Development of technology of cottage cheese enriched with iodine and succinic acid

O L Ladnova, L S Bolshakova, A V Kuzina, E V Izvekova, E G Merkulova and L A Ashikhina

Orel State University of Economics and Trade, 12, Oktyabrskaya Str., Orel, 302028, Russia

E-mail: ladnovaol@mail.ru

Abstract. The creation of innovative food products using natural functional ingredients that can prevent the development of nutrition-dependent diseases is the main state policy in the public health of the Russian Federation. The article considers the possibility of using Succinic Acid (SA) and iodine-containing additives in the production of dairy products. The impact of various dosages of SA on the technological parameters of cottage cheese (cottage cheese yield, acidity, mass fraction of moisture) was studied. The optimal conditions for producing cottage cheese from milk with the addition of "Iodcasein" and "Bioiod" were determined. It was found that the most complete extraction of proteins occurs at a dosage of SA 0.2-0.4% to the mass of milk at 90ºC. It was found that additives have a positive effect on the organoleptic properties of cottage cheese, contribute to an increase in organic acids and iodine. The organic acid content for samples without iodine-containing additives increased by 8.8% (p≤0.05): for samples with "Iodcasein" – by 7.1% (p≤0.05) and with "Bioiod" – by 7.2% (p≤0.05). A sensory evaluation of the organoleptic properties of the obtained product showed a high quality of the creating product.

1. Introduction

Cottage cheese is a protein fermented milk product with high nutritional and dietary properties. The priority areas for the development of technology and assortment of cottage cheese are to increase the mass fraction of protein substances, product yield of the high nutritional and biological value. At present, rich experience by using of various additives in the production of cottage cheese has been accumulated. As additives, honey, vegetable raw materials and products of its processing, natural preservatives are used [1-4]. The use of additives allows one not only to improve the quality, nutritional value, to expand the range of products, but also to give products therapeutic and preventive properties.

The elimination of iodine deficiency remains an important international medical and social problem [5]. The main way to prevent and treat iodine deficiency is to include iodine-rich foods in the diet. According to the principles developed by the World Health Organization, it is necessary to enrich mass consumption products, such as milk and dairy products, as well cottage cheese. Curd formulations with the addition of iodine-containing plant materials, microbiological synthesis products, and inorganic iodine compounds have been developed [6–9]. The most promising ones for use in the technology of iodized cottage cheese are milk iodized proteins. In them, iodine is covalently bound to amino acids, which ensures its safety at all stages of dairy production.
Currently, in the production of cottage cheese, the coagulation of milk proteins is carried out with acid, rennet, acid-rennet, acid curdle and thermo-calcium methods. The acid coagulation method involves coagulation of milk proteins under the action of lactic acid formed from lactose as a result of lactic acid fermentation or as a result of the addition of food acids to milk [10]. SA can be used as an acid component in the production of cottage cheese. This substance has a powerful healing effect without side effects and addiction. SA stimulates the production of energy in cells, enhances cellular respiration, promotes the absorption of oxygen by cells, tissues and organs and has a powerful antioxidant effect; improves the work of most organs (brain, heart, kidneys, liver, etc.), strengthens the immune system, normalizes the nervous system; activates a number of important enzymes. SA suppresses inflammatory processes (normalizes the content of histamine and serotonin), neutralizes a large number of poisons (including from smoking, alcohol and drugs), prevents the onset of tumors and inhibits the growth of existing ones [11].

At present, quite a lot of technologies have been developed for enriched curd products, but given the current high demand for iodized products, as well as the insufficient study of the use of SA as a coagulant of milk protein, the study of the effects of the additives "Iodcasein", "Bioiod" and SA on the curd technology is relevant. The purpose of this study is to develop enriched dairy technology using dairy iodized proteins and SA.

2. Materials and methods
The objects of research were: pasteurized cow's milk with a fat mass fraction of 2.5%, food supplement "Bioiod" (NPO "Chemical Technologies", Russia), food supplement "Iodcasein" (LLC "NPK Medbiofarm", Russia), SA (LLC "Kvadrat-C", Russia).

