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DEVELOPMENT OF AN ASSORTMENT OF SEMI-HARD CHEESE WITH THE ADDITION OF ZA`ATAR AS A FUNCTIONAL INGREDIENT

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Abstract: *Migrating through a healthy diet is a must. Including in the daily diet as high a percentage of functional foods as possible must be a priority for the population. Za`atar is a mix of herbs rich in bioactive compounds that possess beneficial properties on the human body.(Khalil, și alții, 2022)The present study aims to diversify the assortment range of cheeses by obtaining a semi-hard cheese matured in za`atar. In this study, the sensory and physico-chemical effects of za`atar on semi-hard cheese during the ripening period, when za`atar is used as a coating for cheese pieces, were addressed. The ripening period of the semi-hard cheese was 40 days, and the analyses were performed on the first day, in the middle of the period and on the last day, by comparison with a classic semi-hard cheese (without addition) produced under similar conditions. Very good results in terms of sensory analysis using a non-numerical method were obtained by cheese with za`atar coating, especially from the second part of the ripening process. Adding a coating of za`atar to the surface of the cheese does not change much the physico-chemical parameters of the cheese.*

Key words: *semi-hard cheese, za`atar, ripened cheese, ripening conditions.*

1. Introduction

Semi-hard cheeses are characterized by a firm texture but not as dry and crumby as hard cheese. The production of semi-hard cheese involves some particularities in the technological process. Coagulation of semi-hard cheeses takes place at higher temperatures of 32-34°C. The second heating of the curd at a temperature of 38-45°C is applied, followed by strong pressing to remove a large amount of whey, and the maturation period is 1-2 months. Compared to hard cheese, the second heating is at a lower temperature and the ripening period is shorter. The microorganisms used for coagulation differ according to the variety.

Semi-hard cheese has a smooth rind, yellowish color, rare fermentation meshes, elastic consistency, homogeneous throughout the mass.

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Diversification of the range of hard and semi-hard cheeses is a common practice. There are currently on the market cheeses appreciated by consumers with additions of various spices, nettles, garlic, onions, mustard, herbs, clovers, etc.. Besides diversifying the flavor, the objectives of adding herbs to cheese making are to extend the shelf life of the cheese by reducing the microflora leading to a healthy cheese and preventing physical defects by reducing the salt concentration [3, 14].

Including herbs and spices and condiments for replacing the salt in cheese to give the perceived saltiness may be successful especially for lightly-flavoured cheeses [7].

Za`atar is of economic and cultural importance in the Mediterranean region. Za`atar is a mixture of herbs that includes *Origanum*, *Satureja*, *Thymbra*, and *Thymus* with high content of essential oil, especially carvacrol and thymol [1, 9].

The Lebanese herbal mixture "Za'atar" should be considered a healthy food ingredient due to the combined presence of several bioactive compounds with possible beneficial outcomes on human health, as shown by in vitro, in vivo, and clinical studies. The combined action of Za'atar constituents is able to generate comprehensive beneficial effects on several common pathogenic pathways underlying chronic cardio-metabolic diseases and cancer. However, main available evidence derives from animal and in vitro studies. Thus, further human studies are needed to fully characterize Za'atar as a preventive and curative tool [9].

Origanum syriacum & isolate RA possessed in vitro anti-inflammatory, antioxidant and antibacterial properties [12].

Thymbra spicata/ wild thyme also enjoys antibacterial, anti-inflammatory and antioxidant properties. Also an in vitro study shows the antisteatotic and antioxidant activities of Thymbra spicata extracts in liver cells for the treatment of non-alcoholic fatty liver disease [10].

Rhus coriaria / Sumac has the ability to lower blood glucose according to some in vivo studies, has hypolipidemic, hypercholesterolemic properties [5].

Sesamum indicum/ Sesame has in vivo effects and has anti-inflammatory, anti-atherosclerotic and hypercholesterolemic properties [4].

The objectives of this study were to develop an assortment of semi-hard cheese that would include the unique flavor and color that za`atar imparts to the cheese during the ripening process. The physico-chemical effects during the ripening process were also investigated in order to identify if there are major transformations in the cheese due to the addition of za`atar.

