

Проведено аналіз основних методів моделювання рецептур білково-жирових сумішей спеціального призначення. Значну увагу приділено питанню вибору способів стабілізації їх ліпідної складової від окисного псування. Підкреслено актуальність підвищення окисної стабільності білково-жирових сумішей за рахунок природних антиоксидантів, обґрунтовано доцільність комплексних досліджень їх впливу на стабільність до окиснення найбільш лабільних біологічно активних речовин білково-жирових сумішей.

Встановлено вміст фуранових антиоксидантів в насінні кунжуту сортів Глона, Кадет, Боярин, визначено кореляцію між вмістом сезамолу вільного і зв'язаного (сезамоліна). Також досліджено вміст α -ліноленової кислоти і токоферолів в лляному насінні сортів Південна ніч, Ківіка, Симпатік. Обґрунтовано вибір сортів кунжуту і льону для створення білково-жирової суміші спеціального призначення, що є джерелом поліненасичених жирних кислот Ω -3 групи і антиоксидантів сезамолу та сезамоліну.

Досліджено вплив вмісту сезамоліну і вологості в насінні кунжуту сорту Глона на стійкість до окиснення його ліпідної складової, отримана математична залежність, що описує такий вплив. Виявлена закономірність збільшення стабільності до окиснення насіння кунжуту при підвищенні його вологості з 4,0 до 9,5 %, що можна пояснити інтенсифікацією гідролізу сезамоліну з виділенням антиоксидантів сезамолу і саміну.

Досліджено ефект стабілізації α -ліноленової кислоти лляного насіння (сорт Південна ніч) в білково-жировій суміші спеціального призначення вільним сезамолом кунжуту. Доведено, що вагомий вплив на процес гальмування окиснення ліпідів білково-жирової суміші спеціального призначення несе раціональне співвідношення Ω -3 жирних кислот і сезамолу.

Методом сенсорної оцінки обґрунтовано вміст білково-жирової суміші спеціального призначення в соняшниковій халві на рівні 20 %, досліджено окисну стабільність, органолептичні і фізико-хімічні показників якості продукту. Визначено, що стабільність до окиснення (і, звісно, прогнозовані терміни зберігання) модельних зразків соняшникової халви залежать від вмісту в них білково-жирової суміші

Ключові слова: кунжут, льон, сезамол, сезамолін, α -ліноленова кислота, білково-жирова суміш, окисне псування, антиоксиданти, соняшникова халва

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RESEARCH ON OXIDATIVE STABILITY OF PROTEIN-FAT MIXTURE BASED ON SESAME AND FLAX SEEDS FOR USE IN HALVA TECHNOLOGY

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1. Introduction

The newest and most promising direction in the oil and fat industry is development and production of combined

products of lipid-protein composition for special purposes, that is, for nutrition of certain segments of population – children, athletes, pregnant women, the elderly, etc. The composition of such protein-fat mixtures (PFM) is consis-

tent with modern concepts of nutrition. Most often, the raw materials for PFM are meat products, milk proteins (casein, albumin and serum globulins), products of soybean processing (soybean flour, isolates, concentrates, etc.), wheat gluten, oils and fats of various fatty acid composition, etc. [1]. Their application allows food industry enterprises, in particular, confectionery enterprises, to unify production technology and expand the range of products [2].

A tendency of animal proteins replacement with combined vegetable protein mixtures has been observed in food production recently [4, 5]. Their use is due to technological properties, which are understood as proteins behavior in food systems: ability to form emulsions, gels, foams, absorb and retain fat, water, play the role of binding agents, etc. [6]. These semi-finished products can improve technological indicators, replace scarce animal raw materials and enrich food products with essential nutrients (essential amino acids, ω -3 polyunsaturated fatty acids, vitamins, minerals, carotene, chlorophyll, phytosterols, etc.). Studies aimed at the PFM oxidative stability increasing due to natural compounds with antioxidant activity are relevant taking into account the low oxidative stability of most lipophilic biologically active substances of the PFM.

2. Literature review and problem statement

The results of development of the PFM with fatty acid composition of lipids shifted towards saturated fatty acids are presented in [7]. It was found that the duration of product storage was longer than control sample storage. The reason of this was significantly higher lipid component oxidative stability. This method of products shelf life increasing has a disadvantage. It excludes the ability of products to have nutritional and biological values in addition to technological value.

The results of development of the PFM with a balanced ratio of fatty acids, reduced to a natural level content of fatty acids trans isomers and vitamins A and E content are presented in [8, 9]. The authors propose using the developed mixtures as enrichment, improvers or substitutes in the production of new or traditional food products, in particular, in meat processing products and in ice cream technology. A drawback of these developments is obtained food systems stabilization by synthetic antioxidants, in particular, butyl hydroxytoluene (BHT) and butyl hydroxyanisole (BHA). So it is advisable to search the natural antioxidants to stabilize unsaturated lipids of the PFM.

This problem was partially solved in [10]. The possibility of products lipid component stabilizing by complex antioxidants, which include such compounds as synthetic BHA, BHT, propylgallate, and as natural ones – tocopherols and ascorbyl palmitate, was shown. The weak side of this approach is associated with potential toxicity of synthetic compounds for the human body.

