

Обґрунтовано доцільність використання купажу рослинних олій для виробництва молоковісних продуктів збалансованого жирнокислотного складу. Розроблено купаж олій. Методом газорідинної хроматографії визначено жирнокислотний склад сметанного продукту із 50 % заміною молочного жиру купажем. Дана заміна дозволяє значно підвищити вміст поліненасичених жирних кислот та максимально привести жирнокислотний склад молоковісного продукту до рекомендованих дієтологами норм

Ключові слова: оптимізований жирнокислотний склад, молоковісний продукт, сметанний продукт, купаж натуральних рослинних олій, хроматографічний аналіз, заміна молочного жиру

Обоснована целесообразность использования купажа растительных масел для производства молочкосодержащих продуктов сбалансированного жирнокислотного состава. Разработан купаж масел. Методом газожидкостной хроматографии определен жирнокислотный состав сметанного продукта с 50 % заменой молочного жира купажом. Данная замена позволяет значительно повысить содержание полиненасыщенных жирных кислот и максимально привести жирнокислотный состав молочкосодержащих продукта к рекомендованным диетологами нормам

Ключевые слова: оптимизированный жирнокислотный состав, молочкосодержащий продукт, сметанный продукт, купаж натуральных растительных масел, хроматографический анализ, замена молочного жира

UDC 637.146

DOI: 10.15587/1729-4061.2016.81405

OPTIMIZATION OF COMPOSITION OF BLEND OF NATURAL VEGETABLE OILS FOR THE PRODUCTION OF MILK-CONTAINING PRODUCTS

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1. Introduction

It is common knowledge that human health is by more than 70 % depends on proper nutrition, so a daily diet should contain all essential nutrients in digestible ratios (protein – 25 ... 35 %, fat – 30...40 %, carbohydrates – 30...35 %) and a range of micronutrients for normal functioning of all organs and systems. However, an analysis of everyday diet revealed significant deviations from the norms of balanced nutrition, which leads to disruption of the synthesis of enzymes, hormones, antibodies and proteins, which in turn triggers the development of a number of diseases (obesity, impaired metabolic processes, diseases of cardiovascular system and digestive organs).

According to the concept of healthy nutrition, the issue of consumption of fats and fat containing products ranks among the most important. Nowadays, fats are considered not only as being a source of energy and elastic material, but also as the

supplier of physiologically functional ingredients. That is why daily consumption of the required amount of fat is important for normal functioning of every human organism [1, 2].

On the basis of medical and biological research, fatty acids should get to the human body on a daily basis in accordance with the norms established by nutritionists: 80...150 g/day for men and 65...100 g/day for women. And fats of vegetable origin (oils) should contain 30 % of the total amount of consumed fat. Studies conducted at the level of a whole organism and at the cellular and molecular levels demonstrated that physiological effectiveness of food fats depends not only on the existence in them of polyunsaturated fatty acids (PUFA) but also on the optimum ratio between all three groups of fatty acids. Triacylglycerols in food products should contain 10...20 % of polyunsaturated fatty acids (PUFA), 50...60 % of monounsaturated fatty acids (MUFA) and 30 % of saturated fatty acids (SFA). Among PUFA, the ratio of $\omega-6:\omega-3$ groups should make from 4:1 to 10:1. The

British Food Fund considers that an ideal relation between the PUFA family of ω -6 and ω -3 should be 6:1 [3].

However, at present an average person consumes PUFA in the ratio of ω -6 ω -3 from 10:1 to 30:1, which leads to the disruption of lipids metabolism. This excess consumption of fatty acids of the ω -6 class has a detrimental impact on health. The fact is that in the human body arachidonic essential fatty acid that reacts with vitamins of group B is synthesized from linolenic acid. An important factor is that for normal vital activity, the daily norm of arachidonic acid intake should make 2 g, and any of its excess triggers a series of deadly dangerous processes. Therefore, it is always necessary to block the source of synthesis of arachidonic acid by linolenic acid (ω -3) that the vast majority of vegetable oils are rich in [4].

Essential fatty acids should make 4...6 % of the energy value of food ration of a healthy person. It is important for the ratio of PUFA of ω -6 and ω -3 groups to make not more than 10:1, and in the cases of disruption of lipid exchange – 5:1 and even 3:1.