2. Materials and Methods

2.1. Materials

The sheep's milk was purchased from a sheep breeder in Sibiu County.

The cheese culture used was purchased from Choozit, having a composition of *Lactococcus lactis subsp. Lactis* and *Lactococcus lactis subsp. Cremoris*. This was added to the milk according to the manufacturer's instructions.

The rennet powder used to coagulate the milk was purchased from the phytopharmacy.

The calcium chloride used was purchased from the phytopharmacy.

The salt was bought from a local store.

Za`atar spice was purchased from a supermarket.

2.2. Methods

The cheese was made in the laboratory of the Food Biotechnology Research Center, respecting the classic technology for obtaining semi-hard cheese. The technological operations used are: the milk was pasteurized for 30 minutes at a temperature of 62°C, cooled to 30°C and seeded with the starter culture and left to ripen for 30 minutes at the cooling temperature, then calcium chloride was added (15 g / 100 l) and clot. The coagulation time was 45 minutes, following a cutting of the coagulum into cubes up to a size of the coagulum grain of 4 mm. The coagulum mass was left to rest for 5 minutes, after which the second heating was done at a temperature of 42°C, the duration being 10 minutes. After this technological phase, the coagulum grains were placed in molds and subjected to pressing, after which salting was done in brine with a concentration of 18%, at a temperature of 15°C for 2 days. The salted pieces passed through the za`atar, forming a coating, and then passed to the ripening operation. The ripening lasted for 40 days by applying certain ripening conditions, which lead to obtaining a type of cheese with a certain flavor, which can become a unique assortment of cheese. The cheese was stored for ripening in rooms with an air temperature of 15-17°C for 40 days.

2.3. Analysis Methods

2.3.1. Sensory Analysis

The samples were analyzed from a sensory point of view on the first day of storage, the 20th day and the 40th day by a team of 5 amateur tasters, consumers of semi-hard cheese.

To perform the sensory analysis, a non-numerical multi-criteria multi-personal agreement method described by Fadhil et al. [6] was used.

The observed characteristics were consistency, color, stickiness, taste and odor. Table 1 shows the evaluation scale used, and Table 2 shows the level of importance of the criteria based on the scale.

Linguistic assessment scale Table 1

Scale	Description	Abbreviation
1	Like very much	LV
2	Like moderately	LM
3	Like Slightly	LS
4	Neither like nor dislike	NT
5	Dislike slightly	DS
6	Dislike moderately	DM
7	Dislike very much	DV

Criteria importance level Table 2

Scale	Description	Abbreviation
1	Very high	LV
2	High	LM
3	Neither like nor dislike	NT
4	Low	DM
5	Very low	DV

After establishing the evaluation scale and the level of importance of the criteria, a matrix of evaluation criteria was formulated based on the opinion of the evaluators and the chosen alternative. The determination of the negation of the level of importance of the criteria was done using the Equation (1):

$$Neg(W_k) = (W_{a-k+1}) \quad (1)$$

where:
$Neg(W_k)$ is the core negation of criteria k;
k – the index;
q – the scale amount.

For the approval process based on criteria, the Equation (2) was used:

$$V_{ij} = \min[Neg(W_{ak}) \vee V_{ij}(a_k)] \quad (2)$$

where:
V_{ij} is the score of alternative i by person j;
$V_{ij}(a_k)$ – the score of alternative i by person j on criteria k;
k – 1, 2, …., m.

Determining score using the Equation (3):

$$Q_k = Int\left[1+\left(k.\frac{q-1}{r}\right)\right] \quad (3)$$

where:
Q_k is the score k;
Int – the integer;
R – the number of assessors.

Aggregation process for a person (assessor) using the Equation (4):

$$V_i = f(V_i)\cdot\max[Q_j \wedge b_j] \quad (4)$$

wehere:
V_i is the total value for alternative I;
Q_j – the score j;
J – 1, 2, …, *m;*
b_j – the order from the highest alternative score i from alternative score j.