The work [11] describes a method of fat-containing products quality improving by incorporating tocopherol of plant origin. It was found that this provides products shelf life and biological value increasing. But it is worth noting that it is more advisable to use not individual antioxidants, but their mixtures, in oil and fat products production taking into account the increase in their effectiveness due to synergistic interaction.

A method of fat-containing food products stabilizing with a complex natural antioxidant of plant origin was proposed in [12]. The effectiveness of such mixtures is much higher due to the synergism than the use of individual antioxidants. But such additives have a rather high cost, which negatively affects the production cost, which means that the circle of its consumers is reduced.

The use of plant materials rich in antioxidants in PFM technology was described in [13, 14]. A PFM for special purposes, which contains flax, sesame, sunflower seeds and refined corn oil was developed. The product contains ω -3 polyunsaturated fatty acids (PUFAs), vitamins, trace elements, and is resistant to oxidative damage due to plant antioxidants presence. In addition, this PFM contains essential branched-chain amino acids (BCAAs) and can be recommended for athletes as a source of BCAAs. The authors proved that the substantiated component composition of the PFM determined its high biological value and long shelf life. The high biological value is due to the content of flaxseed in the PFM, which is the source of ω -3 PUFA. The long shelf life of the product is ensured by the content of sesame seeds, which is a source of furan lignans, some of which (sesamol, samin) have antioxidant properties [15, 16]. In addition, tocopherols are present in sesame oil. As is known from studies [17], sesamol is a synergist of tocopherols, and therefore these substances can be considered as a complex antioxidant. In addition, the aforementioned scientific papers [13, 14] describe the positive effects of adding the developed PFM to the confectionery product (cream sweets) for the rational nutrition of athletes.

It should be noted that dependence between the shelf life of the PFM, which contain sesame seeds, and mutual influence of factors affecting this process has not been revealed at present. For example, such factors are content of free and bound sesamol of sesame seeds, moisture and PUFA. Accordingly, the shelf life of the PFM is directly related to the oxidation stability (induction period) of its lipid component. This suggests the need for research in this area.

3. The aim and objectives of the study

The aim of the work is to study the oxidative stability of a protein-fat mixture based on sesame and flax seeds for use in halva technology. This will increase the biological value of the PFM and products based on it, as well as increase their shelf life.

The following tasks were set to achieve this aim:

- to identify and select raw materials for PFM for special purposes – sesame variety with the most effective antioxidant complex and flax variety with a maximum content of ω -3 polyunsaturated fatty acids;
- to investigate the effect of bound sesamol (sesamol) content and moisture on seeds lipid component resistance to oxidation in sesame seeds;
- to investigate the effect of stabilization against oxidative damage of α -linolenic acid of PFM for special purposes by free sesamol of sesame seed;
- to substantiate the confectionery product formulation with the addition of PFM for special purposes and determine its organoleptic and physicochemical parameters.

4. Materials and methods for studying the influence of sesame antioxidants on oxidative stability of PFM for special purposes

4.1. Materials and equipment used in the experiment

The following materials were used for research:

- sesame seeds according to DSTU 7012;
- flax seeds according to DSTU 4967;
- granulated sugar according to DSTU 4623;
- syrup according to DSTU 4498;
- soap root extract according to regulatory documents.

PFM for special purposes is a mixture of dried ground flax and sesame seeds in different ratios. The following ratio of PFM components (flax seeds – 50±2.0 %; sesame seeds – 50±2.0 %) was selected to develop a confectionery product.

Photographs of obtained PFM samples are shown in Fig. 1.

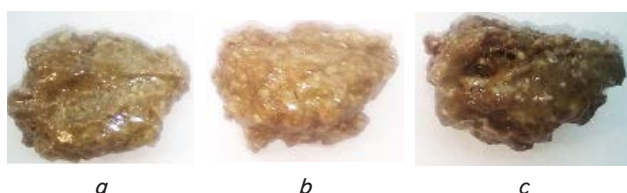


Fig. 1. Photographs of PFM samples with different content of components: *a* – flax seeds – 70 %, sesame seeds – 30 %; *b* – flax seeds – 50 %, sesame seeds – 50 %; *c* – flax seeds – 30 %, sesame seeds – 70 %

Grinding of seeds was carried out on a *Glasser* vertical blade chopper (Infel, Russian Federation) (rotation speed is about 7,000...10,000 rpm). The resulting mixture had a thick paste consistency. *Glasser* vertical blade chopper allows you to grind raw materials to a particle diameter of 150...200 microns.

4.2. Method of determining the content of antioxidants in oilseeds

Lipids were preliminarily extracted from oilseeds to determine the fat-soluble antioxidants in oilseeds. The content of tocopherol in seed lipids was determined by the spectrophotometric method. Analysis of seeds lipids containing free sesamol included extraction of sesamol from oil with an aqueous alkali solution, colorimetric reaction with aqueous sulfuric acid with furfural presence, and spectrophotometric determination. Analysis of seed lipids containing bound sesamol (sesamolin) was carried out in an oil solution after isolation of free sesamol from it. The analysis included measuring the absorption spectrum of the oil solution in the range of 250–320 nm. Sesamolin does not give a purple-colored product of a colorimetric reaction with these reagents.