The composition of "Bioiod" and "Iodkasein" includes milk iodinated proteins. The matrix for iodination in "Iodcasein" is the main milk protein casein, and in "Bioiod" – whey proteins [12,13]. "Bioiod" contains 2% iodine, "Iodkasein" – 7%.

We used generally accepted and special measuring methods for quantitative analysis, organoleptic methods for assessing the quality of raw materials and finished products, and statistical methods for processing information.

Determination of acidity was carried out by titrimetric method according to GOST 3624-92, milk density – according to GOST 3625-84. The mass fraction of protein was determined by the Kjeldahl method, the carbohydrate content was determined by the cyanide method. Determination of active acidity – by potentiometric method on a pH-150 millivoltmeter using an EVL-1M4 glass electrode in accordance with GOST 26781-85. The fat content was determined by using the acid method Gerber. The rate of bacteria of the group of Escherichia coli was determined according to GOST R 53430-2009. The rate of lactic acid microorganisms was determined according to GOST 10444.12. The number of yeast and molds was determined according to GOST 10444.11. The number of mesophilic aerobic and facultative anaerobic microorganisms was determined according to GOST R 53430-2009.

The determination of organoleptic indicators was carried out according to GOST 28283-89 and International standards ISO 6658: 1985 "Sensory analysis. Methodology. General guideline" and ISO 11035: 1994 "Sensory analysis. Identification of the selection of descriptors for establishing a sensory profile in a multi-stage approach" (using a quantitative descriptive profile method); determination of organic acids in cottage cheese by the titrimetric method in terms of milk acid.

The iodine content was determined on a TALab voltammetric analyzer (NPP "Tomanalit", Russia). The technique includes preliminary preparation of samples by mineralization and subsequent analysis of an aqueous solution of a mineralized sample by cathodic inversion voltammetry. In the process of sample mineralization and subsequent ultraviolet irradiation of the mineralized sample solution, all forms of iodine are converted into iodide ions. Iodide ions are concentrated on a modified silver or mercury-film electrode in the form of a sparingly soluble precipitate, followed by cathodic reduction of the precipitate with a linear change in potential. The cathode peak arising in this case at a potential of minus (0.4 ± 0.05) V for the modified silver electrode and minus (0.3 ± 0.05) V for the mercury-
film electrode is an analytical signal. The content of iodide ions in the solution of the prepared sample is determined by the method of additives of a certified mixture of iodide ions.

The results of the study of indicators at different concentrations of SA were processed by parametric variational statistic methods using the t-criterion (p<0.05); and also the reliability of changes in technological parameters when adding iodine-containing additives was calculated using χ²-Pearson (p=0.05).

3. Discussion of the results
When determining the dosages of milk iodized proteins for the preparation of fortified dairy products, it was assumed that 100g of the finished product should contain 30% of the daily intake of iodine (50mg). Given there is concentration of iodine in the additives used, the dosage of the additive "Iodcasein" was 7mg/kg, and the additive "Bioiod" was 25mg/kg of the product.

The additive "Iodcasein" was mixed with water, heated in a water bath at a temperature of 40-50°C until completely dissolved (30-60 min) and added to milk (sample 1). The long cooking time was due to the poor solubility of the additive in water and milk. "Bioiod" supplement was also mixed with water until dissolved and introduced into milk (sample 2). It was noted that the additive "Bioiod" quickly dissolved in water and milk without heating. Pasteurized milk was used as a control sample. Physicochemical, microbiological and organoleptic indicators of the obtained samples were determined (Table 1).

| Table 1. The impact of additives "Iodcasein" and "Bioiod" on the physico-chemical and microbiological parameters of milk |
|-----------------------------------------------|-----------------------------|-----------------------------|
| Indicators                                  | Control Curd samples       | Curd samples Sample 2       |
| Titratable acid, °T                         | 20±1 19±1 21±1             |                             |
| True acid, (pH)                             | 6.61±0.02 6.65±0.02 6.60±0.02 |                             |
| Density, °A                                 | 27±1 27±1 27±1             |                             |
| Fats, %                                     | 2.5±0.1 2.5±0.1 2.5±0.1     |                             |
| Proteins, %                                 | 2.7±0.1 2.7±0.1 2.7±0.1     |                             |
| Thermostability                             | 1 group 1 group 1 group     |                             |
| Escherichia coli bacteria                    | 0.01 cm³ 0.01 cm³ 0.01 cm³ |                             |
| QMA&OAMO, KFU/1 cm³                         | 1.1×10⁵ 3.5×10² 1.1×10³     |                             |