2.3.2. Physico-Chemical Analyses

A. pH Determination

The pH meter was used to determine the pH. The electrodes of the pH meter were inserted into the sample to be analyzed and the results were read and expressed in pH units.

B. Determination of Titratable Acidity

The acidity in a certain volume of the sample prepared for analysis is neutralized by titration with 0.1 n sodium hydroxide solution, in the presence of phenolphthalein as an indicator. The

results were calculated with Equation (5) and were expressed in Thorner degrees [2].

$$A = \frac{V}{m} \cdot 100 \qquad [°C] \qquad (5)$$

where,

V is the volume of sodium hydroxide 0.1 *n* used in the titration [cm^3];

m - the mass of the analyzed sample [g].

C. Determination of Humidity with the Thermobalance

The determination of the dry matter consisted in the determination of the mass loss observed when the sample was heated and determined according to the loss of water content [8, 13].

D. Determination of the Salt Content by the Argentometric Method

Chlorides are extracted from the sample with warm water (70-80°C), and chlorine ions are titrated with a silver nitrate solution in the presence of potassium chromate as an indicator [13].

E. Determination of Water Activity

The water activity of this product was determined using the "Novasina" apparatus. The sample was crushed and inserted into special plastic ampoules, after which the ampoules were inserted one by one into the apparatus, where the activity of the water in the product was determined based on the ratio between the vapor pressure of pure water and the vapor pressure of the water above the sample, the 2 being at the same temperature as the sample (in this case 25°C) [13].

2.4. Statistical Analysis

The results obtained for the physico-chemical analysis of the samples were processed using the Minitab 20 software [11].

3. Results and Discussion

3.1. Sensory Analyses – Determining Alternatives

In the initial stage, the calculation of the negation of the importance level of the criteria was carried out using the Equation (1), thus the negation of the weight value of the criteria was obtained based on each index (*k*). The results of the calculation of the denial of the criteria are presented in Table 4. The opinions of the tasters obtained are presented in Table 5

Negating the importance level of the criteria Table 3

The importance level of the criteria		Negating the importance level of the criteria	
Criterion 1 =	Very high	Criterion 1 =	Very low
Criterion 2 =	High	Criterion 2 =	Low
Criterion 3 =	Neither like nor dislike	Criterion 3 =	Neither like nor dislike
Criterion 4 =	Low	Criterion 4 =	High
Criterion 5 =	Very low	Criterion 5 =	Very high

Evaluation criteria for all alternatives Table 4

Persons	Alternative	Evaluation criteria														
		Consistency			Stickiness			Color			Taste			Odor		
		Day 1	Day 20	Day 40	Day 1	Day 20	Day 40	Day 1	Day 20	Day 40	Day 1	Day 20	Day 40	Day 1	Day 20	Day 40
P1	A1	LV	LM	LM	LS	LS	LM	LV	LV	LV	LM	LV	LV	LM	LM	LV
	A2	LM	LM	LM	LS	LS	LM	LM	LM	LV	LM	LM	LV	LM	NT	LM
P2	A1	LM	LS	LM	LM	LM	NT	LS	LM	LM	LM	LM	LM	LM	LM	LM
	A2	LS	LM	LV	NT	LM	LM	LS	LM	LM	LM	LV	LM	LS	LM	LV
P3	A1	NT	LV	LM	LS	LM	LM	LM	LM	LV	LS	LM	LV	LS	LM	LV
	A2	NT	LM	LM	LS	LM	LM	LM	LM	LV	LS	LM	LV	LM	LM	LV
P4	A1	LS	LM	LM	LM	LM	LM	LM	LM	LS	LS	LM	LM	NT	LS	LM
	A2	NT	LM	LM	LS	LM	LM	LS	LS	LM	LM	LM	LV	LM	LM	LM
P5	A1	LM	LM	LM	NT	LS	LS	LM	LM	LM	LM	LM	LM	LM	LV	LV
	A2	LM	LV	LV	LS	LS	LS	LS	LM	LM	LM	LV	LM	LM	LM	LV

where:

A1 is the semi-hard cheese classic;

A2 – the semi-hard cheese with Za`atar.