4.3. Method of determining the moisture content in oilseeds

Moisture determination of sesame seeds was carried out according to standard methods. The essence of the method is to dehydrate a sample of ground seeds in an air-heat cabinet at fixed parameters (temperature – 110 °C, drying time – 10 minutes) and determine its weight loss.

4.4. Method of determining the stability to oxidation of oilseeds, PFM and model samples of sunflower halva

The oxidative stability of ground flax and sesame seeds, as well as their mixtures, was studied using the acceler-

ated “active oxygen” method. This method is based on the exposure of the ground seeds at a constant elevated temperature and determination of the degree of oxidation of oil in it at regular intervals, which is characterized by the peroxide value. 50 g of the studied sample was introduced into the weighing bottle and placed in a drying cabinet heated to a temperature of 85±2 °C. Samples of ground seeds for peroxide value (PV) determining were taken with a spatula in the amount of 5.0±0.02 g in a pre-weighed ground-glass stopper flask; the flask was re-weighed after cooling the sample. The oxidation indicators were determined according to the mass difference of the taken sample. The oil was extracted and the PV was measured. The oxidation of oils was carried out to the PV equal to 10 mmol ½ O/kg, taking into account the inappropriateness of further oxidation. The values of the induction period were determined graphically from the curves of peroxide values growth.

4.5. Method of determining the α-linolenic acid content in oilseeds

The fatty acid composition of the oils extracted from oilseeds was determined by the standard method of gas-liquid chromatography on a Shimadzu chromatograph (Japan). Evaporator temperature – 240 °C; detector temperature – 250 °C; speed of carrier gas (hydrogen) – 1.0 ml/min., flow division – 1:60. Fatty acids were identified by comparing their retention times with the retention times of reference samples. The content of fatty acids, in particular α-linolenic, was calculated as a percentage of their total.

4.6. Method of sunflower halva obtaining

Sunflower halva obtaining included the following stages: obtaining caramel mass from granulated sugar and syrup, obtaining whipped caramel mass from the original caramel mass and soap root extract, and actually mixing the whipped caramel mass with the mass of fried ground sunflower seeds, to which a certain amount of the PFM for special purposes is added.

4.7. Methodology of the study of sunflower halva quality indicators

Sensory evaluation of halva samples was performed by experts according to ISO 8586-1 and ISO 8586-2. The olfactory, gustatory, tactile sensitivities of the experts were determined in accordance with ISO 5496: 1992, ISO 3972: 1991 and ISO 11036. A special system of scoring for sensory assessment was used. Scoring quantitatively expresses a number of quality indicators of the studied halva samples. The organoleptic evaluation of halva samples was determined according to DSTU 4188. The mass fraction of moisture in halva samples was determined according to GOST 5900, the mass fraction of fat – according to GOST 5899, the mass fraction of total sugar – according to GOST 5903.

4.8. Experiments designing and statistical processing of research results

Mathematical methods were applied to plan the experiment and process the data using the software packages Microsoft Office Excel 2003 (USA) and Stat Soft Statistica v6.0 (USA). We used a three-level plan for the two-factor response function to study the dependence of the induction period of lipid oxidation of oilseed and PFM samples at the temperature of 85±2 °C on the content of free and bound sesamol (sesamo-

lin), α -linolenic acid and the mass fraction of moisture. The studies were carried out in triplicate. For a given degree of probability $P=95\%$, the relative error did not exceed:

- 2% in determining the tocopherol fraction of seed lipids;
- 4% in determining the content of free and bound sesamol in oilseeds;
- 0,5% in determining the fatty acid composition of oilseed lipids;
- 4% in determining the peroxide value of lipids of oilseed and the PFM;
- 5% in determining the induction periods of lipids oxidation of oilseed and the PFM;
- 0.25% in determining the mass fraction of moisture of oilseeds and sunflower halva;
- 0.5% in determining the mass fraction of fat in sunflower halva;
- 1% in determining the mass fraction of sugar in sunflower halva.

5. Results of the study of sesame antioxidants effect on oxidative stability of the PFM for special purposes

5.1. Study of the target components of raw materials for the PFM for special purposes

Samples of sesame seeds of Ilona, Kadet and Boyarin varieties were studied to determine the content of tocopherols and the sesamol specific antioxidant – free and bound (sesamol). The results are presented in Table 1.

Table 1

Content of antioxidants in sesame seeds of different varieties

Sesame variety	Tocopherols, mg/100 g of lipids	Sesamol, mg/100 g of lipids	
		free	bound (sesamol)
Ilona	35.5	15.3	1,130
Kadet	30.2	10.1	880
Boyaryn	36.0	12.6	1,050

It has been established that sesame seeds contain tocopherol from 30.2 mg/100 g of lipids (Cadet variety) to 36.0 mg/100 g of lipids (Boyaryn variety). The largest amount of free and bound sesamol was recorded in Ilona variety – 15.3 mg/100 g of sesamol and 1130 mg/100 g of sesamol.

A correlation between the content of free and bound sesamol in sesame seeds of different varieties was established. This is graphically shown in Fig. 2. The equation describing this dependence is as follows:

$$c_{sn}(c_{sl})=79.428 \cdot c_{sl}+4.672, (R=1) \tag{1}$$

where c_{sl} – content of free sesamol in sesame seed samples, mg/100 g (in the range of $c_{sl}=10.1...15.3$ mg/100 g); c_{sn} – content of bound sesamol (sesamol) in sesame seed samples, mg/100 g (in the range of $c_{sn}=880...1,130$ mg/100 g).

