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# Biogenic amines contents of Van herby cheese matured by different methods

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**Abstract:** In this study, biogenic amines levels of Van herby cheese (Van Otlu peynir) matured in dry-salted/filling (basma) and brine (salamura)-salted techniques were investigated. For this purpose, a total of 100 herby cheese samples matured by dry-salted and brine-salted techniques (50 dry-salted and 50 brine-salted) were purchased from the grocery stores in Van province, and chemical characteristics and biogenic amines contents of the samples were determined. The mean chemical composition for Van herby cheese matured by dry-salted method and brine-salted methods were, respectively, as follows: pH value 4.62 and 5.16, acidity 1.50% and 1.08%, salt content 7.85% and 7.15%, dry matter content 59.07% and 49.22%, fat 27.00% and 23.43%, protein content 23.39% and 17.17% and protein hydrolysis of 100.92 mM and 79.57 mM, indicating that dry-salted Van herby cheese had significantly lower pH values and significantly greater acidity and protein, dry matter, and fat content than brine-salted Van herby cheese ($P < 0.05$). In addition, only the tyramine levels were significantly greater in the dry-salted group than the brine-salted group approximately twice high ($P < 0.001$). In terms of the other biogenic amines, no significant difference was found between two groups ($P > 0.05$). In conclusion, none of the biogenic amines levels measured in Van herby cheese produced by both techniques were above the levels considered to be dangerous for human health. More detailed research is needed to better elucidate the importance of present findings in terms of human health.

**Keywords:** Biogenic amines, brine-salted, dry-salted, Van herby cheese

## 1. Introduction

Although white cheese, kashar cheese, and tulum cheese are the most commonly consumed cheese in Turkey, there are some other local cheese (i.e. circassian cheese, curd cheese, cottage cheese, dil cheese, herby cheese and etc.) available in grocery stores and largely consumed by Turkish people (Demirci et al., 1994; Durlu-Özkaya and Gün, 2017).

Herby cheese is produced by dry-salted and brine-salted techniques in Van, Ağrı, Batman, Bitlis, Diyarbakır and Siirt provinces located in Eastern and Southern Anatolia with the supplementation of special herbs (Coşkun, 2005; Çakmakçı, 2011; Tunçtürk and Tunçtürk, 2020). In recent years, there has been an increase interest to Herby cheese from the other regions in Turkey. This cheese is made from sheep milk. The intensive production of herby cheese occur in Van province because the region is richer in terms of the wild plants adding in the Herby cheese and called " Van herby cheese". More than 60 plant species belonging to 9 different families are included in Van herby cheese. The most important herbs are included in Van herby cheese; these herbs belong to Apiaceae, Liliaceae and Lamiaceae families including *Ferula* sp. (siyabo), *Allium* (sirmo), *Chaerophyllum spp.* (mendo), *Heracleaum* (Sov), *Thymus* (kekik), *Prangos* sp. (heliz), *Zizophora* (catır) genus. It has been determined that these herbs added to the cheese enrich the local cheese in terms of vitamin C, raw fiber, macro and micronutrients and also provide the cheese with antimicrobial and antioxidant properties (Tunçtürk and Tunçtürk, 2020).

Cheese ripening is a complex process including biochemical reactions, various microorganisms, and enzymes. During cheese ripening, casein is initially degraded into larger-size peptides by enzymes, then peptides are degraded into small peptides and amino acids by proteinase and peptidases (Ünsal, 1997). Biogenic amines are defined as low-molecular weight, alkaline nitrogenous organic compounds generated through various metabolic activities of plants, animals, and microorganisms (Ordóñez et al., 2017). With the degradation of carboxyl groups of amino acids, amines of the relevant amino acid are formed. Such a process is called 'decarboxylation' and catalyzing enzyme is called 'decarboxylase'. The enzymes responsible for decarboxylation may exist in animal and plant tissues or may also be produced by microorganisms (Yerlikaya and Gökoğlu, 2002). Microbial degradation-

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originated decarboxylation is more frequent in foodstuffs (Vatansever, 2004; Şanlıbaba and Uymaz, 2015). Previous studies revealed that pH value, reciprocal interactions of microorganisms, number and type of microorganisms, salt contents, storage and ripening conditions, and production techniques play an important role in biogenic amines formation (Joosten and Van-Boekel, 1988; Durlu-Özkaya et al., 1999, 2000; Durlu-Özkaya and Tunail, 2000; Karahan et al., 2001).