3.2. Sensory Analyses - Determination of Criteria

According to the opinion of the tasters, the approval criteria for each alternative were calculated using Equation (2), so each alternative, the following results were obtained:

1. Day 1 of storage

The results of the approval criteria for alternative 1 are = LS, LS, LS, LS, NT.

The results of the approval criteria for alternative 2 are = LS, NT, NT, NT, LS.

2. Day 20

The results of the approval criteria for alternative 1 are = LS, LS, LS, LS, LS.

The results of the approval criteria for alternative 2 are = LS, LM, LS, LM, LS.

3. Day 40

The results of the approval criteria for alternative 1 are = LM, NT, LM, LM, LM.

The results of the approval criteria for alternative 2 are = LM, LM, LM, LM, LM.

3.3. Sensory Analyses - Determination of Tasters

Before calculating the approval process of a taster, we used Equation (3) to determine the value weights.

The value weights for Q1, Q2, Q3, Q4, Q5 are DM, DS, NT, LS, LS.

To determine the approval process of the tasters, we used Equation (4).

1. Day 1

The result of the tasters' approval process for alternative 1 on day 1 is LS (Like slightly).

The result of the tasters' approval process for alternative 2 on day 1 is NT (Neither like nor dislike).

2. Day 20

The result of the tasters' approval process for alternative 1 on day 20 is LS (Like slightly).

The result of the tasters' approval process for alternative 2 on day 20 is LS (Like slightly).

3. Day 40

The result of the tasters' approval process for alternative 1 on day 40 is LS (Like slightly).

The result of the tasters' approval process for alternative 2 on day 40 is LS (Like slightly).

On the first day of storage, the sample of classic semi-hard cheese obtained a higher score (like slightly), which is preserved during the storage period. The semi-hard cheese coated with Za`atar obtained a lower score on the first day of storage (Neither like nor dislike), which increased on days 20 and 40 (Like slightly). This may be due to the fact that the spice mixture on the surface of the cheese became uniform with the aroma of the matured cheese during the storage period, as compared to the first day when the two aromas were distinguished differently.

3.4. Physico-chemical analyses

3.4.1. pH

As can be seen in Figure 1, during the 40 days of storage, the pH of the cheese samples decreases due to the accumulation of lactic acid. The lowest results for pH were obtained for the classic semi-hard cheese, the semi-hard cheese with Za`atar coating scored slightly higher.

3.4.2. Determination of Titratable Acidity

Figure 2 shows that the acidity of cheeses increases during the storage period, due to the continuation of the fermentation process through the action of lactic bacteria on lactose. Lower results for acidity were obtained by cheese with semi-hard paste and Za`atar coating throughout the storage period.