At the same time, there are some known data about the effectiveness of applying acids of the ω -3 group when treating various diseases. The increase in dietary content of the ω -3 fatty acids increases the effectiveness of dietary therapy and promotes the correction of disorders of lipid metabolism in patients with type II diabetes. In this case, there is a decrease in the previously increased activity of phospholipases A₁ and A₂ responsible for degeneration of phospholipids in the process of cell metabolism [5].

Taking into account all of the above mentioned arguments, we can conclude that today's relevant task is to develop technologies of products of balanced fat and acid composition with enhanced biological and nutritional values. In this case, the use of natural vegetable raw materials is promising. Therefore, an alternative variant of the strategy of improving and preserving health is the correction of lipid and acid composition of fat containing products of everyday use. Since the fat and acid composition of certain fats does not correspond to an optimum ratio of saturated, monounsaturated and polyunsaturated fatty acids, and considering the lack of oil with "perfect" fat containing composition in the native form, the most rational option of solving the problem of improvement of physiological properties of fats is to create blends of natural vegetable oils and their combination with animal fats in products of everyday use. In this case, an important advantage is that vegetable oil is a traditional food product throughout the world.

Further use of the blend, developed on the basis of natural vegetable oils, is promising and relevant for the development of dairy industry. In this case, a partial replacement of the fat component with the created blend of vegetable oils will optimize the fat and acid composition of milk containing products and enrich its with biologically active substances of vegetable origin, and thus create a product of functional direction. The use of vegetable raw materials (blending of natural vegetable oils) in the technology of milk containing products will make it possible to expand their product range, partly solve a problem of the shortage of raw milk and prevent the seasonal fluctuations of the components of raw milk. The creation and implementation of such products for mass consumption will be economically beneficial for dairy industry and, which is not less important, will have social effect on the Ukrainian population.

2. Literature review and problem statement

Sour milk products are the products that nutritionists advise to include in the daily diet. They are useful both for the development of children and for maintaining normal functioning of all organs and systems of an adult person. Sour milk products should be consumed on a daily basis by elderly people to improve and maintain health. However, it should be taken into account that milk fat is not "ideal". In its composition there is an excessive amount of saturated fatty acids, the average content of which is 60...65 %. At the same time, the content of unsaturated, especially polyunsaturated fatty acids are considerably below the recommended standards [6].

The use of vegetable oils and fats allows for compensating the lack of unsaturated fatty acids in animal fats. In addition, natural vegetable oils are a source of fat-soluble vitamins, in particular, vitamin E.

For example, corn oil is extracted from the nuclei of corn seeds and contains up to 60 % of unsaturated fatty acids but the vast majority of polyunsaturated fatty acids belong to the ω -6 group (86 %). In addition, corn oil contains glycerides of fatty acids: saturated, such as palmitic and stearic, monounsaturated, such as oleic, and polyunsaturated, such as linoleic acids. Phospholipids in amount of 1500 mg %, stearins up to 1000 mg %, protein, starch and pentoza are also found in it. It contains vitamin PP, vitamins of group B (B₁, B₂, B₅, B₆), provitamin A – 0,058...0,155 mg %, vitamin K – 0.058 mg %, vitamin-like compounds, biotin, provitamin D – 0,42...1.38 mg %, vitamin E – 120...250 mg %. In addition, the isomer composition of vitamin E is different: α – 10...20 mg %, β – 2...5 mg %, γ – 68...85 mg % and δ – 3...8 mg %, the increased amount of γ -tocopherol allows storing oil longer without losing its physiological activity. It is the existence of γ -tocopherol in corn oil that helps slow down the processes of oxidation of unsaturated bonds and later form aldehydes, which provoke rancidity with the accompanying specific taste and smell. This oil is also rich in bioflavonoids, having a wide range of effects on the body: luteolin (anti-inflammatory, spasmolytic effects), myricetin (gastroprotecting, diuretic, cardio-stimulating effects), isoquercetin (has a hypotensive effect), quercetin (P-vitamin activity), epicatechin (anti-diabetic effect), scopoletin – compounds of coumarin raw that has a spasmolytic and hypoglycemic effect [9].