It was reported that during ripening, when the sufficient amount of amino acid was released with the effect of protein hydrolysis and if the number and type of microorganisms were sufficient, then biogenic amines formation may reach to toxic levels (Joosten and Van- Boekel, 1988; Büyük and Marangoz, 2018; Aktop and Şanlıbaba, 2018). Therefore, excessive ripening and resultant increased protein hydrolysis were reported to increase biogenic amines quantities to upper most level (Joosten and Weerkamp, 1994). Biogenic amines released by foodstuffs may result in various symptoms including nausea, spots and ecthyma, vomiting, fever, perspiration, sore throat, hypo or hypertension (Joosten and Stadhouders, 1987; Chander et al., 1989; Stratton et al., 1991). Increasing biogenic amines quantities indicate microbial degradation of foodstuffs (Karahan, 2003; Vatansever, 2004). Therefore, biogenic amines quantities are most of the time used to identify food quality. Cadaverine, putrescine, spermidine, spermine, tyramine, histamine, tryptamine and 2- phenylethylamine are important biogenic amines that determine food quality (Karahan, 2003).

This study was conducted to determine biogenic amines levels of dry-salted and brine-salted Van herby cheese sold in Van province. Chemical composition of these cheese was also determined and correlated with biogenic amines formation.

Biogenic amines have potential risks for public health and used as a hygiene indicator. Thus, present findings will provide an insight into whether biogenic amines of Van herby cheese produced by dry-salted and brine-salted techniques will pose a risk on human health, or if so, which one of these cheese will pose a greater risk. Then, a scientific approach will be applied to consumers in selection of Van herby cheese, and contributions will be provided to preservation of public health accordingly. Present literature reviews revealed that there were no study comparing biogenic amines levels of dry-salted and brine-salted Van herby cheese. Therefore, present study is the first one in terms of comparing biogenic amines levels of Van herby cheese matured by dry-salting and brine-salting techniques.

## 2. Materials and methods

In this study, a total of 100 Van herby cheese samples produced by dry-salting and brine-salting techniques were collected in winter (50 dry-salted and 50 brine-salted) from the grocery stores in Van province, and biogenic amines and chemical analyses were performed on these samples. Chemicals used in present analyses were all in analytical purity and quality. Analyses were performed in duplicate.

Van herby cheese samples were subjected to several chemical analyses. pH and titration acidity values of the samples were determined in accordance with Anonymous (2013); salt ratios which inverse document frequency (IDF) standard method was used. Example IDF with Metin (2012); dry matter quantities with IDF (2004); fat ratios with Anonymous (2015); total nitrous substance quantities with AOAC (2002); Protein hydrolysis ratios with TNBS method given by Polychroniadou (1988) and modified by Tunçtürk (1996). Biogenic amines analyses were conducted with high-performance liquid chromatography (HPLC) method as recommended by Eerola et al. (1993).

Pieces of Van herby cheese were sliced with a clean stainless-steel knife in order to prepare the cheese for analysis. Some parts of the Van herby cheese (2g of the sample) were randomly chosen and transferred into falcon plastic tubes, then homogenized with a metallic staff homogenizer tools (T-25 digital Ultra-Turrax from IKA-Works, Inc. Wilmington, NC, USA) for about 2 min. The homogenization was done by adding 125 µL of internal standard (1.7-diaminoheptane) with 10 mL of 0.4M perchloric acid (Merck, Darmstadt, Germany). In the next step, the homogenate samples were centrifuged (3000 rpm for 10 min under 4 °C) by high-speed refrigerated centrifuge (Hitachi Koki Co., Ltd., Tokyo, Japan) then, the extraction solvents were transferred and filtered with filter paper (Schleicher and Schuell 589 Black ribbon Ø 70mm) into a volumetric flask. The remaining (supernatant) part again was centrifuged with 10 mL perchloric acid and filtered into the same volumetric flask and then was completed to 25 mL with 0.4M perchloric acid. An aliquot of 1mL of the final extract was then used for analysis after derivatization while the remaining volume was stored at 4 °C for no more than one week.