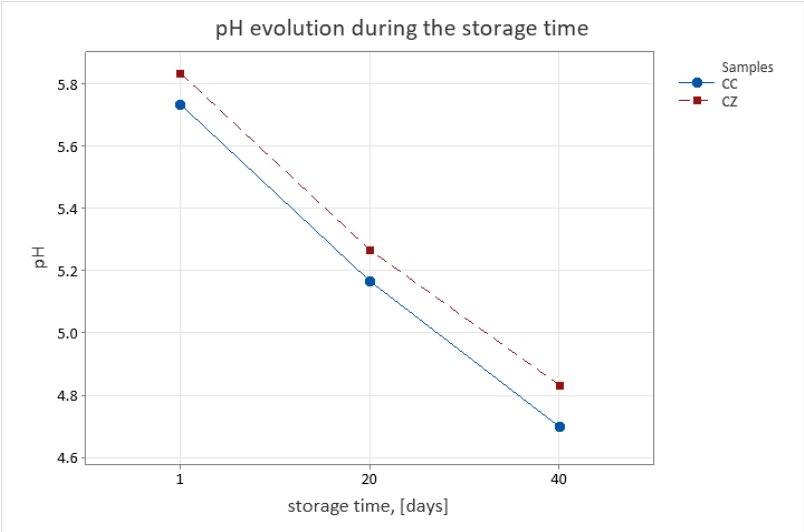

Fig. 1. *pH evolution during the storage time*

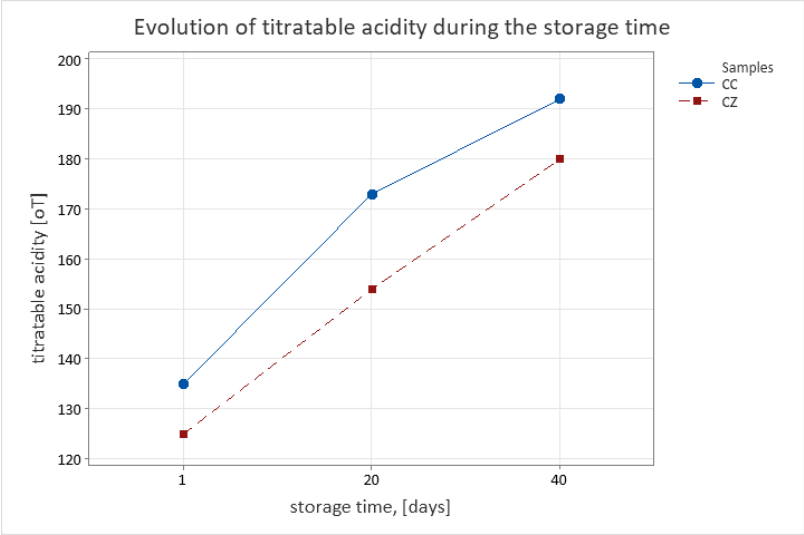

Fig. 2. *Evolution of titratable acidity during the storage time*

3.4.3. Determination of Dry Matter with the Thermobalance

As can be seen in Figure 3, during storage days, the dry substance content of the samples increases due to the qualitative and quantitative changes that take place in the ripening process, such as the dehydration of the cheese, which will give the specific consistency of each variety of cheese.

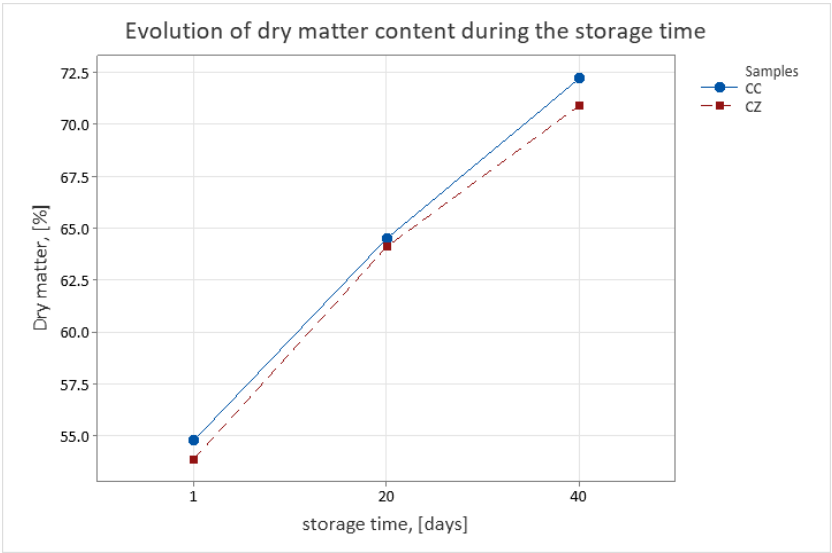

Fig. 3. *Evolution of dry matter content during the storage time*

3.4.4. Determination of the NaCl Content

As can be seen in Figure 4, during the storage period the sodium chloride content of the cheese samples increases, this is due to the dehydration that occurs during the ripening process. Higher results in terms of sodium chloride content were observed for the cheese without additions, but also a more intense dehydration.

3.2.5. Determination of water activity

During the 40 days of storage, the water activity decreases in the case of both Pecorino cheese samples, as this can be seen in Figure 5.