An analysis of the data showed that the additives "Iodcasein" and "Bioiod" do not affect the physico-chemical and microbiological properties of milk. An organoleptic assessment showed that the samples of milk with the addition of "Iodcasein" had the smell of iodine, while the samples of milk with the addition of "Bioiod" did not have any foreign odors or taste. The resulting iodine rich milk was used in the following-up studies.

The essence of thermo-acid coagulation of milk proteins is the simultaneous exposure to high temperatures and the acid factor. The consequence of this technological treatment is thermal denaturation and acid coagulation of proteins. The advantage of this method is the precipitation of both protein fractions of casein and whey proteins.

To select the optimal dosages and modes of coagulation of milk protein, SA in the amount of 0.1, 0.2, 0.4, 0.6, and 0.8% by weight of milk was combined with milk and heated at a temperature of 75, 85, and 90°C. When SA was added in an amount of 0.1%, regardless of temperature, protein coagulation was not observed. This was explained by the fact that SA has a low degree of dissociation and the addition of acid in an amount of 0.1% is insufficient for the precipitation of milk proteins. At a temperature of 75°C, protein flakes formed in other samples, whey was white, cloudy. At 85°C, in samples with a dosage of SA 0.2%, the curd clot formed poorly and had a smearing consistency, while in samples with a dosage of 0.4, 0.6, and 0.8%, the clot formed well, was fairly dense, but had an
acidic taste, which intensified with increasing dosage of SA. At 90ºC, the samples with a dosage of SA 0.2 and 0.4% had a soft curd, and with a dosage of 0.6 and 0.8% they were thick and rubbery. For samples with a dosage of SA 0.2% and 0.4%, the taste of the curd clot was pleasant, sour-milk, and at a dosage of 0.6% and 0.8%, a sharp sour taste appeared, so for further studies we chose a dosage of SA 0.2 and 0.4%.

At the next stage, we studied the possibility of obtaining cottage cheese enriched with SA and iodine. To prepare samples without iodine-containing additives, milk was heated to 90°C and combined with SA in the amount of 0.2 and 0.4% by weight of milk, kept until a protein clot was obtained and subjected to self-pressing (curd sample 1 and 2). To obtain the experimental samples used milk with the addition of "Iodcasein" (sample 3 and 4) and "Bioiod" (sample 5 and 6). The yield of cottage cheese, the acidity of cottage cheese and serum, the mass fraction of dry and organoleptic indicators were determined (Table 2).

Table 2. The impact of various dosages of SA on technological indicators of cottage cheese

| Indicators                        | Curd samples |
|----------------------------------|--------------|
|                                  | 1            | 2            | 3            | 4            | 5            | 6            |
| Moisture content, %              | 76.4±0.5     | 77.4±0.5     | 77.4±0.5     | 75.3±0.5     | 78.3±0.5     | 76.0±0.5     |
| Yield of charge(curd), %         | 17.8±0.5a    | 19.8±0.5a    | 18.8±0.5b    | 21.5±0.5b    | 18.2±0.5c    | 20.8±0.5c    |
| Titratable acid of curd, °T       | 82±3d        | 92±3d        | 82±3e        | 91±3e        | 79±3f        | 90±3f        |
| Titratable acid whey, °T          | 53±3g        | 65±3g        | 54±2h        | 68±2h        | 51±2i        | 63±2i        |
| Milk whey proteins, %            | 7.4±0.1j     | 6.6±0.5j     | 7.4±0.1k     | 6.3±0.1k     | 7.9±0.1l     | 6.1±0.1l     |

\( i = \alpha, l− \) have statistical differences at \( p \leq 0.05 \)

An analysis of the data showed that the values of the mass fraction of moisture of all samples were at the same level (no statistical differences). It was found that increasing the dosage of SA leads to an increase in the yield of cottage cheese by 2.0, 2.7, and 2.6% (\( p \leq 0.05 \)) in samples without iodine-containing additives and samples with additives "Iodcasein" and "Bioiod", respectively. This is confirmed by a decrease in serum proteins. An increase in the dosage of SA also leads to an increase in the acidity of the curd clot by 8.5% (\( p \leq 0.05 \)) for samples without iodine-containing additives, by 10.9% (\( p \leq 0.05 \)) and 13.9% (\( p \leq 0.05 \)) for samples with the addition of "Iodcasein" and "Bioiod", respectively.