### 2.1. Statistical analysis

Experimental data were subjected to statistical analysis using SPSS 20 software (IBM Corp., Chicago, Illinois, USA). Frequency distribution and descriptive statistics were used in statistical analyses. Kolmogorov–Smirnov test was applied to check data normality. Student-t test was used for parametric tests, and Mann–Whitney U analysis was used for nonparametric tests. Correlations were identified by Spearman's correlation test. Significance level was considered as $P < 0.05$.

## 3. Results and discussion

The results of pH values of dry and brine-salted Van herby cheese were presented in Table 1. Lower pH values of dry-

**Table 1.** Chemical characteristics of dry and brine-salted matured Van herby cheese Mean ± SD.

| Characteristics | | N | Min | Max. | Mean | P |
|---|---|---|---|---|---|---|
| pH value | Dry-salted | 50 | 3.98 | 5.34 | 4.624 ± 0.332 | < 0.001 |
| | Brine-salted | 51 | 4.03 | 6.38 | 5.161 ± 0.618 | |
| Acidity (%) | Dry-salted | 50 | 0.63 | 2.64 | 1.500 ± 0.426 | < 0.001 |
| | Brine-salted | 51 | 0.21 | 2.27 | 1.080 ± 0.599 | |
| Salt (%) | Dry-salted | 50 | 5.12 | 17.55 | 7.845 ± 2.367 | 0.281 |
| | Brine-salted | 51 | 4.24 | 11.26 | 7.150 ± 1.566 | |
| Dry matter (%) | Dry-salted | 50 | 47.9 | 77.35 | 59.065 ± 5.761 | |
| | Brine-salted | 50 | 31.05 | 70.80 | 49.222 ± 8.065 | < 0.001 |
| Fat (%) | Dry-salted | 50 | 17 | 37 | 27.000 ± 4.629 | |
| | Brine-salted | 51 | 4 | 42 | 23.431 ± 9.611 | 0.036 |
| Protein (%) | Dry-salted | 49 | 16.75 | 32.73 | 23.392 ± 3.390 | |
| | Brine-salted | 51 | 10.81 | 22.55 | 17.169 ± 2.958 | < 0.001 |
| Proteolysis (mM) | Dry-salted | 50 | 43.59 | 187.67 | 100.092 ± 31.27 | |
| | Brine-salted | 50 | 30.06 | 199.31 | 79.050 ± 38.82 | < 0.001 |

salted Van herby cheese were attributed to inclusion of concentrated acidic molecules formed through glycolysis into cheese matrix. Mean pH values of dry-salted cheese were compatible with the results of Coşkun and Öztürk (2001), while they lower than the values obtained by Çelik et al. (1998) for herby cheese and higher than the values obtained by Doğan (2012) for Siirt herby cheese. Mean pH values of brine-salted Van herby cheese were lower than the results found by Coşkun and Öztürk (2001) and Çelik et al. (1998) and higher than the values found by Doğan (2012) for herby cheese. Differences in pH values were mostly attributed to differences in raw milk, heat treatment, salt addition, additives, and maturation conditions (Demirci and Dıraman, 1990).

In our study, mean % lactic acid values of dry and brine-salted Van herby cheese were also calculated (Table 1). Higher % lactic acid levels of dry-salted Van herby cheese than its brine-salted counterparts were attributed to the same reasons explained for pH values. The % lactic acid content of dry-salted cheese samples were greater than the values of Coşkun (1998) reported for herby cheese and lower than the values of Sancak (1990) and Doğan (2012) reported for herby cheese. Mean % lactic acid content of brine-salted Van herby cheese were relatively close to the values of Sancak et al. (1996) reported for herby cheese, greater than the values of Coşkun (1998) and lower than the values of Sancak (1990) reported for herby cheese. Such differences in acidity of cheese samples were mainly resulted from the herbs added to raw material and cheese.