Rapeseed oil has low specific cost and rapeseed crops occupy about 10 % of the total area of oilseed crops in the world. It contains 99,9 % of lipids and only 0,1 % percent of water; carbohydrates and proteins are absent at all, which is its distinguishing feature among all other vegetable oils. The low content of saturated (palmitic and stearic) fatty acids <7 % is characteristic for this oil. It contains the following phospholipids: phosphatidilcholines – 0,8 %, phosphatidiletanolamins – 0,6 % and galactolipids: monogalaktosil-diacylglycerols – 0,7 %, digalaktosil-diacylglycerols, as well as a small amount of phospholipids of non-hydrated forms. According to its chemical composition, rapeseed oil contains sterols, vitamin E – 55 mg %, which is responsible for the processes of regeneration of organism, provitamin D – 0,34...0,59 % and rare vitamin F which takes part in the process of forming new cells, enhances immunity and is responsible for revitalizing of the entire body. In this case, the important function of this biologically active substance is to excrete accumulated toxins [10].

According to the content of tocopherol isomers of rapeseed oil, their total quantity is within 20,7...22.6 mg %. The specific feature of this oil is a high content of β – tocopherol (67,4...73.1 % of the total sum of tocopherols), which is characterized by the most pronounced antioxidant properties that prevent oxidation of polyunsaturated fatty acids. Thanks to its fat and acid composition, this oil has high biological value. The content of saturated fatty acids is insignificant – 6,86, opposite to the majority (4 times) of polyunsaturated fatty acids – 27.81, which positively affect the blood circulation and improve condition of the vessels. Rapeseed oil has therapeutic and prophylactic properties, it is able to regulate the content of cholesterol in human blood and thereby reduce the threat of thromb formation and prevent cardiovascular diseases [10].

Walnut oil is extracted from the core of walnuts, picked up from trees in the young degree of maturity or when they are not completely ready to use. Within several months, walnuts ripen in special premises. During this time, the amount of natural oils in their content increases by times [11].

Chemical composition of walnut oil is enriched with such useful compounds as ascorbic acid, magnesium, iodine, cobalt, zinc, co-enzyme Q10 and lots of fat-soluble vitamins – A, D, E, and water-soluble vitamins – C, P, PP. Walnut oil has excellent anti-inflammatory and antimicrobial effects that help treat certain diseases. Its daily use contributes to improvement of the organs of the gastrointestinal tract, heart, joints, lungs, brain and enhances the immune and endocrine systems. It is widely used in the treatment of tuberculosis, furunculosis, eczema, psoriasis, varicose of vessels. Nut oil protects the body from the effects of carcinogenic substances and increases the resistance of the entire body, including to radiation exposure, due to the ability to excrete radio nuclides. The inclusion of this oil to the food ration contributes to improving indicators of cellular immunity, reducing the concentration of circulating immune complexes, increasing the resistance of an organism to respiratory diseases [12].

But the use of any of the vegetable oils does not provide the optimal ratio of particular groups of fatty acids. Therefore, a promising direction of research is blending natural vegetable oils.

Thus, the well known is the development [12] of the blend of vegetable oils, the basis of which is made of sunflower oil – 60...90 %, and grape and apricot seeds oil – 40...10 %. However, this blend has a number of disadvantages. First, the selected vegetable oils, like grape or apricot, have high cost, and therefore, the blend with their use will be economically viable. Second, the above mentioned blend on the basis of natural oils from seeds is positioned by developers as a standalone product for expanding the assortment of products of oil and fat industry; the possibility and expediency of its combination with milk basis is not experimentally proven.

Authors of papers [13–15] proposed using hemp, pumpkin and camelina oils combined with the oil of wheat nuclei to create a blend of vegetable oils. However, obtaining the blends of vegetable oils on their basis on the industrial scale is highly unlikely due to the high cost. It should also be noted that each of them has specific organoleptic properties, which, combined with milk base, will create unattractive taste and aroma of the product.

The developments of blends [16] with the use of rapeseed, linseed and soybean oils are also known. However, the fact is undeniable that soybean oil is expedient to be added to the blend in the amount that does not exceed 20...30 %, the amount of linseed oil should not exceed 5 %, because exceeding these limits worsens taste properties of the product.