Samples of flax seeds of Southern Night, Kivika and Sympatik varieties were studied to determine the content of α -linolenic acid (ω -3 groups PUFA) and tocopherol antioxidants. The results are presented in Table 2.

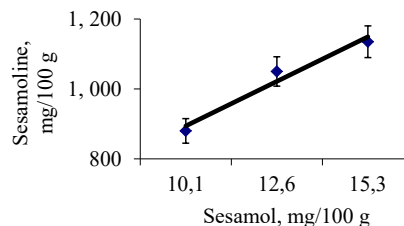


Fig. 2. Dependence of bound sesamol (sesamol) content versus free sesamol content in various types of sesame seeds

Table 2

Content of α -linolenic acid and tocopherols in flax seeds of different varieties

Flax variety	Content of a-linolenic acid, % of total fatty acids	Tocopherols, mg/100 g of lipids
Southern Night	55.9	40.7
Kivika	50.3	38.1
Sympatik	54.1	35.9

It has been established that flaxseed contains tocopherol from 35.9 mg/100 g of lipids (Sympatik variety) to 40.7 mg/100 g of lipids (Southern Night variety). The highest amount of α -linolenic acid (55.9%) was recorded in Southern Night variety. It should be noted that the higher the α -linolenic acid content in flaxseed samples, the higher the tocopherols content in them.

5.2. Study of the effect of physicochemical composition of sesame seeds on oxidation stability

We studied the change of induction period of lipid oxidation of ground sesame seeds of selected varieties with different moisture contents in the next stage of the work. The research results are shown in Fig. 3.

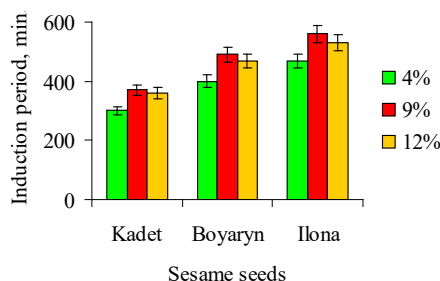


Fig. 3. Dynamics of the induction period of lipids oxidation of sesame seeds with different moisture contents

It is known that with increasing moisture content of fat-containing raw materials, oxidative damage processes are intensified, which leads to a decrease in the induction period of lipid oxidation. A different dependence is observed in the case of an increase in moisture content in samples of sesame seeds of all varieties. As can be seen from Fig. 3, an increase in moisture content in sesame seed samples from 4 to 9% leads to an increase in the induction period of lipid oxidation. The induction period practically does not decrease

with an increase in seeds moisture from 9 to 12 %. It has been revealed that sesame seeds of Ilona variety are characterized by the highest oxidative stability (560 minutes at a moisture content of 9 %).

We used the multivariate regression method with the construction of response surfaces to determine the dependence between the induction period of lipid oxidation of samples of sesame seeds of Ilona, Kadet and Boyarin varieties at the temperature of $85 \pm 2^\circ\text{C}$ and bound sesamol (sesamol) and moisture content. The method of full factorial experiment was used to build the model. The content of bound sesamol (sesamol) in sesame seeds samples was varied in the range of 880...1130 mg/100 g in increments of 125 mg/100 g. The moisture content in sesame seeds samples was varied in the range of 4.0...12.0 % in increments of 4.0 %. The obtained values of the induction period of lipid oxidation of sesame seeds samples were within 300...560 minutes. The surface of this dependence is shown in Fig. 4.

The equation of the two-factor polynomial regression model of the second degree, describing this dependence and obtained using mathematical processing of experimental data has the next form:

$$\begin{aligned} \tau_i(c_{sn}, WC) = & -2131.4 + 4 \cdot c_{sn} + \\ & + 53.2 \cdot WC - 0.002 \cdot c_{sn} \cdot WC - 2.92 \cdot WC^2, \\ R^2 = & 0.91, \end{aligned} \tag{2}$$

where $\tau_i(c_{sn}, WC)$ – induction period of accelerated oxidation of sesame seeds samples at 85°C , min.; c_{sn} – content of bound sesamol (sesamol) in sesame seeds samples, mg/100 g (in the range of $c_{sn}=880\text{...}1130$ mg/100 g); WC – moisture content in sesame seeds samples, % (in the range of $WC=4.0\text{...}12.0$ %).

The coefficients of this regression equation were determined using the least squares method. The significance of individual regression coefficients was determined using Student's criterion t by testing the hypothesis that the corresponding equation parameter is equal to zero. The calculated absolute value of Student's criterion $t(6)$ was compared with its critical tabular value $t_{ctv}(6)=2.45$ at the significance level $p=0.05$ and the number of degrees of freedom for multiple regression $df=6$ when assessing individual regression coefficients. If the calculated absolute Student's criterion was greater than its tabular value, the null hypothesis was rejected and the value of the corresponding coefficient of the regression equation was considered significant with a probability of 0.95 (or 95 %), otherwise the regression coefficient was recognized insignificant and excluded from the equation. Data and conclusions regarding the determination of coefficients significance of the regression equation are given in Table 3.