In the study, mean salt contents of dry and brine-salted Van herby cheese were found as 7.845% and 7.150%, respectively. Although dry-salted cheese had greater mean salt values than the brine-salted ones, the difference between the salt values of both groups were not found to be significant since salt values varied in broad range and had high standard deviation values (Table 1). Mean salt values of dry-salted cheese samples were in accordance with the values found in Sancak's (1990) study and greater than the values found in the studies of Sönmezsoy (1994) and Doğan (2012) on herby cheese. Mean salt values of brine-salted samples were similar with the values obtained by Sancak (1990) and greater than the values of Sönmezsoy's (1994) study on herby cheese. The differences in salt values were resulted from nonstandardized production and different ripening durations of Herby cheese.

Mean dry matter contents of dry and brine-salted Van herby cheese samples were 59.065% and 49.222%, respectively (Table 1). Dry matter content of dry-salted samples was about 10% greater than the dry matter content of brine-salted samples. Such a case was resulted from upside-down placement of containers of dry-salted cheese and thus more water loss in these cheeses. Mean dry matter content of dry-salted cheese samples was greater than the values obtained by Sancak (1990) and Doğan (2012) on herby cheese and lower than the values in Kiraz's (2018) study on Kargı tulum cheese. Mean dry matter content of brine-salted Van herby cheese was greater than the one found in the studies of Sönmezsoy (1994) and Akyüz and Özçelik (1993) and lower than the one obtained by Sancak (1990) on herby cheese. Differences in dry matter ratios were mainly attributed to differences in chemical composition of raw milk, ripening conditions, and random purchase of cheese samples.

In the study, fat contents of dry and brine-salted Van herby cheese samples were analyzed, and results were given in the Table 1. Mean fat content of dry-salted samples was greater than the one in the study of Akyüz and Özçelik (1993) and Yetişmeyen et al. (1992) and lower than the values found by Doğan (2012) in their studies on herby cheese. Mean fat content of brine-salted Van herby cheese samples was similar with the one of herby cheese studied by Sancak (1990), lower than the one found in Sönmezsoy's (1994) study on herby cheese and Rençber's (2016) study on Muş tulum cheese. Mean fat content of brine-salted Van herby cheese samples used in this study was also greater than the one obtained in the study of Akyüz and Özçelik (1993) and Doğan (2012) on herby cheese. Differences in cheese fat ratios were resulted from the differences in fat ratios of milk processed into cheese, nonstandardized use of raw milk.

In the protein analysis, mean protein value was identified as 23.392 % for dry-salted cheese samples and 17.169 % for brine-salted samples (Table 1). The factors affecting cheese dry matter and fat ratios were also effective in protein ratios. Mean protein content of dry-salted cheese were in compliance with the values of Kurt and Akyüz (1984), lower than the related values in Sancak et al.'s (1996) study and greater than the values in Sönmezsoy's (1994) and Doğan's (2012) study on herby cheese. Mean protein content of brine-salted Van herby cheese was lower than the related values in Sancak et al.'s (1996) and Yetişmeyen et al.'s (1992) study and greater than the values in Doğan's (2012) study on herby cheese. Such differences in cheese protein ratios were mainly resulted from differences in chemical composition of raw milk used in cheese production, use of milk of different animals, and nonstandardized production techniques.

Protein hydrolysis levels were measured over free amino groups and values of dry-salted Van herby cheese were significantly greater than the values of brine-salted ones (Table 1). In dry-salted Van herby cheese group, protein hydrolysis had significant positive correlations with tryptamine, phenylethylamine, putrescine and cadaverine levels; in brine-salted Van herby cheese group, protein hydrolysis had significant positive correlations with tryptamine, phenylethylamine, putrescine, cadaverine, histamine, and tyramine. Protein hydrolysis is among the most important processes during ripening. Protein hydrolysis softens cheese and provides significant quantity of substrate for biogenic amines formation through leading formation of free amino acids. Therefore, increasing protein hydrolysis also increases free amino acid quantities and consequently increase biogenic amines formation by microorganisms (Büyük and Marangoz, 2018).

