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DEVELOPMENT OF NEW TYPES OF VEGETABLE OIL BLENDS WITH BALANCED FATTY ACID COMPOSITION ON THE BASIS OF KAZAKHSTAN COTTON OIL AND BELARUSIAN LINSEED OIL

Abstract. The article presents the results of research on the development of new types of vegetable oils, based on the combination of oils with higher content of such acids as linolenic and lenolic acids with oils in which these contents are lower. It has been established that the content of linoleic acid in cotton oil exceeds all other oils practically twice, and linseed oil in the content of α-linolenic acid practically 50 times. Consequently, the optimal fatty acid composition is a blend of cotton and linseed oils in ratios of 5:1 and 10:1. Such ratio allows to balance the blend by ω-3 and ω-6 acids, as well as to reduce the oxidizing ability of vegetable oils, affecting the shelf life of the final product.

Keywords: cottonseed oil, linoleic acid, blended vegetable oils, linseed oil, edible vegetable oils, linolenic acid, polyunsaturated fatty acids.

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Introduction. The introduction of effective physiological regulators of biochemical processes in the human diet is becoming increasingly important nowadays. There are many nutrients among them that are necessary for normal development and functioning of the organism, the composition of which should be adjusted depending on sex, age, condition (pregnancy, lactation, diseases, gerontology, etc.) [1].

Wide medical and hygienic studies of diets of various population groups [2,3] have shown a significant imbalance of the main components, including low consumption of polyunsaturated fatty acids (PUFA) that are a part of the phospholipids of cell membranes, where they participate in the regulation of impulse transmission from receptors. Their proper concentration triggers the synthesis of some hormones, such as eicosanoids, that are in charge of immune responses at the cellular level [4-6]. Increasing the share of PUFAs in the diet reduces the concentration of soft cholesterol in biological fluids and thus the risk of cholesterol deposits in blood vessels.

Bringing PUFAs consumption to the acceptable level is an important factor in supporting healthy lifestyle and preventing the growth of chronic non-infectious diseases among the population [2,3,7]. is to Enriching the traditional food with ω-3 and ω-6 polyunsaturated fatty acids is among of the ways to achieve this goal.

PUFAs of the ω-3 family are represented at Figure 1 over the example of α-linolenic acid; PUFAs of the ω-6 family are shown at Figure 2 through the example of linoleic acid.

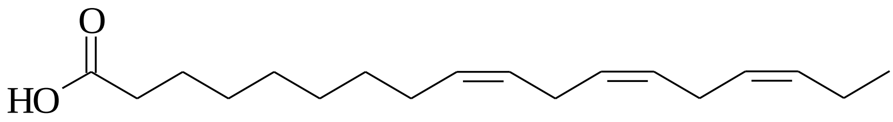

Fig. 1. Alpha-linolenic acid

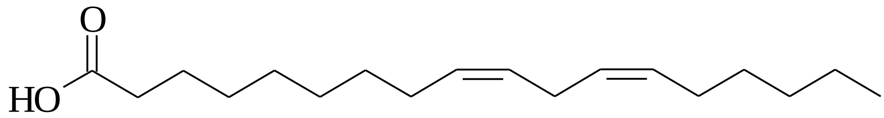

Fig. 2. Linoleic acid

Alpha-linolenic acid (C18:3, ω-3), from which cells synthesize long-chain PUFAs like eicosatetraenoic acid (C20:5, ω-3) and docosahexaenoic acid (C22:6, ω-3), is among the most important polyunsaturated fatty acids of the ω-3 class. However, the productivity of synthesis of these acids is insufficient, and with age it is significantly reduced or completely lost. This requires their supplementation to obtain a balance.

On the other hand, essential linoleic acid (C18:2, ω-6), which can be converted in the body to arachidonic acid (C20:4, ω-6), is found in cell membranes at a 10-fold ratio to α-linolenic acid. Almost all the vegetable oils (coconut oil is the exception) contain linoleic acid in their formulas. It is also produced as a dietary supplement in capsule form.

It is equally important when formulating the diet to take into account that the chain elongation and desaturation reactions of ω-3 and ω-6 fatty acids are catalyzed by the same enzymes, i.e. the fatty acids are the competitors. Such competition results in excess of fatty acids from one family by inhibition the synthesis of the corresponding acid from the other family, which emphasizes the need for a balanced composition of omega-3 and omega-6 PUFAs in the diet, because the synthesis of longer molecules can’t improve the balance.