The determination coefficient R^2 was determined to assess the quality of the model and the completeness of selected factors influence. The obtained value $R^2=0.91$ allows us to conclude that there is a very significant effect (more than 91 %) of variations in bound sesamol (sesamol) and moisture content on variations in the induction period of lipid oxidation of the studied sesame seeds samples. The Fisher-test F was calculated to establish the significance of the regression model based on the assumption that the equation is statistically insignificant ($R^2=0$ – the null hypothesis). The calculated value of Fisher-test was $F(2, 6)=30.13$ and was greater than

its critical tabular value $F_{ctv}(2, 6)=5.14$ with the significance level $p=0.05$ and the number of freedom degrees $df_1=2$ and $df_2=6$. This result allows us to reject the null hypothesis and recognize significance of determination coefficient value $R^2=0.91$ and the model with a probability of 0.95 (or 95 %).

Table 3

Data and conclusions regarding determination of coefficients significance of the regression equation (2)

Coefficient of the regression equation at	Coefficient value in physical units	t(6)	tctv(6)	Estimated probability of null hypothesis for the coefficient of the regression equation (p-level)	Conclusion about coefficient significance
Intercept	-2131.4	-3.26820	2.45	0.017073	Significant
csn	4	7.19402		0.000365	Significant
WC	53.2	2.91529		0.026795	Significant

Based on the obtained results, it can be stated that there is a regularity of increasing the induction period of PFM oxidation with increasing moisture content from 4.0 to 9.5 %. This can be explained by bound sesamol hydrolysis intensification. But there is a decrease in the induction period of PFM lipid oxidation with a further increase in moisture content from 9.5 to 12.0 %, which can be explained by an increase in triglycerins hydrolysis rate with the formation and, correspondingly, faster oxidation of free fatty acids.

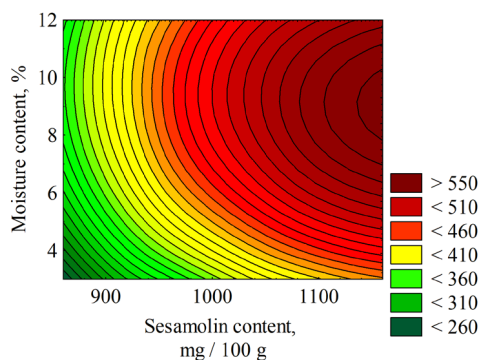


Fig. 4. Dependence of the induction period of lipid oxidation of sesame seeds samples versus sesamol bound (sesamol) and moisture content

As can be seen from Fig. 5, hydrolysis of bound sesamol (sesamol) is accompanied by release of substances with antioxidant activity (proton donors) – free sesamol and samin, which inhibit lipid oxidation.

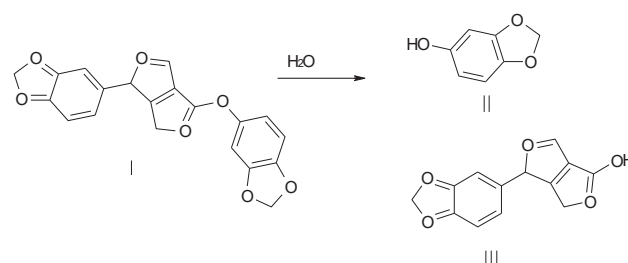


Fig. 5. Scheme of hydrolysis of bound sesamol (sesamol) (I) with free sesamol (II) and samin (III) release

5. 3. Investigation of stabilization effect of α -linolenic acid in the PFM for special purposes with sesame free sesamol

It is known that ω -3 PUFAs (so-called vitamin F) are extremely deficient in the body. It is difficult to overestimate their biological value [3, 5, 15], but resistance to oxidative damage of these compounds is extremely low. Therefore, a study of mutual influence of sesamol antioxidant content of sesame seeds and α -linolenic acid of flax seeds on the induction period of the PFM for special purposes (source of ω -3 polyunsaturated fatty acids) was conducted. As you know, the induction period of fat-containing products is proportional to their shelf life.

A method of multivariate regression with the construction of response surfaces was chosen to determine the dependence of the induction period of lipid oxidation of PFM samples at the temperature of 85 ± 2 °C versus antioxidant sesamol and α -linolenic acid content in it. A method of full factorial experiment was used to build the model. Free sesamol content in PFM samples varied in the range of 0...15.3 mg/100 g. α -linolenic acid content in PFM samples varied in the range of 0.1...55.9 % of total fatty acids. The obtained values of the induction period of lipid oxidation of sesame seeds samples were within 65...475 min. The equation of the two-factor polynomial regression model of the second degree obtained using mathematical processing of experimental data has the next form:

$$\tau_i(c_{sl}, c_{la}) = 135.71 + 26.38 \cdot c_{sl} - 1.43 \cdot c_{la} - 0.26 \cdot c_{sl}^2 - 0.29 \cdot c_{sl} \cdot c_{la} + 0.003 \cdot c_{la}^2, \quad R^2 = 0.98, \quad (3)$$

where $\tau_i(c_{sl}, c_{la})$ – induction period of accelerated oxidation of the PFM at 85 °C, min.; c_{sl} – free sesamol content in the PFM, mg/100 g (in the range of $c_{sl} = 0.00 \dots 7.65$ mg/100 g); c_{la} – α -linolenic acid content, % of total fatty acids (in the range of $c_{la} = 0.1 \dots 55.9$ % of total fatty acids).