The mean proteolysis results of dry and brine-salted Van herby cheese can be seen from the Table 1. As it was expected, dry-salted Van herby cheese had greater protein hydrolysis values than brine-salted cheese. Protein hydrolysis products of dry-salted Van herby cheese were hold in cheese matrix except for losses through package during the initial days. However, majority of protein hydrolysis products formed in brine-salted cheese are water-soluble and pass into brine until a balance of concentration between cheese matrix and brine water. Therefore, even the same quantity of protein hydrolysis was realized in dry and brine-salted cheese, lower protein hydrolysis concentrations are measured in brine-salted cheese because of dilution. Present protein hydrolysis values of dry and brine-salted Van herby cheese were greater than the values found in Tunçtürk's (1996) study on herby cheese. Different protein hydrolysis values were resulted from differences in raw milk, production techniques, storage conditions, cheese cultures, and compositions.

The results of tryptamine contents of dry and brine-salted cheeses as mean values were provided in the Table 2. There were positive correlations between protein hydrolysis and tryptamine values of both dry and brine-salted cheese (Tables 3–4). The present mean tryptamine values of dry and brine-salted cheese were lower than the values reported by Vale and Gloria (1997) and Koehler and Eintenmiller (1978) for different types of cheese and greater than the values reported by Şenel et al. (2012) for Urfa and Van herby cheese and by Yıldız-Akgül et al. (2019) for Tulum and Kashar chesses. Such differences were mainly attributed to differences in type of milk (sheep or cow), heat treatments, microflora and production processes (Andiç et al., 2010).

In the biogenic amines analyses, the obtained mean phenethylamine contents of dry and brine-salted Van herby cheese were presented in the Table 2. There were significant differences in phenethylamine contents of two cheese groups, in other words, there was a large variation in phenethylamine values of cheese and standard deviations were high (Table2). However, there were positive correlations between protein hydrolysis and phenethylamine values of both cheese types (Table 3-4). The present phenethylamine values of dry and brine-salted cheese were lower than the values reported by Koehler and Eitenmiller (1978) for different types of cheese, by Durlu-Özkaya et al. (2000) for Tulum cheese and by Durlu-Özkaya and Tunail (2000) for White cheese and greater than the values reported by Vale and Gloria (1997) for different cheese and by Yetişmeyen (2005) for Herby cheese. Differences in phenethylamine values were resulted from the differences in production processes and places.

**Table 2.** Biogenic amines levels of dry and brine-salted Van herby cheese Mean ± SD (mg/kg)

| Biogenic amines | | N | Min | Max. | Mean | P |
|---|---|---|---|---|---|---|
| Tryptamine | Dry-salted | 50 | 0 | 68.87 | 3.782 ± 9.849 | |
| | Brine-salted | 50 | 0 | 41.13 | 3.026 ± 11.550 | 0.171 |
| Phenylethylamine | Dry-salted | 49 | 0 | 70.75 | 11.449 ± 15.804 | |
| | Brine-salted | 48 | 0 | 99.38 | 9.621 ± 21.475 | 0.064 |
| Putrescine | Dry-salted | 49 | 0 | 430 | 98.447 ± 102.050 | |
| | Brine-salted | 48 | 0 | 458.72 | 81.852 ± 104.844 | 0.369 |
| Cadaverine | Dry-salted | 49 | 0 | 1976.13 | 325.127 ± 505.013 | |
| | Brine-salted | 48 | 0 | 2277.7 | 360.758 ± 683.714 | 0.994 |
| Histamine | Dry-salted | 49 | 0 | 472.5 | 124.826 ± 127.773 | |
| | Brine-salted | 48 | 0 | 565 | 133.002 ± 152.713 | 0.994 |
| Tyramine | Dry-salted | 49 | 0 | 1374.37 | 419.421 ± 330.764 | |
| | Brine-salted | 48 | 0 | 1393 | 228.792 ± 340.360 | 0.001 |
| Spermidine | Dry-salted | 49 | 0 | 0.04 | 0.001 ± 0.006 | |
| | Brine-salted | 48 | 0 | 0.04 | 0.008 ± 0.058 | 0.977 |
| Spermine | Dry-salted | 49 | 0 | 2305.63 | 279.937 ± 458.073 | |
| | Brine-salted | 48 | 0 | 350.6 | 79.769 ± 121.216 | 0.517 |