There was the research into the change in fat and acid composition of milk and immune indexes of cows, after adding the ω -3 fatty acids from algae “Schizochytrium” to their diets [17]. According to the obtained results, the changes in enhancing antibody reactions occurred in 4 weeks after the introduction of fatty acids of the ω -3 group to their diet, which also contributed to the change in the profile of polyunsaturated fatty acids of milk.

It is worth noting that the possibilities and prospects of using vegetable oils as substitutes for milk fat in the dairy industry have the highest index in butter manufacturing sector [18]. Thus, the technology of butter with the complex “OmegaTrin” with a balanced content of polyunsaturated fatty acids was developed. Introduction of this complex increases the temperature of milk fat melting by 3.4 %, slightly increases heat resistance by 0,03 and leads to balancing the ratio of content of polyunsaturated fatty acids, which enhances biological value of the product, the output of production increases by 8.1 %. However, it should be noted that “OmegaTrin” was developed specifically to improve the fat and acid composition of butter. Experimental studies on using it in other food technologies were not carried out.

Therefore, a relevant direction of scientific research is the development of fat components for milk containing products of the balanced fat and acid composition. Criteria for selection are the availability of vegetable oils and their lipid and acid composition, structure, and specific organoleptic characteristics.

3. The aim and tasks of the study

The purpose of the studies was to create special blend based on natural vegetable oils for combination with a milk base and further development of sour cream product with partial replacement of milk fat with the blend. A developed sour cream product should have maximally balanced and optimized fat and acid composition according to the standards established by nutritionists, in order to provide the product with the highest possible degree of assimilation of essential fatty acids by the body.

The set goal was accomplished by solving the following tasks:

- to examine possibility and feasibility of combination of selected vegetable oils with a milk base and with one another as a part of the blend;
- to develop a program in the MATLAB mathematical programming environment for optimizing the ratio of components comprising the blends of natural vegetable oils for the purpose of their further use in the technology of milk containing products;
- to determine experimentally the fat and acid composition of the milk containing product with a partial substitution of milk fat with the developed vegetable oil blend;
- to prove the expediency of using the developed blend as a part of milk containing products.

4. Materials and methods of studying the influence of partial replacement of milk fat, created and optimized by lipid and acid composition with the blend of vegetable oils, on lipid and acid composition of a sour cream product

4.1. Materials and equipment used in the experiment

On the basis of the previous research, for the introduction to a sour cream product, we selected vegetable oils based on organoleptic parameters, compatibility with the milk base and with one another. Substantiation of the composition of blends of vegetable oils was carried out by using contemporary ideas about the role of fats and their components in human nutrition and a balanced ratio of individual fatty acids. The important factors in choosing vegetable oils for blending were their technological properties, pricing policy and territorial prevalence. Considering all the listed requirements, the authors chose three natural vegetable oils: corn oil, rapeseed oil and walnut oil, (the latter two are not refined and deodorized) [19].

4.2. Procedure of determining the fat and acid composition of experimental samples

The studied samples "A" and "B" for determining the fat and acid composition by gas-liquid chromatography were prepared according to the instructions of GOST P51486-99 and DSTU ISO 5509-2002.

Methyl esters of fatty acids were prepared by the method, in which sodium methylate was used as a reagent for etherification. A necessary condition for the proper preparation of the sample is the use of antioxidant – 0,05 % solution of BHT (butylhydroxytoluol) in heptane because it prevents premature oxidation of prepared methyl esters. A weight portion of molten fat (100 mg) was solved in 2 ml of BHT in heptane. 5–6 drops (about 100 μ l) of sodium methylate was added to the resulting solution, stirred for 2 minutes and left for 15 minutes for stilling. The sample was neutralized using 1–2 g of $\text{Na}_2\text{SO}_3 \cdot \text{H}_2\text{O}$. The washed sample passed through anhydrous Na_2SO_4 for dehydration and was transferred into another test tube, another 2 ml of solvent – BHT in heptane were added, shaken and filtered in another test tube. The filter was washed with 1 ml of BHT in heptane and the resulting sample was transferred to a vial for further chromatographic analysis.