The coefficients of this regression equation were determined using the least squares method. The significance of individual regression coefficients was determined using Student's criterion t by testing the hypothesis that the corresponding equation parameter is equal to zero. The calculated absolute value of Student's criterion $t(9)$ was compared with its critical tabular value $t_{ctv}(9) = 2.26$ at the significance level of $p = 0.05$ and the number of degrees of freedom for multiple regression $df = 9$ when assessing individual regression coefficients. If the calculated absolute Student's criterion was greater than its tabular value, the null hypothesis was rejected and the value of the corresponding coefficient of the regression equation was considered significant with a probability of 0.95 (or 95 %), otherwise the regression coefficient was recognized insignificant and excluded from the equation. Data and conclusions regarding the determination of coefficients significance of the regression equation are given in Table 4.

The determination coefficient R^2 was determined to assess the quality of the model and the completeness of selected factors influence. The obtained value $R^2 = 0.98$ allows us to conclude that there is a very significant effect (more

than 98 %) of variations in free sesamol and α -linolenic acid content on variations in the induction period of lipid oxidation of the studied PFM samples. The Fisher-test F was calculated to establish the significance of the regression model based on the assumption that the equation is statistically insignificant ($R^2 = 0$ – the null hypothesis). The calculated value of Fisher-test was $F(2, 9) = 240.74$ and was greater than its critical tabular value $F_{ctv}(2, 9) = 4.26$ with the significance level $p = 0.05$ and the number of freedom degrees $df_1 = 2$ and $df_2 = 9$. This result allows us to reject the null hypothesis and recognize significance of determination coefficient value $R^2 = 0.98$ and the model with a probability of 0.95 (or 95 %).

Table 4

Data and conclusions regarding determination of coefficients significance of the regression equation (3)

Coefficient of the regression equation at	Coefficient value in physical units	t(9)	tctv(9)	Estimated probability of null hypothesis for the coefficient of the regression equation (p-level)	Conclusion about coefficient significance
Intercept	135.71	11.48667	2.45	0.000001	Significant
csl	26.38	16.27938		0.000000	Significant
cla	-1.43	-535396		0.000460	Significant

The surface of the dependence of the induction period of PFM oxidation of the PFM based on flax and sesame seeds versus sesamol and α -linolenic acid content at the temperature of 85 ± 2 °C is shown in Fig. 6.

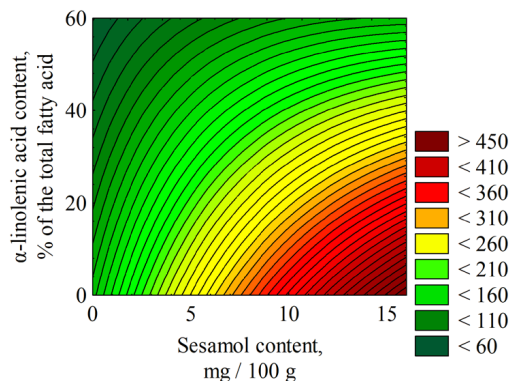


Fig. 6. Dependence of the induction period of lipids oxidation of the PFM based on flax and sesame seeds versus sesamol and α -linolenic acid content

The graph in Fig. 6 illustrates the mutual influence of sesamol and α -linolenic acid on the values of the induction period of lipids oxidation of the PFM based on flax and sesame seeds with different proportions of components.

5. 4. Substantiation of halva formulation with the PFM for special purposes and study of halva quality parameters

The next stage of research was development of the formulation of confectionery with addition of the PFM for special purposes (sample 2, Fig. 1). The indicated ratio of components (50 % of each flax and sesame seeds) makes the product a source of α -linolenic PUFA (23.0 ± 0.7 % of total

fatty acids), which is stabilized against oxidative damage by free sesamol effective concentration (10.0 ± 0.3 mg/100 g). The PFM can be used both in daily nutrition and as part of confectionery products for the rational nutrition of athletes, hard physical workers (for example, miners, geologists), and military personnel. Sunflower halva was chosen as such confectionery product. Usually this product is consumed during tea drinking, and its components (not only carbohydrates, but also proteins with dispersed lipids, vitamins, minerals, etc.) enter the body in the form of a warm concentrated aqueous solution. This speeds up their metabolism in the body. Due to the high energy value of halva (more than 520 kcal/100 g), athletes often eat it as a snack between workouts and competitions. Therefore, it makes sense to increase the biological value of this confectionery product by introducing into its composition ω -3 group polyunsaturated fatty acids, stabilized by a complex of natural antioxidants. The formulations of model samples of sunflower halva with the PFM are given in Table 5.

Table 5

Formulations of model samples of sunflower halva with different contents of the PFM

Component	Raw material content, kg			
	a	b	c	d
Sunflower mass	510.0	460.0	410.0	310.0
PFM	–	100	200	300
Syrup	330.0	330.0	330.0	330.0
Granulated sugar	150.7	150.7	150.7	150.7
Soap root extract	9.0	9.0	9.0	9.0
Vanillin	0.3	0.3	0.3	0.3
Total, %	1000.0			

Photos of model samples of sunflower halva are shown in Fig. 7.