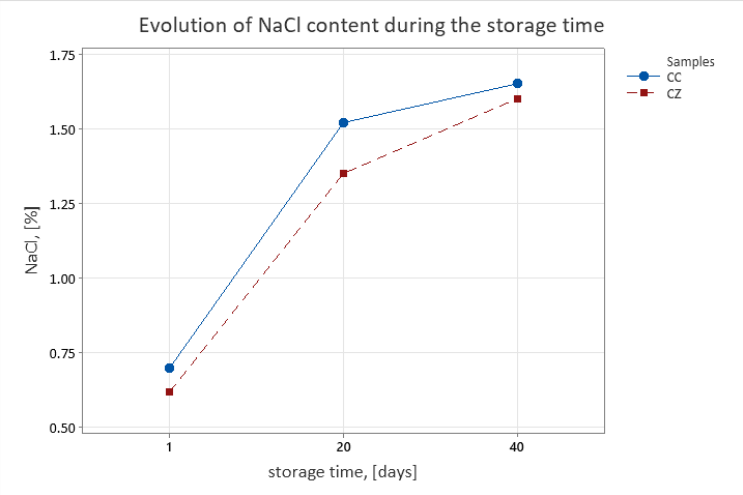

Fig. 4. *Evolution of NaCl content during the storage time*

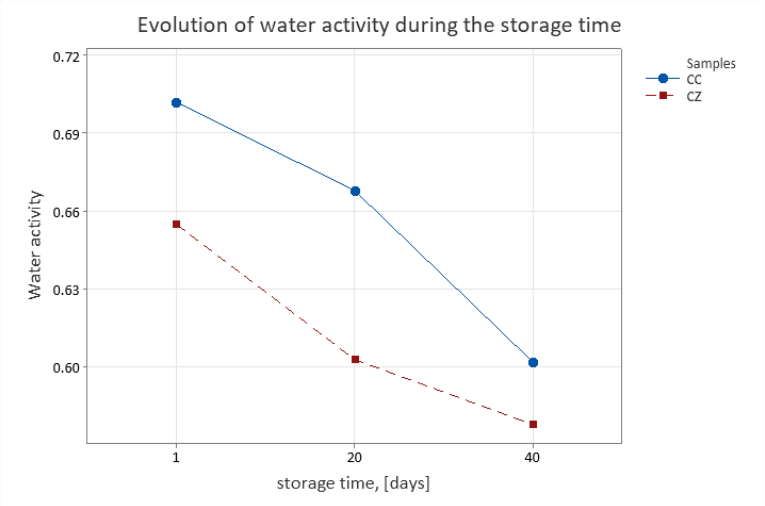

Fig. 5. *Evolution of water activity during the storage time*

Water activity is an important indicator of food safety for consumption. When the values exceed 0.60, the product may undergo changes. If a food has a water activity of 0.60, and the humidity in the air is 70%, the product will absorb water vapor from the air, until the water activity in the product reaches a balance with the humidity in the air.

The cheese without the addition of Za`atar coating obtained higher values, from which we can conclude that the coating of spices on the surface of the cheese can modify the moisture transfer between the product and the ambient environment.

4. Discussion

Consumer interest in functional food is constantly growing. The development of foods that also include functional ingredients in their recipe should be a common practice especially if these ingredients can be consumed as such, without being thermally processed.

The development of a semi-hard cheese with Za`atar represents a potential for the cheese industry, especially because the health benefits that these plants contain are known.

Regarding the sensory analysis carried out over a period of 40 days on the first day, the 20^{th} day and the 40^{th} day, the cheese with Za`atar obtained good scores especially from the second part of the technological process. This may be due to the fact that with ripening, the flavors that the Za`atar imparts to the cheese have also become uniform.

By the addition of Za`atar, significant changes were registered for the color of the cheese, which acquired a reddish brown color on the outside, the taste became slightly spicy specific to the herbs in the Za`atar composition, and the smell was also modified. These things were appreciated by the 5 tasters.

In terms of physico-chemical analysis, Za`atar does not greatly modify the characteristics of the cheese. As we can see from the previous graphs, the results show that the water activity has been improved. Slightly lower values were also obtained for acidity, dry matter and salt content.

