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Biogenic Amines in the Different Types of Cheese

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Abstract

The aim of the experiment was to analyse the content of biogenic amines (BA) in the main groups of commercially produced cheeses and in cheese matured under standard conditions. The content of biogenic amines in commercially produced cheeses was monitored on the last day of consumption, and on the 1st, 30th and 60th days after production in the cheese matured under standard conditions. The highest content of biogenic amines was found in semi- hard cheeses, mainly in Eidam slices (tyramine123.12 mg.kg^{-1} putrescine 23.02 mg.kg^{-1}). The cheese was not treated after the production and was cut and packed after production, which significantly affected the formation of biogenic amines. Also, "Salámový syr" - cheese had a high content of biogenic amines (tyramine 65.12 mg.kg^{-1} putrescine 29.25 mg.kg^{-1}). High content of BA was also found in the other semi- hard cheeses - "Hranol neúdený" (tyramine 56.02 and putrescine 51.49 mg kg^{-1}). In general, the content of biogenic amines in semi- hard cheeses is higher than in semi-soft, because they have a longer ripening time.

1. Introduction

Biogenic amines (BA) are low molecular weight aliphatic organic compounds derived from amino acids. They commonly participate in metabolic processes in living tissues **(Komprda, 2005).**
According to the chemical structure, BA are composed of aromatic (tyramine, phenylethylamine), heterocyclic (histamine, tryptamine), aliphatic (putrescin, cadaverine) and polyamines (spermidine, spermine, or agmatine) **(Velíšek, 2002; Čuboň *et al.,* 2017).**
Proteolytic processes, including the release of free amino acids from the protein matrix, result mainly from the activity of the enzymatic apparatus of the SLAB and NSLAB present. The product of histidine decarboxylation is histamine, and cadaverine is formed from lysine **(Buňka *et al.,* 2012; Pachlová *et al.,* 2015).**
The BA content in certain foods may be very different. Typical levels of biogenic amines in foods range from 10 mg.kg^{-1} to 100 mg.kg^{-1}. BA content detected in food can exceed 1000 mg. kg^{-1} **(Buňková, 2010).** The BA concentration in fresh cow milk is less than 1 mg.kg^{-1}. These are primarily histamine and tyramine. The histamine content in milk varies from 0.5 to 0.8 mg. kg^{-1}, the histamine content of the dried milk is around 131 mg. kg^{-1}, tyramine content 42 mg.kg^{-1}. The BA content in the cheese may be higher than10 g.kg^{-1} **(Greif and Greifová, 2006).**
BA content of all cheeses gradually increases during ripening process. Their kinetics also depends on the type of cheese and the technology used. Hard cheeses contain less BA than soft cheeses. The highest values were in the tyramine content (up to 146 mg.kg^{-1}) and histamine up to 85 mg.kg^{-1}. Also, tryptamine, phenylethylamine, putrescine, cadaverine, spermine, spermidine, adrenaline and noradrenaline were identified in the cheeses **(Kolesarová, 1995).**
The aim of the experiment was to analyse the content of biogenic amines in the main groups of commercially produced cheeses and in cheese matured under standard conditions.

2. Material and methods

In our study, a total of 40 samples of natural cheeses were analysed. They were purchased from various stores in the Slovak Republic.
The cheeses were divided according to the consistency (expressed as the water content in the non-fatty matter of the cheese - VBHS%) into groups (hard 49-56%, semi- hard 54-63%, semi-soft 61-69%, and soft 67%).
In the experiment, the following samples of cheese were analyzed according to the following consistency:
- Hard cheese: A - Primator (n = 5),
- Semi- hard cheese: B - Eidam slices (n = 5), C- „Salámový syr neúdený"- cheese (n = 5), D- „Hranol neúdený"–cheese (n = 5),
- Semi - soft cheeses: E - Mold cheese (n = 5), F - Half-horsepowder (n=5),
- Soft cheese: G- Plesnivec (n = 5), H-Encian (n = 5).
The cheese was analysed at the end of expiration date. From the purchase until the analysis, the samples were stored at 10 ± 2 °C.