Fig. 7. Photos of model samples of sunflower halva: a – without PFM addition; b – with 10 % of PFM content; c – with 20 % of PFM content; d – with 30 % of PFM content

The obtained halva model samples were subjected to thermal oxidation at the temperature of 85 ± 2 °C. The induction periods of lipid oxidation of halva samples are shown in Fig. 8.

The diagram in Fig. 8 shows that oxidation of the lipid component of halva samples is significantly inhibited when the PFM content is from 20 to 30 % (induction period values are 460 and 480 minutes in comparison with 270 minutes in the control sample).

A sensory assessment of organoleptic parameters of model halva samples was carried out. The products were evaluated by such indicators as appearance, taste, smell, texture and appearance in the break. The results of sensory evaluation are reflected in the profilogram, which is presented in Fig. 9.

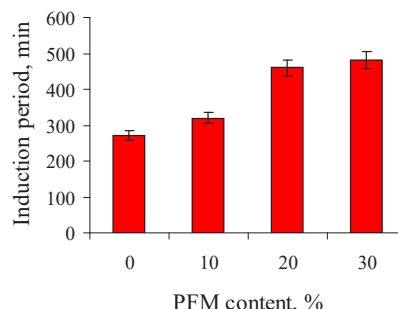


Fig. 8. Induction period of oxidation of sunflower halva model samples at the temperature of 85 ± 2 °C

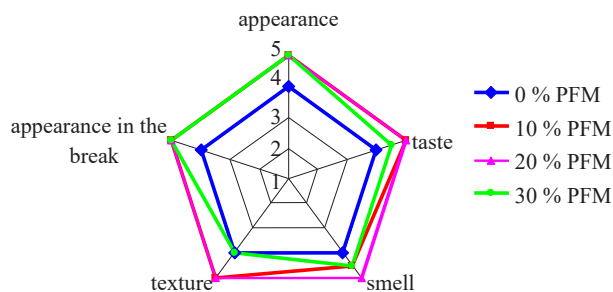


Fig. 9. Profilogram of organoleptic parameters of sunflower halva model samples with of PFM different amounts addition

The analysis of profilograms of organoleptic parameters of halva samples has shown the advantage of a sample containing 20 % of the PFM, mainly in terms of taste, smell and appearance in the break (5 points versus 4...4.5 points). In particular, piquant nutty aroma and taste typical of sesame seeds are evident in the halva samples with 20 and 30 % content of the PFM. But, the scores for taste (a feeling of “powderiness”), smell (“fishy” smell) and consistency (“powdery”) were reduced for the sample with 30 % of the PFM. Thus, the results of profilograms confirm the choice of the PFM content in sunflower halva at the level of 20 %.

The physicochemical parameters of the halva model sample with 20 % of PFM addition were studied in comparison with the halva sample without the PFM. The data are presented in Table 6.

Table 6

Physicochemical parameters of the studied halva model samples

Physicochemical parameters	Sunflower halva		
	control sample (0 % PFM)	sample with 20 % PFM	Norm according to DSTU 4188
Moisture content, %	3.40	3.15	less than 4 %
Fat content, %	32.80	32.60	28–34 %
Total sugar in terms of sucrose, %	42.70	42.30	25–45 %

As can be seen from Table 4, the physicochemical parameters of the halva sample with the PFM do not differ from the control ones and meet the requirements of regulatory documentation.

6. Discussion of results of the study of sesame antioxidants effect on oxidative stability of the PFM for special purposes

The results of the study of samples of sesame seeds of domestic varieties (Ilona, Boyarin and Kadet) indicate a rather high content of tocopherols, sesamol and sesamol. Inclusion of tocopherol-rich sesame seeds in daily diet will help increase the body's antioxidant status. Obviously, inclusion of sesame seeds as a raw material in the PFM for special purposes is a factor in regulating the shelf life of a product due to effective antioxidant complex. It is seen that between the samples of different sesame varieties with approximately the same tocopherols content, a significant difference in free and bound sesamol content is observed by analyzing the antioxidant composition of sesame seeds. Given the above, Ilona variety sesame having the most effective antioxidant complex has been selected as a raw material for the PFM for special purposes.

The analysis of the induction periods of lipid oxidation of sesame seeds with different contents of moisture, free and bound sesamol and α -linolenic PUFA allows us to state the following:

- increase in moisture content in the PFM containing sesame seeds plays a double role – on the one hand, the process of hydrolysis of triacylglycerols is intensified, which initiates their oxidative damage, and on the other hand, the process of release of antioxidants – free sesamol and samin from sesamol (Fig. 5), whose action leads to inhibition of PFM lipid oxidation, – is accelerated. This can make certain adjustments to the technological process of production and storage;

- rational moistening of raw materials has a significant impact on production and storage of the PFM with sesame seeds. This will ensure the prolonged release of antioxidant complex (Fig. 5) to inhibit the oxidation of labile biologically active compounds in the product;

- correct variation in the content of ω -3 fatty acids and sesamol in the product has a significant effect on lipid oxidation inhibition of the PFM for special purposes.