Among natural sources of polyunsaturated fatty acids, first of all, we should mention almost all common nuts and pumpkin seeds, sunflower seeds, legumes, including peanuts, vegetable oils, fish oil and fish of fatty and semi-fatty species (salmon, mackerel, herring, sardines, mackerel, trout, tuna and others), cod liver and shellfish [8]. However, the ratio of ω-3 and ω-6 fatty acids in them is usually far from optimum [9-12]. This requires to blend the edible vegetable oils to increase the proportion of the desired lipids in the final product to reach the desirable amount of ω-3 and ω-6 PUFAs [3,9,10].

In the connection with the above mentioned, the aim of the present work was to study the fatty acid composition of various types of vegetable oils and to develop on the basis of this analysis the composition of a new type of blend with the optimal ratio of ω-3 and ω-6 polyunsaturated fatty acids with the assessment of oxidative stability of the final product during storage.

Materials and methods. As the objects of research there were chosen:

- *sample No.1* – cotton refined deodorised oil, isolated from cotton seeds by Kazakhstani producer JSC "Shymkentmai", as the most widespread in the southern regions of Kazakhstan;
- *sample No. 2* – linseed oil, extracted from flax seeds, differing from other types of oils, high content of ω-3 PUFAs, produced in Belarus;
- *sample No.3* – corn oil extracted from corn seeds, also produced in Belarus;
- *sample No.4* – rapeseed oil, produced in Belarus, which is extracted from black rapeseed seeds.

Of all the listed types of vegetable oil, linseed oil is referred to the little studied oils in our country, because in industrial scale, it grows in the Republic of Belarus. Corn and rapeseed oil are rich with ω-6 polyunsaturated fatty acids.

The study of fatty acid composition of vegetable oils of selected samples was carried out by a gas chromotograph "Chromatek Crystal-5000" using the method of gas-liquid chromatography. The device "Chromatek Crystal-5000" is equipped with a flame ionisation detector (FID), a quartz capillary column with a diameter of 0.25 mm and a length of 100 m, with the applied phase – cyanopropyl phenyl polysiloxane. Nitrogen was used as the gas. The volume of the injected sample was 1 μl. The method of measurements corresponded to GOST 30418-96 [11]. Preparation of fatty acid methyl esters was carried out in accordance with GOST 31665-2012 [12].

The following temperature regimes were used for measurements. Prior to analysis the column thermostat had an initial temperature of 140°C and was heated at this level for 4 minutes. The temperature was then programmatically increased at a rate of 3°C/min to 180°C and maintained for 40 minutes. Further, the temperature was increased at a rate of 3°C/min to 240°C. The isothermal regime was maintained for 25 minutes.

Chromatograph calibration and subsequent identification were carried out by Restek 35077 and Restek 35079 environmental fatty acid mixtures, FAME Mix, Supelco 37-component fatty acid methyl esters standard mixture, and literature data on retention indices.

Sample preparation: vegetable oil samples were weighed 0.1±0.002 g and dissolved in 2.0 cm^3 of hexane, then shaken well. Then 0.1 cm^3 of sodium methylate solution in methanol with molar concentration of 2 mol/cm^3 was added to the obtained solution by pipette, corked and stirred vigorously for 2 minutes. Then the reaction mixture was allowed to stand for 5 min and the upper layer containing the methyl esters was filtered through a paper filter. 0.1 to 2 mm^3 of the fatty acid methyl esters solution was taken from the test sample and inserted onto the column.

Using Unichrome® software, the quantification of fatty acids in the tested samples was carried out by the internal normalisation method. Also, there were conducted organoleptic evaluation of blends by colour analysis in transmitted and reflected light on a white background, as well as by smell analysis at a sample temperature of about 50°C and taste characteristics that were determined by the commission, which consisted of five trained testers who used a 5-grade scale under the principles of GOST ISO 13299-2015[13] and GOST ISO 11037-2013 [14].

The main indicators of oxidative deterioration during storage of vegetable oils and their blends under ultraviolet radiation and oxygen access at the air temperature of 20±5°C were estimated by the value of acid number according to GOST 31933-2012 [15] and peroxide number according to GOST 26593-85 [16]. A storage regime was chosen as close as possible to the conditions of household use. Every fortnight samples were taken for further testing.

The values of the quality indicators of the obtained vegetable oil samples are presented in Table 1.