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2.1 Ripening experiment

In the second part of the experiment, an Eidam brick was produced in a dairy plant (n = 5) from five milk samples. The cheese was produced to monitor the content of biogenic amines during maturation. Samples for analysis were taken on 1st, 30th and 60th day after production. They were stored at 10 ± 2 °C all the time.

In the study, there are limits for analysed parameters (mg.kg^{-1}) for a complex matrix, such as: histamine - 1.07, tyramine - 1.41, putrescin - 1.65, cadaverin - 1.72, agmatin - 2.54, spermidine - 0.71, spermin - 1.57. The actual detection limits for biogenic amine standards are approximately at a quarter of these values.

Free amino acids and biogenic amines were determined by using ion-exchange chromatography (AAA400 Amino Acid Analyzer; Ingos, Prague, Czech Republic) according to **Buňková *et al.* (2010).** Each cheese sample was analysed twice. Standards were supplied by Sigma–Aldrich.

The data were processed in statistical analysis using the Statistic Analysis System (SAS) package (SAS 9.3 using of application Enterprise Guide 4.2).

3. Results and discussion

In commercial cheese production in the Slovak Republic, concentrations of biogenic amines (histamine, tyramine, putrescin, cadaverine, agmatine, spermidine, spermine) were analysed by an ion exchange chromatography method using the AAA400 analyser. The cheeses were analysed at the end of the expiration date.

The content of biogenic amines in extruded cheeses is shown in Table 1.

In the hard cheese (Primator) the tyramine content was 11.05 mg.kg^{-1} and putrescine 11.15 mg.kg^{-1}. Other analysed biogenic amines were below the limit of analysis (Table 1). In semi- hard cheese – „Eidam slices", tyramine content was 123.12 mg.kg^{-1} and putrescine 23.02 mg.kg^{-1}. In „Salámový syr neúdený" - cheese, tyramine content was 65.12 mg.kg^{-1}, putrescine 11.05 mg.kg^{-1} and cadaverine 11.05 mg.kg^{-1}. In the „Hranol neúdený" –cheese tyramine content was 56.02 mg.kg^{-1} and putrescine 51.49 mg.kg^{-1}.

In semi soft cheese – „Plesňový syr" cheese, the tyramine content was 24.05 mg.kg^{-1} and putrescine 21.62 mg.kg^{-1}. In the „Gazdovský polooštiepok" - cheeses, only the cadaverine content of 3.25 mg.kg^{-1} was found. Other biogenic amines levels were under the analysis limit.

Higher contents of tyramine - 180.4 mg.kg^{-1} in the cheese is reported by **Buňková (2010).** However, tyramine content in the cheese can also reach 500 mg.kg^{-1} **(Leuschner *et al.,* 1999).** The highest content of biogenic amines was found in semi- hard cheeses mainly in Eidam slices (tyramine - 123.12 mg.kg^{-1}, putrescine - 23.02 mg.kg^{-1}). The cheese was not heat-treated after production and was cut and packaged after production, which significantly affected the formation of biogenic amines. Also, „Salámový syr neúdený"- cheese had a high content of biogenic amines (tyramine - 65.12 mg.kg^{-1}, putrescine - 29.25 mg.kg^{-1}). The high content of BA was also in the other „Hranol neúdený"- cheese (tyramine - 56.02 and putrescine - 51.49 mg.kg^{-1}). Generally, the content of biogenic amines in semi- hard cheeses is higher than that of semi-soft cheese because they have a longer maturing time.

Soft cheeses including „Bryndza"– cheese had higher concentration of biogenic amines (300 mg.kg^{-1}) in spring bryndza **Greif, Greifová (2006)**.

Also, **Dičaková and Dudriková (2006)** found high tyramine content (52.4-410 mg.kg^{-1}) and also indicate that the content of biogenic amines in food is also increasing during storage of products.

In comparison to our results, **Standarova *et al.* (2008)** found significantly higher concentrations of biogenic amines in soft ripened cheeses. The highest concentrations were also found in the „Bryndza"- cheese (417 mg.kg^{-1} of tyramine, 591 mg.kg^{-1} of putrescine and 1110 mg.kg^{-1} of cadaverine) and „Hermelín" - cheese (187 mg.kg^{-1} of tyramine).