In the obtained trials of samples, the fat and acid composition was explored by the method of gas-liquid chromatography on the gas chromatographer Hewlett Packard HP-6890 using the capillary pump HP-88 (88 % – cyanopropyl aryl-polysiloxane, Agilent Technologies), 100 m length, with the inner diameter of 0,25 mm and thickness of the immobile phase of 0,2 microns under the following conditions: flow rate of gas-carrier – 1,2 ml/min, coefficient of flow separation of 1:50, vaporizer temperature of 280 $^{\circ}\text{C}$, temperature of detector (PID) – 290 $^{\circ}\text{C}$, the temperature mode of the pump – gradual heating from 60 $^{\circ}\text{C}$ to 230 $^{\circ}\text{C}$.

The volume of injection is 2 μ l for lymphocytes, 1 μ l for liver and muscles.

For the identification of chromatographic peaks and calculation of chromatograms, we used a mixture of methyl esters of fatty acids 37 Component FAME Mix of Supelco trade mark (Cat No. 47885-U). Registration and processing of chromatograms was performed with the use of a personal computer equipped with the software "HP ChemStation" [20].

5. Results of research into the fat and acid composition of experimental samples with partial substitution of milk fat with the developed vegetable oil blend

Results of research into the fat and acid composition by the method of gas-liquid chromatography of sour cream are presented in chromatogram (Fig. 3).

The results of research into the fat and acid composition by the method of gas-liquid chromatography of a sour cream product with 50 % substitution of milk fat with the developed blend based on natural vegetable oils are presented in chromatogram (Fig. 4).

The corresponding numerical values obtained by the method of gas-liquid chromatography for the experimental sample with 50 % replacement of milk fat with the blend of vegetable oils (sour cream product) compared with sour cream of corresponding fat content (control) are presented in Table 3.

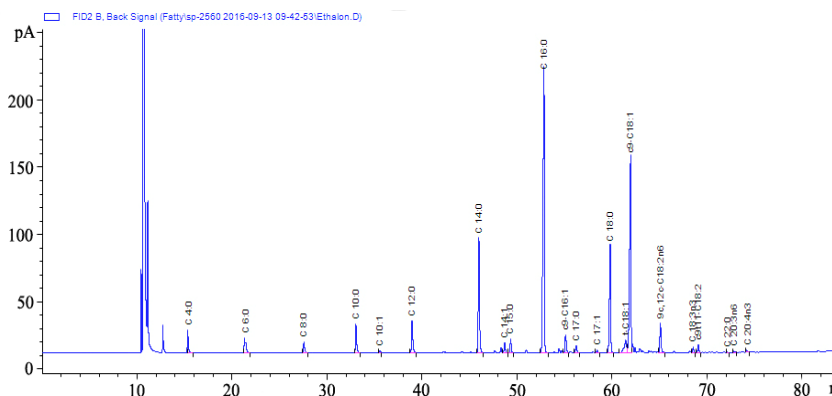


Fig. 3. Chromatogram of the fat and acid composition of sour cream with 20 % mass fraction of fat (control sample)

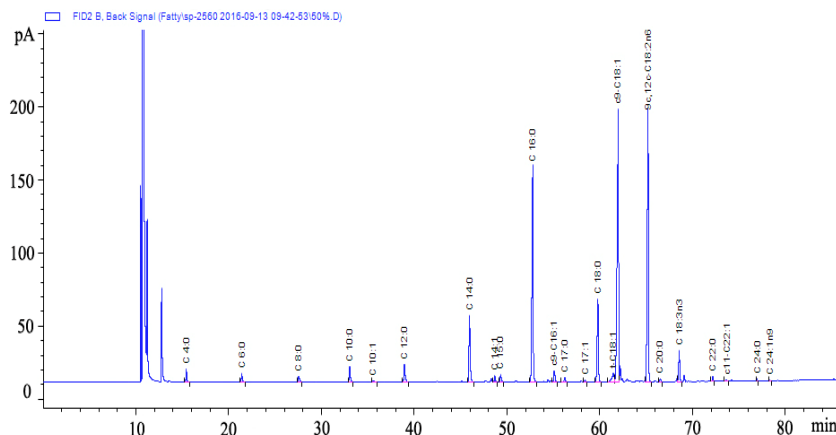


Fig. 4. Chromatogram of the fat and acid composition of experimental sample of a sour cream product with 50 % substitution of milk fat with the developed vegetable oil blend