5. Conclusion

The resulting Za`atar cheese variant has a firm texture, salty and slightly spicy taste, the outer part has a brown color due to the Za`atar coating. Between the control sample and the sample with Za`atar there are no significant differences related to texture, acidity, pH, moisture, but the taste and smell differ from the classic one.

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References

1. Alwafa, R.A., Mudalal, S., Mauriello, G., 2021. *Origanum syriacum* L. (Za'atar) from raw to go: a review. In: Plants, vol. 10(5), ID article 1001. DOI: 10.3390/plants10051001.
2. AOAC, 2015. Official methods of analysis (18th Edition). Association of Official Analytical Chemists, Maryland, U.S.A.
3. Charles, D.J., 2013. Antioxidant properties of spices, herbs and other sources. Springer, Science+Business Media, New York, U.S.A., 612 p. DOI: 10.1007/978-1-4614-4310-0.
4. Deme, P., Narasimhulu, C.A., Parthasarathy, S., 2018. Identification and evaluation of anti-inflammatory properties of aqueous components extracted from sesame (*Sesamum indicum*) oil. In: Journal of Chromatography B, vol. 1087-1088, pp. 61-69. DOI: 10.1016/j.jchromb.2018.04.029.
5. Doğan, A., Çelik, I., 2016. Healing effects of sumac (*Rhus coriaria*) in streptozotocin-induced diabetic rats. In: Pharmaceutical Biology, vol. 54(10), pp. 2092-2102. DOI: 10.3109/13880209.2016.1145702.
6. Fadhil, R., Agustina, R., Hayati, R., 2020. Sensory assessment of sauerkraut using a non-numeric approach based on multi-criteria and multi-person aggregation. In: Bulletin of the Transilvania University of Brasov, Series II – Forestry, Wood Industry, Agricultural Food Engineering, vol. 13(62), no. 2, pp. 111-118. DOI: 10.31926/but.fwiafe.2020.13.62.2.10.
7. Farkye, N.Y., Guinee, T.P., 2017. Low-fat and low-sodium cheeses. In: Cheese chemistry, physics and microbiology, 4th Edition. Elsevier Academic Press, London, United Kingdom, pp. 699-714.
8. ISO 5534, 2004. Cheese and processed cheese. Determination of the total solids content (Reference method). Available at: https://www.iso.org/standard/35249.html. Accessed on: October, 2023.
9. Khalil, M., Caponio, G.R., Diab, F. et al., 2022. Unraveling the beneficial effects of herbal Lebanese mixture "Za'atar". History, studies, and properties of a potential healthy food ingredient. In: Journal of Functional Food, vol. 90, ID article 104993. DOI: 10.1016/j.jff.2022.104993.
10. Khalil, M., Khalifeh, H., Baldini, F. et al., 2019. Antisteatotic and antioxidant activities of *Thymbra spicata* L. extracts in hepatic and endothelial cells as in vitro models of non-alcoholic fatty liver disease. In: Journal of Ethnopharmacology, vol. 15(239), ID article 111919. DOI: 10.1016/j.jep.2019.111919.
11. Minitab, 2023. Minitab. Available at: https://www.minitab.com/en-us/. Accessed on: October, 2023.
12. Shen, D., Pan, M.-H., Wu, Q.-L. et al., 2010. LC-MS method for the simultaneous quantitation of the anti-inflammatory constituents in oregano (*Origanum* species). In: Journal of Agricultural and Food Chemistry, vol. 58(12), pp. 7119-7125. DOI: 10.1021/jf100636h.
13. Tița, M., 2002. Handbook of Quality Analysis and Control in the Dairy Industry (in Romanian). Lucian Blaga University Publishing House, Sibiu, Romania.

14. Witkowska, D. Hickey, D., Alonso-Gomez, M. et al., 2013. Evaluation of antimicrobial activities of commercial herb and spice extracts against selected food-borne bacteria. In: Journal of Food Research, vol. 2(4), pp. 37-54. DOI: 10.5539/jfr.v2n4p37.