In the second part of the experiment, an Eidam brick was produced in a dairy plant (n = 5). The content of biogenic amines was analysed during maturation (on the 1st, 30th and 60th day after production). Cheeses were stored at 10 ± 2 ° C throughout the maturing time. The observed concentrations of biogenic amines are shown in Table 2.

During the 60 days of Eidam brick cheese maturation at 10 ± 2 °C, the content of biogenic amines was analysed. No biogenic amines were found in samples on the 1st day post-production. On the 30th day after processing, we found tyramine content of 8.256 mg.kg^{-1}, putrescine of 4.81 mg.kg^{-1} and cadaverine of 12.22 mg.kg^{-1}. The content of histamine, agmatine, spermidine and spermine was below the detection limit.

In cheeses on the 60th day after processing, we found tyramine content of 14.25 mg.kg^{-1}, putrescine of 10.25 mg. kg^{-1}, cadaverine of 26.42 mg. kg^{-1} and spermidine of 1.31mg. kg^{-1}. Other analysed biogenic amines (histamine, agmatine and spermine) were below the detection limit.

Pachlová *et al.* (2018) did not detect the content of biogenic amines in cheeses with microorganism without decarboxylation activity. But when using *Lb. paracease DEPE T52,* content of biogenic amines on the 30th day was 61.4 mg. kg^{-1} and on the 60th day 77.4 mg. kg^{-1}. Tyramine content on the 30th day was 20.6 mg.kg^{-1} and 29.9 mg.kg^{-1} on the 60th day.

Table 1. Content of biogenic amines in commercialized cheeses (mg.kg^{-1})

Cheese	HIS	TYR	PUT	CAD	AGM	SPD	SPM
Hard cheese **A**	ND	11.05 ± 1.09	11.15 ± 0.95	ND	ND	ND	ND
Semi- hard cheese **B**	ND	123.12 ± 9.02	23.02 ± 0.94	ND	ND	ND	ND
C	ND	65.12 ± 4.21	29.25± 1.42	11.05±0.45	ND	ND	ND
D	ND	56.02 ± 1.72	51.49 ± 2.82	ND	ND	ND	ND
Semi - soft cheese **E**	ND	24.05 ± 2.48	21.62 ± 0.98	ND	ND	ND	ND
F	ND	ND	ND	3.25 ± 0.45	ND	ND	ND
Soft cheese **G, H**	ND	ND	ND	ND	ND	ND	ND

Legend: HIS – Histamine, TYR - Tyramine, PUT - Putrescine, CAD – Cadaverine, AGM – Agmatine, SPD – Spermidine, SPM – Spermine, ND = non detected

Table 2. The biogenic amines contents in the Eidam brick in the course of maturing (mg.kg^{-1})

HIS	TYR	PUT	CAD	AGM	SPD	SPM
1^{-st} day						
ND	ND	ND	ND	ND	ND	ND
30^{-th} day						
ND	8.25 ± 0.62	4.81 ± 0.48	12.22 ± 0.51	ND	ND	ND
60^{-th} day						
ND	14.25 ± 0.62	10.25 ± 0.91	26.42 ± 0.95	ND	1.31 ± 0.21	ND

Legend: HIS – Histamine, TYR - Tyramine, PUT - Putrescine, CAD – Cadaverine, AGM – Agmatine, SPD – Spermidine, SPM – Spermine, ND = non detected

Conclusion

The formation of biogenic amines is affected by several factors. The microflora and production technology used have a great impact. The highest content of biogenic amines was found in semi- hard cheeses, mainly in Eidam slices (tyramine - 123.12 mg.kg^{-1}, putrescine - 23.02 mg.kg^{-1}). The cheese was not heat-treated after production and was cut and packaged after production, which significantly affected the formation of biogenic amines. Also, „Salámový syr neúdený"- cheese and „Hranol neúdený" had a high content of biogenic amines. In general, the content of biogenic amines in semi- hard cheeses is higher than in semi-soft, because they have a longer maturing time. At the experiment during the maturation we found approximately two times the increase of tyramine, putrescine and cadaverine from the 30th to the 60th day of maturing.

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Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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