Table 1

Values of quality indicators of tested oil samples

A trivial name	Nomenclature name	Fatty acid content, wt. %			
		Sample No.1	Sample No.2	Sample No.3	Sample No.4
Alpha-linolenic	cis-9,12,15-octadecatrienoic	0.1	51.7	8.1	1.0
Linoleic	cis-9,12-octadecane	51.5	15.6	22.7	43.0
Myristic	Tetradecanoic	0.8	-	0.1	0.1
Palmine	Hexadecanoic	23.1	5.8	4.9	5.4
Stearic	Octadecanoic	2.3	4.6	1.9	2.9
Oleic	Cis-9-octadecenoic acid	19.2	19.8	58.6	39.5

Moscow State University of Food Production has developed a methodology for calculating the composition of multi-component blended oils, which can be used as a method to calculate the ratio of linolenic and linoleic acids and the initial content of these acids in the oil. Formulas (1) and (2) that are presented below are intended for their calculation:

$$\frac{m_a \cdot c_a^1 + m_b \cdot c_b^1}{m_a \cdot c_a^2 + m_b \cdot c_b^2} = 10; \tag{1}$$

$$m_a + m_b = 1, \tag{2}$$

where: m_a, m_b – mass of vegetable oil, kg; c_a^1, c_b^1 – concentration of linoleic acid in vegetable oil, wt. %; c_a^2, c_b^2 – concentration of linolenic acid in vegetable oil, wt. %.

The blends were obtained by preliminary mixing of two basic oils in the laboratory at temperature of 20°C under continuous stirring by a magnetic mixer and subsequent introduction of minor blend components up to the required proportion.

Research results and discussion. To optimise the fatty acid composition of the studied blends and the data obtained for each of the vegetable oils, the most acceptable is linseed oil, due to its significant content of polynasaturated fatty acids, unlike other types of oils, which predetermines as the most preferable raw material. Production of linseed oil at the industrial scale in Belarus is conducted under natural conditions of obtaining significant amounts of flax seeds.

However, the results of gas chromatographic analysis of the content of individual fatty acids in triglycerides of the oil samples that are presented at Figure 3 revealed significant differences.

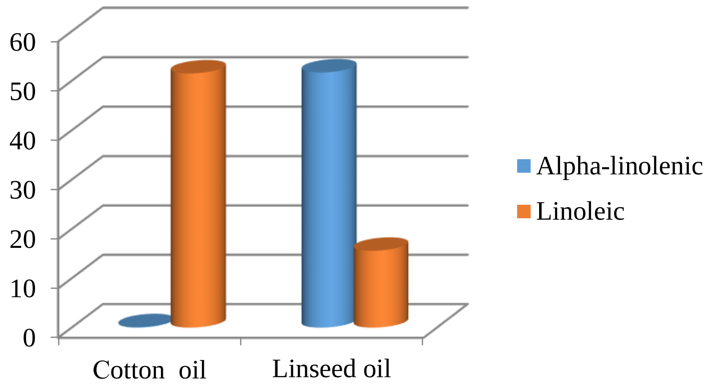

Fig. 3. Fatty acid content

The results for the composition of sample No. 1 (cotton oil) shows the largest amount of linoleic acid, approximately 50% by mass, and a very small amount of linolenic acid, less than 0.1% by mass. This correlates with the results that are available from literature data [6] and confirmes the imbalance in the fatty acid composition of refined and unrefined cotton oils, which are widely used in the southern regions of Kazakhstan.

Rapeseed oil and cottonseed oil have similar fatty acid composition. Rapeseed oil contains about 40% linoleic acid and 1% linolenic acid. Corn oil, on the other hand, contains 22% linoleic acid and 8% linolenic acid. Because of this, corn oil can be used to enrich the composition of cottonseed oil.

The highest amount of linolenic acid is found in bilberry oil with a content of about 54%. This makes it the most promising ingredient of blends with a balanced fatty acid composition and that is why it was chosen by us as a source of linolenic acid. But it could be found to be too expensive for mass production.

Based on the results obtained, we proposed two blends based on cottonseed oil and linseed oil. The proposed blend No. 1, in which the ratio of polyunsaturated fatty acids is 10:1, can be recommended for daily use and prophylactic mean in diet.

Sample No. 2 is a product that is characterised by an increased content of flaxseed oil. This is a wonderful supplement that provides a 5:1 ratio of polyunsaturated fatty acids. The richness by flaxseed oil in this product makes it an ideal choice for those interested in therapeutic nutrition. Table 2 shows the compositions of recommended oil blends.

Table 2

Vegetable oil content in blends No. 1 and No. 2

Object number	Actual ratio of polyunsaturated fatty acids	Linseed oil	Cotton oil
Blending 1	10:1	0.09	0.91
Blending 2	5:1	0.25	0.75

The results of physicochemical and organoleptic parameters of the samples of blends 1 and 2 are presented in Table 3.

