The first taste deterioration (slight sour) occurred around 4th day of milk storage at 10°C and 7th day at 2°C, in both samples, namely from June and September. Similarly, in żentyca a slight deterioration of taste was observed after 7 and 28 days of storage.

In order to characterize the process of proteolysis, chromatographic separations (HPLC) of amino acids and peptides released during storage were carried out, and the obtained chromatograms are summarized in tables 2 and 3. Generally storage of milk did not seem to cause substantial changes in the relative intensity of amino acids peaks, but increase in the number and relative area of peaks assigned to peptides were recorded. On the other hand, in the case of stored żentyca, the increase in relative area of peaks representing non- aromatic amino acids was observed.

Table 2. HPLC analysis of proteinaceous fractions in fresh and stored ewe's milk collected in June and September.

Storage conditions	Relative area (%)						Number of peaks	
	A.As*	Tyr	Phe	Trp	Peptides	Poly-peptides	Peptides	Poly-peptides
June								
Fresh milk	2.71	0.09	nd**	0.16	6.61	91.30	12	5
2°C, 10 days	4.74	0.44	nd	0.14	16.01	79.36	50	8
10°C, 6 days	2.63	0.39	nd	0.28	14.07	82.80	24	5
September								
Fresh milk	3.07	0.06	nd	0.13	13.98	82.92	28	3
2°C, 10 days	2.92	0.08	nd	0.20	21.08	76.54	40	6
10°C, 6 days	3.62	0.12	nd	0.11	17.05	79.49	63	7

A.As*- non-aromatic amino acids; Tyr- tyrosine; Phe- phenylalanine; Trp- tryptophan; nd**- not detected

Table 3. HPLC analysis of proteinaceous fractions in fresh and stored żentyca produced from milk collected in June and September.

Storage conditions	Relative area (%)						Number of peaks	
	A.As*	Tyr	Phe	Trp	Peptides	Poly-peptides	Peptides	Poly-peptides
June								
Fresh żentyca	32.63	1.78	0.07	2.86	36.79	25.88	45	5
2°C, 10 days	58.56	0.22	0.28	0.16	24.71	16.11	35	7
10°C, 6 days	53.21	0.31	0.20	0.29	27.40	18.65	35	7
September								
Fresh żentyca	43.96	1.24	0.65	2.52	30.56	21.07	38	6
2°C, 10 days	57.78	0.63	0.31	0.47	24.94	15.88	35	8
10°C, 6 days	54.25	0.39	0.36	0.53	26.72	17.76	36	8

A.As*-non-aromatic amino acids; Tyr- tyrosine; Phe- phenylalanine; Trp- tryptophan.

In this work, nine BAs have been determined. Ewe's milk contained only four and table 4 illustrates changes in their contents during storage. In żentyca there was no agmatine, while there were histamine and tyramine (Table 5). The levels of detected BA contents are slight, and therefore do not bring risk to safety of the analyzed products (EFSA, 2011).

Table 4. Concentration of biogenic amines in fresh and stored ewe's milk collected in June and September.

Temp. (°C)	Storage time (days)	Biogenic amine (mg/L)			
		Putrescine	Cadaverine	Tryptamine	Agmatine
		June			
2	0	1,41	nd*	10,22	0,43
2	6	6,58	1,44	10,17	2,10
2	10	18,21	2,23	9,65	6,21
10	0	1,41	nd	10,22	0,43
10	3	7,68	nd	14,31	0,82
10	6	9,37	nd	16,23	3,62
		September			
2	0	1,25	0,44	10,87	nd
2	6	6,22	2,12	6,19	nd
2	10	10,12	3,84	4,85	nd
10	0	1,25	0,44	10,87	nd
10	3	1,44	2,45	4,47	nd
10	6	8,25	6,21	1,29	nd

*nd- not detected

Table 5. Concentration of biogenic amines in fresh and stored żentyca produced from milk collected in June and September.

Temp. (°C)	Storage time (days)	Biogenic amine (mg/L)				
		Putrescine	Cadaverine	Tryptamine	Histamine	Tyramine
		June				
2	0	6,23	nd*	6,17	1,05	0,87
2	14	8,07	1,54	6,07	1,80	6,07
2	28	8,42	1,41	4,18	2,14	6,23
2	35	8,14	0,89	4,09	1,96	6,17
10	0	6,23	nd	6,17	1,05	0,87
10	7	8,25	nd	4,68	1,60	4,18
10	14	14,78	0,87	4,15	1,39	6,03
		September				
2	0	2,69	2,89	4,08	1,69	1,21
2	14	2,47	2,10	4,47	2,54	1,04
2	28	2,95	0,85	4,19	1,98	1,29
2	35	3,12	1,24	4,08	1,84	1,47
10	0	2,10	2,89	4,08	1,69	1,21
10	7	4,84	2,33	6,07	1,89	1,37
10	14	6,08	2,78	4,97	1,67	1,19

*nd- not detected

CONCLUSIONS

1. Storage at 2°C instead of 10°C allows to extend milk shelf-life from 4 up to 7 days and żentyca from 7 to 28 days in comparison to higher temperature.
2. During both products storage limited fat oxidation and protein hydrolysis occur.
3. Fresh and stored products contain biogenic amines in a concentration which is not hazardous for consumer health.

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Acknowledgments: Research were conducted in frame of Doctus project nr MCP.ZS. 4110.-214.1/2009.

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