These conclusions may be appropriate from a practical point of view, as they allow to determine the ratio of components in the PFM. From a theoretical point of view, the feasibility of conclusions is to determine the fundamental possibility of the process of hydration of pro-antioxidant compound in the PFM with active antioxidants formation (Fig. 5). These are the benefits of the research. However, it is worth noting that the mathematical dependence (1) analysis indicates an ambiguous effect of moisture content on product oxidative stability. In the framework of this study, this ambiguity is not resolved. This is the task of further research, which, in particular, should be focused on identifying the equilibrium value of moisture content of the system. The rate of inhibition of oxidation of sesamol and samin formed as a result of hydrolysis of sesamol is equal to the oxidation rate of free fatty acids formed as a result of triacylglycerols hydrolysis at this point. The results of such a study will significantly streamline the storage processes of raw materials and finished products. The obtained data should be of interest to both oil and fat and confectionery enterprises producing the PFM and confectionery products with its addition.

Rational concentrations of biologically active compounds in the PFM for special purposes were selected by experiment

results analyzing (Fig. 4, 6, eq. (3), (4)). They are as follows: α -linolenic PUFA content is 20...23 % of total fatty acids, free sesamol – 10...12 mg/100 g, bound sesamol (sesamol) – 740...890 mg/100 g. The ratio of components is 35...50 % of flax seeds and 50...65 % of sesame seeds at the same time.

The studies have shown that the antioxidant complex of sesame seeds has a stabilizing effect on the lipid component of the product with PFM addition. Fig. 8 shows that the oxidation stability (and, of course, predicted shelf life) of sunflower halva model samples depends on PFM content in them. The induction period of sunflower halva lipids with 10 % of PFM exceeds the induction period of the control sample by only 19 %, but the induction periods of halva samples containing 20 % and 30 % of the additive exceed the control sample induction period by 70 % and 78 %, respectively.

It can be seen from the profilogram of organoleptic parameters of sunflower halva model samples with different PFM content (Fig. 9) that the use of the PFM in product composition has a significant effect on taste and smell organoleptic indicators values, which are higher in experimental samples with 10 and 20 % of PFM, than in the control sample. A further increase in PFM content more than 20 % leads to the appearance of "mealy" flavor and "fishy" smell of ground flaxseed. Thus, PFM effective concentration in sunflower halva was chosen at the level of 20 % based on the results of sensory analysis.

The results of determining the physicochemical quality parameters of halva model samples (Table 4) indicate that when 20 % of the PFM is added to this confectionery product, there are practically no changes in moisture, fat and sugar content.

7. Conclusions

1. The content of tocopherols, free and bound sesamol in sesame seeds of Ilona, Kadet, Boyarin varieties was established in the study. It was determined that the Ilona variety sesame seeds samples contain the largest amount of free and bound sesamol (15.3 mg/100 g and 1130 mg/100 g, respectively). Due to this, it can be argued that the Ilona variety sesame seeds in the PFM will exhibit a high ability to inhibit oxidative damage, thereby reducing the amount of this type of raw material. The content of α -linolenic acid and tocopherols in samples of flax seeds of Southern Night, Kivik, Sympatik varieties was also established. It was determined that Southern Night variety flax seeds contain the highest content of α -linolenic acid and tocopherols (55.9 % and 40.7 mg/100 g of total fatty acids, respectively). Thanks to this, it can be argued that Southern Night variety flax seeds as part of the PFM will carry the greatest biological value.

2. The mathematical dependence of the induction period of lipid oxidation of sesame seeds samples versus the content of bound sesamol (sesamol) in the range of 880...1130 mg/100 g and moisture content in the range of 4.0...12.0 % was obtained. This dependence has shown that the factor of increased moisture of the PFM (from 4.0 % to 9.5 %) leads to an increase in the induction period of product lipid oxidation due to sesamol hydrolysis mechanism with sesamol and samin antioxidants release. The described dependence was not observed with a further increase in moisture. This indicates the prevalence of hydrolysis of triacylglycerols and oxidation of free fatty acids.

3. The mathematical dependence of the induction period of lipid oxidation of samples of the PFM for special purposes versus the content of free sesamol in it in the range of 0.00...7.65 mg/100 g and α -linolenic acid in the range of 0.1...55.9 % of fatty acids amounts has been obtained. The calculated dependence has proved the possibility of directional regulation of the process of oxidative damage by adjusting these factors, which, in turn, can significantly simplify the selection of rational storage conditions for the PFM for special purposes with a given composition of ω -3 fatty acids. Rational concentrations of biologically active compounds have been selected: α -linolenic PUFA content is 20...23 % of total fatty acids, free sesamol content is 10...12 mg/100 g, bound sesamol (sesamol) content is 740...890 mg/100 g.

4. The formulation of sunflower halva with the addition of the PFM for special purposes has been scientifically sub-

stantiated. It has been determined that the PFM contributes to an increase in stability to oxidative damage of sunflower halva, and it positively affects such organoleptic parameters as taste and smell when added in an amount of up to 20 %. The organoleptic and physicochemical parameters of the developed confectionery product have been determined (moisture content is 3.15 %, fat content is 32.60 %, total sugar content in terms of sucrose is 42.30 %), they are within the limits defined in DSTU 4188. Based on the obtained results, it can be argued that the studied sesame antioxidant complex and the revealed dependences of its stabilizing action are promising for oil and fat and food industries, as well as for producers of biologically active additives. However, it is necessary to continue further studies of sesame antioxidant complex effect on the oxidative damage stabilization of other biologically active substances labile to oxidation.

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