Figure 1. The total sensory evaluation of organoleptic characteristics of cottage cheese samples

The organoleptic properties of the samples were studied, we determined the appearance, taste and smell, color and texture, each of the indicators was evaluated on a 5-point scale (Figure 1).
An analysis of the data showed that the additives did not affect the color of the cottage cheese, the color of all samples was white with a cream tint, but for samples with SA 0.4% a denser small-grained texture and a more acidic taste were noted.

Nutritional and energy value was determined by experimental and calculation methods (Table 3).

**Table 3. The impact of various dosages of succinic acid on nutrition and energy value of cottage cheese**

| Indicators                  | Cottage cheese samples |
|-----------------------------|------------------------|
|                             | 1          | 2          | 3          | 4          | 5          | 6          |
| Proteins, g                 | 15.8±0.5  | 16.9±0.5  | 16.4±0.5  | 17.0±0.5  | 16.0±0.5  | 17.2±0.5  |
| Fats, g                     | 12.5±0.5  | 13.2±0.5  | 12.5±0.5  | 13.0±0.5  | 12.3±0.5  | 11.9±0.5  |
| Carbohydrates, g            | 10.1±0.5  | 9.2±0.5   | 9.8±0.5   | 9.2±0.5   | 10.2±0.5  | 9.8±0.5   |
| Organic acid, g             | 0.68±0.1\textsuperscript{a} | 0.74±0.1\textsuperscript{a} | 0.70±0.1\textsuperscript{b} | 0.75±0.1\textsuperscript{b} | 0.69±0.1\textsuperscript{c} | 0.74±0.1\textsuperscript{c} |
| Iodine, mkg/100 g           | 4.1±0.5\textsuperscript{de} | 3.7±0.7\textsuperscript{fg} | 46.2±1.1\textsuperscript{d} | 46.4±0.9\textsuperscript{f} | 48.5±0.9\textsuperscript{e} | 48.2±1.1\textsuperscript{g} |
| Energy value\textsuperscript{b}, kcal/kJ | 216.9     | 223.2     | 217.3     | 221.8     | 215.5     | 215.2     |
| kcal/kJ                     | 893.68     | 924.31     | 898.99     | 919.34     | 891.05     | 889.73     |

\(i = \text{a, f} \) – have statistical differences at \(p<0.05\)

\(\text{b} \) – calculated data

Analysis of the data showed that the amount of proteins, fats and carbohydrates in the samples did not change. An increase in organic substances in the product and a higher iodine content in samples with iodine-containing additives were noted. With an increase in the dosage of SA, the content of organic acids for samples without iodine-containing additives increased by 8.8\% (\(p<0.05\)), for samples with "Iodcasein" – by 7.1\% (\(p<0.05\)) and with "Bioiod" – by 7.2\% (\(p<0.05\)). The iodine content did not change with increasing dosage of SA, while the iodine content in the samples with "Iodcasein" and "Bioiod" was significantly higher.

**Figure 2. The impact of product storage time on iodine content in cottage cheese**

An important indicator of iodized products is the preservation of iodine during the shelf life of the product, so the loss of iodine during storage was determined. The shelf life of cottage cheese at a temperature of from -2\°C to +4\°C is 72 hours, and for heat-treated samples – 5 days or more. Samples of cottage cheese were stored at a temperature of +4\°C. The iodine content in the samples
immediately after preparation, after 1, 3 and 5 days is in figure 2. An analysis of the data showed that during storage of cottage cheese for 120 hours, the iodine content in all samples did not change, which allows us to conclude that the cottage cheese is enriched with iodine.