Table 3

Physic-chemical parameters of blended oils No. 1 and No. 2

Blend number	Linoleic acid content, wt.	Mass fraction of moisture and volatile substances, %	Linolenic acid content, wt.	Peroxide number, ½ O mol/kg	Acid number, mg KOH/g
Blending 1	44.73	0.05	5.83	4.4	0.4
Blending 2	42.68	0.06	7.27	4.7	0.5

The results obtained for the values of acid and peroxide numbers for all blends corresponded to the requirements to unrefined edible oil blends.

It should be noted that the samples with a higher content of linseed oil have lower values of acid and peroxide numbers, which provides some advantage of these blends during production, bottling and storage due to lower oxidative capacity, and, therefore, better preservation of chemical and microbiological influence.

Thus, the results of the conducted research prove the possibility of producing all the proposed blends of vegetable oils, as they all fully meet to the established requirements by organoleptic and physico-chemical parameters.

In addition, the application of gas chromatography method allows to evaluate the compliance with the calculated ratio of PUFAs in the composition of the obtained vegetable oil blends. The results that are presented in Table 3 concerning the ratio of linoleic and linolenic acids in them fully correlate with the previously planned results.

Conclusion. The studies of this work resulted in two new blended vegetable oils based on cottonseed oil that include additives of linseed oil, corn oil and rapeseed oil, which are little used in our country, but widely produced in Belarus and Kazakhstan. Such blending allows to provide the best proportion of ω-3 and ω-6 fatty acids and will increase the biological value of fat goods, and, as well, in technological terms, will enhance high-quality and safe transportation and storage of such a product.

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ҚАЗАҚСТАНДЫҚ МАҚТА МАЙЫ ЖӘНЕ БЕЛАРУСЬ ЗЫҒЫР МАЙЫНЫҢ НЕГІЗІНДЕ ТЕҢЕСТІРІЛГЕН МАЙ ҚЫШҚЫЛДЫ ҚҰРАМЫ БАР ӨСІМДІК МАЙЛАРЫНЫҢ ЖАҢА ТҮРІН ӘЗІРЛЕУ

Аңдатпа. Мақалада линол және линолен қышқылдары сияқты қышқылдығы жоғары майларды құрамындағы азырақ майлармен біріктіру негізінде өсімдік майларының жаңа түрлерін әзірлеу бойынша зерттеулердің нәтижелері берілген. Мақта майы құрамындағы линол қышқылының мөлшері барлық басқа майлардан 2 есеге жуық жоғары, ал зығыр майы құрамындағы а-линолен қышқылының мөлшері бойынша барлық басқа майлардан 50 есеге жуық артық екені анықталды, бұл май қышқылдарының оңтайлы құрамы 5:1 және 10:1 қатынасындағы мақта және зығыр майларының қоспасы болып табылады деп қорытынды жасауға мүмкіндік береді. Мұндай арақатынас ω-3 және ω-6 қышқылдарының қоспасын теңестіруге мүмкіндік береді, сонымен қатар соңғы өнімнің жарамдылық мерзіміне әсер ететін өсімдік майларының тотықтырғыш қабілетілігін төмендетеді.

Тірек сөздер: мақта майы, линол қышқылы, өсімдік май қоспалары,зығыр майы, тағамдық өсімдік майлары, линолен қышқылы, полиқаныққаған май қышқылдары.

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РАЗРАБОТКА НОВОГО ВИДА КУПАЖЕЙ РАСТИТЕЛЬНЫХ МАСЕЛ СО СБАЛАНСИРОВАННЫМ ЖИРНО-КИСЛОТНЫМ СОСТАВОМ НА ОСНОВЕ КАЗАХСТАНСКОГО ХЛОПКОВОГО МАСЛА И БЕЛАРУССКОГО ЛЬНЯНОГО МАСЛА

Аннотация. В статье приведены результаты исследований по разрботке новых видов растительных масел, основанных на комбинировании масел с более высоким содержанием таких кислот, как линоленовая и ленолевая с маслами, в которых эти содержания более низки. Установлено, что по содержанию линолевой кислоты хлопкового масло, превосходит все остальные масла практически в два раза, а льняное по содержанию α-линоленовой кислоты – практически в 50 раз. Следовательно, оптимальным по жирокислотному составу является купаж из хлопкового и льняного масел в соотношениях 5:1 и 10:1. Такое соотношение позволяет сбалансировать купаж по ω-3 и ω-6 кислотам, а также снизить окислительную способность растительных масел, влияющих на сроки хранения конечного продукта.

Ключевые слова: хлопковое масло, линолевая кислота, купажи растительных масел, льняное масло, пищевые растительные масла, линоленовая кислота, полиненасыщенные жирные кислоты.