Mean putrescine values of dry and brine-salted Van herby cheese which calculated from obtained results of HPLC analysis were presented in the Table 2. Present values were lower than the values reported by Durlu-Özkaya et al. (2000) for Tulum cheese and by Durlu-Özkaya and Tunail (2000) for White cheese and greater than the values reported by Yetişmeyen (2005) for Herby cheese, by Şenel et al. (2012) for Urfa and Van herby cheese and by Yıldız-Akgül et al. (2019) for Tulum and Kashar cheese. Biogenic amines content of a cheese is close closely related to existence of microorganisms, production processes and ripening durations. Biogenic amines production of cheese generally attributed no-starter lactic acid bacteria and *Enterobacteriaceae*. Therefore, especially for sensitive individuals, there may a toxicological risk about consumption of raw milk cheese (El-Zahar, 2014).

The mean values of cadaverine belonging to dry and brine-salted Van herby cheese can be seen from the Table 2. There were positive correlations between protein hydrolysis and cadaverine values of both cheese types (Table 3-4). The present mean cadaverine values of dry and brine-salted Van herby cheese were greater than the values reported by Vale and Gloria (1997) for different types of cheese, by Yetişmeyen (2005) for Herby cheese, by Valsamaki et al. (2000) for Feta cheese, by Şenel et al. (2012) for Urfa and Van herby cheese and by Yıldız-Akgül et al. (2019) for Tulum and Kashar cheese. The differences in cadaverine values of the cheese were resulted from production processes and contaminations (Durlu-Özkaya et al., 2000). *Enterobacteriaceae* family and *pseudomonas* species are considered as the primary cadaverine sources (Bunka et al., 2012). High cadaverine values were attributed to production and accumulation of biogenic amines in cheeses and the other fermented foods facilitated by physiochemical attributes (free amino acids, water activity, pH, salt, moisture and temperature) and microorganism (Gardini et al, 2005; Schirone et al, 2011). The cheeses with long maturation period also contribute to high biogenic amines quantities because of pyrolysis.

In the sample analyzed; the mean histamine values of dry and brine-salted Van herby cheese are provided in (Table 2). There were not any positive correlations between protein hydrolysis and histamine values of dry-salted Van herby cheese, but positive correlations were observed between protein hydrolysis and histamine values of brine-salted ones (Table 3-4). The present mean histamine values of dry and brine-salted Van herby cheese were greater than the values reported by Vale and Gloria (1997) for different types of cheese, by Yetişmeyen (2005) for Herby cheese, by Valsamaki et al. (2000) for Feta cheese, by Noyan et al. (2004) for White cheese, by Durlu-Özkaya et al. (2000) for Tulum cheese, by Andiç et al. (2015) for Herby cheese, by Şenel et al. (2012) for Urfa and Van herby cheese and by Yıldız-Akgül et al. (2019) for Tulum and Kashar cheese. It is assumed that various herbs used in cheese production resulted in increased histamine quantity.

The mean tyramine values of dry and brine-salted Van herby cheese can be seen from the Table 2. There were

**Table 3.** Correlation levels between the parameters measured in the Van Herb cheese group matured by the pressing method.