4. Conclusion
We studied the possibilities of using Succinic Acid and iodine-containing additives in the production of cottage cheese. It has been established that the additive "Iodcasein" is poorly soluble in water and milk, and also gives the milk a pronounced odor of iodine, the additive "Bioiod" is highly soluble in water and milk under ordinary conditions. The impact of various dosages of SA on the parameters of coagulation of milk protein and technological rates of cottage cheese (yield, acidity, mass fraction of moisture) was studied. The technology to product of cottage cheese with additives "Iodcasein" and "Bioiod" was developed by using thermoacid coagulation of SA.

It was found that the most complete extraction of proteins occurs at a dosage of SA 0.2-0.4% to the mass of milk and at 90ºC. It was found that additives have a positive effect on the organoleptic properties of cottage cheese, contribute to an increase in organic acids and iodine. The organic acid content for samples with SA and without iodine-containing additives increased by 8.8% (p<0.05), for samples with "Iodcasein" - by 7.1% (p<0.05) and with "Bioiod" - by 7.2% (p<0.05).

The iodine content did not change with an increase in the dosage of SA, while the iodine content in the samples with the addition of "Iodcasein" and "Bioiod" was significantly higher than that of the samples without iodine-containing additives.

The content of iodine in the cottage cheese was determined by the cathodic inversion volt-ammetry method, and product safety was established during processing and storage. The additives "Iodcasein" and "Bioiod" provide a significant increase in the iodine content in the product, which was stored for 120 days.

Thus, the additives of SA and iodine-containing additives, such as "Iodcasein" and "Bioiod" allowed developing a product with high organoleptic properties while maintaining the basic physicochemical and structural-mechanical properties. The data obtained allow us to recommend a developed food product for the prevention of iodine deficiency.

References
[1] Aleksandrova L I, Zabodalova L A and Skvortsova N N 2016 Study the possibility of use of extracts of the mushroom Boletus edulis in the production of functional dairy products Proceedings of the Voronezh State University of Engineering Technologies 2 131-139
[2] Pilipenko T V and Roginskaya E O 2018 Development of milk dessert enriched by functional vegetable additives Bulletin of the South Ural State University Ser. Food and Biotechnology 6 (1) 40–48
[3] Dobriyan E I, Ilina A M and Medvedeva T A 2018 Increasing the biological value of the curd product Proceedings of the Voronezh State University of Engineering Technologies 80 (3) 124-127
[4] Dolmatova O I and Zyalgava E I 2018 Biotechnology of curd product with vegetable origin components Proceedings of the Voronezh State University of Engineering Technologies 80 (1) 129-132
[5] Spirichev V B and Shatnyuk L N 2010 Enrichment of articles of food by micronutrients: scientific principles and practical decisions Food industry 4 20-24
[6] Hamagaeva I S and Badlueva A V 2009 Effects of potassium iodide on activity of bifido- and propionic bacteria Dairy Industry 7 74
[7] Hamagaeva I S and Badlueva A V, RU Patent No. 2294645 Method for production of iodinated products
[8] Tomchany O V, Cyb A F, Roziev R A, Bozadgiev L L, Skrypnik D G, Skvortsov V G and Chernyaev S I 2001 Fortification of dairy products with iodine casein Dairy Industry 12 31-32
[9] Orlova O Yu, Pilipenko T V and Nikulina M V 2015 Traditional and perspective vegetable sources of iodine for enrichment of foodstuff *Scientific journal NRU ITMO Series "Processes and Food Production Equipment"* 4 26-38

[10] Lipatov N N 1973 *Curd production. Theory and practice* (Moscow: Food Industry)

[11] Yakovleva E G, Anisko R V and Gorshkov G I 2015 Succinic acid – a natural adaptogen and immunostimulant *Bulletin of the Kursk Agricultural Academy* 7 164-167

[12] Ljublinskij S L, Savchik S A and Smirnov S V RU Patent No. 2212155 *Method for obtaining a biologically active food additive*

[13] Cyb A F, Roziev R A, Skvorcov V G, Klepov A N, Skobelev I V, Us P.P., et al. RU Patent No. 2151611 *Means for regulating iodine metabolism or preventing iodine deficiency*