Table 3
Results of gas-liquid chromatography of the fat and acid composition of experimental samples

Group of fatty acids	Sour cream product (sample)	Sour cream (control)
SFA	(36,64±5) %	(64,81±5) %
MUFA	(34,40±5) %	(29,76±5) %
PUFA	(28,94±5) %	(5,42±5) %
ω -6: ω -3	5,8:1	4,2:1

According to results of chromatographic analysis, the decrease in the amount of saturated fatty acids is clearly observed – by 28 % compared with the control (sour cream), the percentage of groups of unsaturated fatty acids increases: monounsaturated fatty acids to 5 %, polyunsaturated fatty acids to 15 %, the ratio of ω -6: ω -3 is 5,8:1, which meets the recommended standards.

6. Discussion of results of comparative analysis of the fat and acid composition of the sour cream product, obtained with the help of mathematical simulation and experimentally

In order to obtain milk containing products with the balanced fat and acid composition, the use of natural vegetable oils – corn, rapeseed and walnut oils – was theoretically substantiated and experimentally proved.

In the MATLAB mathematical programming environment we defined the optimum ratio of the aforementioned oils included in the blend with regard to the lipid and acid composition of milk fat.

The ratio of saturated, mono- and polyunsaturated fatty acids, as well as the ratio of essential fatty acids of the ω -6 ω -3 groups, was defined as the criteria of optimization.

We performed chromatographic analysis of the lipid and acid composition of the sour cream product with 50 % substitution of milk fat with the developed blend of vegetable oils. A sour cream with similar fat content was used as a reference sample.

According to the obtained data, the fat and acid composition of the studied sample was more balanced: the content of saturated fatty acids decreased almost by 2 times to 36,64 %, while in the control this index was 64,81 %. In this case, the percentage of polyunsaturated fatty acids in the sour cream product increased by more than 5 times and amounted to 28,94 % (control – 5,42 %).

The error in the quantitative index between the results obtained in the environment of the MATLAB mathematical

package and the results obtained experimentally using chromatographic laboratory analysis is justified by such factors as seasonal fluctuations in the fat and acid composition of the oils, used in the blend (corn, rapeseed, walnut oils), as well as by an error in the readings of the chromatographer. The difference between these data is not higher than 1 %, which, in turn, does not exceed a generally permissible error of 5 %. On this basis, the obtained results testify to the accuracy of mathematical calculations and the appropriateness of using the blend developed on the basis of natural vegetable oils in the technology of milk containing products.

A mathematical method of calculation, proposed in the paper, may be used for the development of enriching compositions based on a wider range of vegetable oils and fats, which would expand the range of milk containing products with the balanced fat and acid composition.

The production of such products will decrease the deficit of polyunsaturated fatty acids, including the ω -3 groups in the diet of ordinary consumers, which would have a positive impact on the state of their health and would allow preventing the development of a number of dangerous diseases.

7. Conclusions

1. Taking into account the fat and acid composition of certain vegetable oils, the possibility of their combination with one another in the composition and with the milk base, we substantiated the expediency of their introduction to the composition of the blend of corn, rapeseed and walnut oils.

2. In order to optimize the composition of the blend of natural vegetable oils, we used the program in the environment of MATLAB mathematical package; based on its calculations, we defined the optimal ratio of corn, rapeseed oil and walnut oil in the blend composition – 1:1.1:1.

3. The data on the fat and acid composition of our cream product with 50 % substitution of milk fat with the developed blend of vegetable oils, obtained by the method of gas-liquid chromatography, confirm the calculations in the environment of the MATLAB mathematical package.

4. It was established that the use of the blend of vegetable oils can significantly enrich a product with polyunsaturated fatty acids and bring its fat and acid composition to the recommended standards. Thus, the ratio of SFA:MUFA:PUFA in the sour cream product with 50% substitution of milk fat was 1.3:1.2:1, whereas in the control (sour cream with similar fat content) – 12:5,5:1; the ratio of fatty acid of the ω -6 ω -3 groups was 5,8:1, respectively, whereas in the reference – 4,2:1.

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