| Analitler | pH value | Acidity | Salt | Fat | protein | Dry matter | Tryptamine | Phenylethylamine | Putrescine | Cadaverine | Histamine | Tyramine | Spermidine | Spermine | Proteolysis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH value | 1.000 | **–.540**** | .051 | .132 | .134 | .227 | .124 | -.172 | .104 | .106 | .032 | -.098 | -.174 | .200 | -.137 |
| Acidity | | 1.000 | –.056 | –.104 | –.007 | –.057 | –.044 | .231 | .161 | .049 | .106 | .224 | .051 | –.215 | .231 |
| Salt | | | 1.000 | –.126 | –.207 | .003 | **–.317*** | **–.563**** | **–.526**** | **–.431**** | .097 | –.226 | –.133 | **–.285*** | **–.420**** |
| Fat | | | | 1.000 | .217 | **.564**** | –.165 | .138 | .167 | .242 | .259 | .239 | 0.000 | –.176 | –.015 |
| Protein | | | | | 1.000 | .252 | –.212 | **.319*** | .233 | .188 | .163 | .074 | .163 | –.119 | .221 |
| Dry matter | | | | | | 1.000 | –.108 | .011 | .211 | **.294*** | .280 | .086 | .051 | –.188 | –.008 |
| Tryptamine | | | | | | | 1.000 | .272 | .220 | .268 | **–.516**** | .046 | –.068 | **.553**** | **.400**** |
| Phenylethylamine | | | | | | | | 1.000 | **.463**** | **.465**** | .081 | **.413**** | –.073 | .083 | **.610**** |
| Putrescine | | | | | | | | | 1.000 | **.798**** | .264 | **.372**** | .051 | –.171 | **.408**** |
| Cadaverine | | | | | | | | | | 1.000 | .189 | **.289*** | .082 | –.107 | **.368**** |
| Histamine | | | | | | | | | | | 1.000 | **.503**** | .005 | **–.638**** | –.132 |
| Tyramine | | | | | | | | | | | | 1.000 | .112 | –.198 | .250 |
| Spermidine | | | | | | | | | | | | | 1.000 | –.132 | .061 |
| Spermine | | | | | | | | | | | | | | 1.000 | .256 |
| Proteolysis | | | | | | | | | | | | | | | 1.000 |

* $P < 0.05$ , ** $P < 0.01$.

**Table 4.** Correlation levels between the parameters measured in the Van herby cheese group matured by the brine method.

| Analitler | pH value | Acidity | Salt | Fat | Protein | Dry matter | Tryptamine | Phenylethylamine | Putrescine | Cadaverine | Histamine | Tyramine | Spermidine | Spermine | Proteolysis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH value | 1.000 | **–.814**** | –.035 | **–.332*** | –.150 | **–.289*** | .123 | –.281 | **–.402**** | **–.453**** | **–.472**** | **–.562**** | –.079 | –.125 | **–.473**** |
| Acidity | | 1.000 | .103 | **.394**** | **.368**** | **.397**** | .166 | **.346*** | **.499**** | **.578**** | **.686**** | **.564**** | .237 | .212 | **.718**** |
| Salt | | | 1.000 | .050 | –.048 | –.027 | –.044 | –.258 | –.064 | .033 | .211 | .072 | .221 | .099 | –.121 |
| Fat | | | | 1.000 | .033 | **.489**** | –.002 | .007 | .174 | .255 | **.455**** | .204 | .237 | .174 | .269 |
| Protein | | | | | 1.000 | **.450**** | .126 | .188 | .116 | .079 | .216 | .187 | .237 | –.190 | **.493**** |
| Dry matter | | | | | | 1.000 | .014 | .022 | .144 | .193 | **.384**** | .244 | –.076 | .007 | **.455**** |
| Tryptamine | | | | | | | 1.000 | **.490**** | **.457**** | **.474**** | **.448**** | .252 | –.044 | .128 | **.292*** |
| Phenylethylamine | | | | | | | | 1.000 | **.729**** | **.631**** | **.357*** | **.432**** | .141 | –.081 | **.341*** |
| Putrescine | | | | | | | | | 1.000 | **.883**** | **.480**** | **.487**** | .111 | –.124 | **.415**** |
| Cadaverine | | | | | | | | | | 1.000 | **.603**** | **.583**** | .153 | .071 | **.506**** |
| Histamine | | | | | | | | | | | 1.000 | **.568**** | .134 | **.409**** | **.599**** |
| Tyramine | | | | | | | | | | | | 1.000 | .174 | .118 | **.440**** |
| Spermidine | | | | | | | | | | | | | 1.000 | .049 | .079 |
| Spermine | | | | | | | | | | | | | | 1.000 | .159 |
| Proteolysis | | | | | | | | | | | | | | | 1.000 |

* $P < 0.05$ , ** $P < 0.01$.

not any positive correlations between protein hydrolysis and tyramine values of dry-salted Van herby cheese, but significant positive correlations were observed between protein hydrolysis and tyramine values of brine-salted Van herby cheese (Table 3-4). The present tyramine values of dry and brine-salted Van herby cheese were lower than the values reported by Valsamaki et al. (2000) for Feta cheese and greater than the values reported by Yetişmeyen (2005) for Herby cheese, by Durlu-Özkaya and Tunail (2000) for White cheese, by Andiç et al. (2015) for Herby cheese, by Şenel et al. (2012) for Urfa and Van herby cheese and by Yıldız-Akgül et al. (2019) for Tulum and Kashar cheese. Greater tyramine values indicated enterococci contamination of the cheese before, during and after production (Joosten and Northolt,1987).

The mean spermidine values of dry and brine-salted Van herby cheese were given in the Table 2. The present mean spermidine values of dry and brine-salted Van herby cheese were lower than the values reported by Ekici et al. (2019) for Herby cheese (0.17 mg/kg), by Komprda et al. (2007) for Netherland type hard cheese (0.3 mg/kg) and by Bonczar et al. (2018) for acid and rennet coagulated cheese (7.74 mg/kg). Existence of this biogenic amines indicates poor hygiene of the raw milk used in cheese production (Andiç et al.,2010).

The mean spermine values calculated using the results obtained in our study for dry and brine-salted Van herby cheese can be seen from the Table 2**.** Although the difference between the mean values of two cheese groups is too high, the difference was not found statistically significant as a result of large variation in both groups' values and high standard deviation values (Tables 2–4). The present mean spermine values of dry and brine-salted cheese were greater than the values reported by Ekici et al. (2019) for herby cheese (0.25 mg/kg), by Komprda et al. (2007) for Netherland type hard cheese (0.2 mg/kg), and by Bonczar et al. (2018) for acid and rennet-coagulated cheese (5.70 mg/kg).

As discussed here, there are several previous studies conducted about biogenic amines levels of various types of cheese as well as Van herby cheese. However, present literature reviews revealed that there were not any studies comparing biogenic amines levels of dry-salted and brine-salted Van herby cheese. Therefore, present study is the first one in terms of comparing biogenic amines levels of cheese matured through dry-salted and brine-salted techniques. Within the scope of this study, 8 different biogenic amines (tryptamine, phenethylamine, putrescine, cadaverine, histamine, tyramine, spermidine, and spermine) levels of cheese samples produced with two different techniques were measured and compared. Among the investigated biogenic amines, only tyramine levels of dry-salted Van herby cheese were significantly greater (almost double) than the tyramine levels of brine-salted ones. There were not any significant differences in other biogenic amines levels of dry and brine-salted Van herby cheese.

There were significant differences in pH value, acidity, dry matter content, protein content, and protein hydrolysis values of dry and brine-salted Van herby cheese. Greater tyramine levels of dry-salted Van herby cheese were attributed to these chemical differences; dry-salted Van herby cheese had significantly greater protein content than brine-salted ones. Such a case indicated that dry-salted ones might have greater tyrosine amino acid content and thus greater tyramine contents because of greater tyrosine decarboxylation. However, correlations between protein hydrolysis and tyramine values of both groups were not supporting that idea (Tables 3–4). Thus, while there were not any significant correlations between protein hydrolysis and tyramine values of dry-salted Van herby cheese, there was a significant positive correlation in brine-salted ones. There was a negative correlation between tyramine and pH and a positive correlation between tyramine and acidity in brine-salted group, not in dry-salted group. There were significant differences in acidity and pH values of dry and brine-salted Van herby cheese; such differences may also result in greater tyramine levels of dry-salted Van herby cheese. Further studies are needed to better elucidate the differences in tyramine levels of both groups. The findings revealed that biogenic amines levels of both cheese groups were below the toxic level of 1000 mg/kg.

## 4. Conclusion

In conclusion, it was observed that dry-salted cheese had almost twice as much tyramine levels as brine-salted ones, and such a difference was found to be significant. Significance of such findings should be proved with further research to be conducted with immunologist for "cheese reaction" of sensitive individuals. Such detailed studies may bring limitations to sensitive people prone to allergic reactions for the consumption of dry-salted Van herby cheese. However, the findings are not sufficient to bring a preference between dry and brine-salted Van herby cheese based on biogenic amines levels. Therefore, there is a need for further detailed and supportive research. Considering the differences in tyramine levels, it can now only be recommended that individual's prone allergic reactions should always keep that issue in mind.

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