THE STUDY OF INFLUENCE OF NATURAL ANTIOXIDANTS ON QUALITY OF PEANUT AND LINSEED OIL BLENDS DURING THEIR STORAGE

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1. Introduction

Vegetable oils play an extremely important role in daily human nutrition providing the body with 50–60 % of daily need of fats and energy.

Biological value of vegetable oils is determined by fatty acid composition: the content of polyunsaturated fatty acids and the ω-3:ω-6 acid ratio. Sunflower oil is the main vegetable oil consumed in the diet of Ukrainians and the ratio ω-6:ω-3 of polyunsaturated fatty acids is 33:1. That is, there is a significant excess of the level of ω-6 fatty acids. Americans consume corn oil more often than other oils. Annually, about one million tons of corn oil is produced for the US domestic market. This oil features an unbalanced
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Fatty acid composition as well. Residents of southern Europe prefer olive oil which is characterized by high content of oleic (about 70% of total fatty acids), palmitic (15%) and linoleic (up to 10%) acids. That is, an unbalanced content of fatty acids is also observed in the oils. Mustard, sesame, rape, linseed, pumpkin, cedar oils are also among consumer demands but they are more often used in small quantities for salad dressing. It is primarily because of their high cost. The recommended ω-6:ω-3 ratio is 4:1–18:1, that is, people should endeavor to increase share of omega-3 fatty acids [1, 2]. It can be achieved by combining several types of oils with a necessary fatty acid composition.

It is known that polyunsaturated fatty acids ω-3 and ω-6 are unstable and feature a high degree of oxidation and degradation in conditions of production and storage of vegetable oils. In order to prevent degradation of polyunsaturated fatty acids, numerous studies have proved effectiveness of antioxidants. However, nature of the proposed substances is not universal since their inhibitory ability was proven just for particular products. In addition, taking into account consumer’s demands for natural food products, it is necessary to substitute natural ingredients with proven antioxidant properties for synthetic antioxidants.

Therefore, selection of natural inhibitors to improve oxidative stability of peanut and linseed blends as well as the study of their effects on organoleptic characteristics and preservation of unsaturated fatty acids are topical issues.

2. Literature review and problem statement

Analysis of scientific literature has shown [3–5] that activities are under way at present to create products with an optimal fatty acid composition by means of blending. Sunflower, soybean, corn, olive, rape, linseed and false flax oils are most commonly used for blending. Also, pumpkin, thistle, amaranth, wheat germ oils which are uncommon for this industry but possess biological activities and pharmacological properties along with their nutritional benefits have found their use. However, no data on the use of peanut oil in blends were found. However, presence of numerous vitamins, macro- and trace elements, polyphenols, phospholipids, phytosterols in composition of this oil makes it particularly valuable for a healthy nutrition.

There is practically no essential ω-3 fatty linolenic acid in peanut oil. Therefore, for the balance of ω-6:ω-3 ratio, it is worth to select such an oil with a highest content of linolenic acid. Among the vegetable oils, linseed oil is the richest source of this acid. It is known that pure linseed oil is rarely used in the food industry as a separate ingredient. This is because it has a pronounced specific odor and a slight bitter aftertaste. At low concentrations, this oil does not worsen organoleptic characteristics of the blends. Due to the therapeutic and prophylactic properties of linseed oil, it is used in a dietary nutrition.

Because of chemical instability of unsaturated ω-3 and ω-6 fatty acids, some substances are formed in the process of production and storage of oils. They not only worsen qualitative characteristics but can also be harmful to human health. In view of this, there is a problem of maintaining blend quality consisting in protection of lipids against oxidation.

Numerous studies have proven the promising use of plant antioxidants with a high oxy-stabilizing effect. Mainly these are oil, water and alcohol extracts of leaves and/or flowers of basil, calendula, self-heal, mullein, larch-tree, meadowsweet, Japanese sophora, purple amaranth, John's-wort, rosemary, peppermint, melissa, thyme, walnut, sage, green tea, coffee. It is also advisable to use hips, white-rod, mountain ash, grape seeds, haricot beans, essential oils of orange, lemon, carnation, cinnamon, pomegranate skin, tropical rambutan fruit, a biomass extract of ripe aleplosporous of Haematococcus pluvialis. For example, work [6] recommends the use of antioxidant concentrates from calendula, basil, self-heal, mullein in an amount of 2 mg/kg. Since the study objects were sunflower and rapeseed oils, it is impossible to assert effectiveness of the extracts selected for other types of vegetable oils.

Antioxidant effect of essential oils and extracts of melissa, mint, sage and thyme on sunflower oil in its storage at room temperature was estimated in [7]. It was found that the induction period of sunflower oil increased with increasing concentrations of mint and melissa extracts. At the same time, sage extract accelerated formation of peroxides in the oil sample. It is unclear from the study what concentration of plant extracts is optimal for maximal retarding oxidative processes and preservation of the organoleptic properties characteristic of sunflower oil.

Antioxidant activity of essential oils, alcoholic and aqueous extracts of melissa of sunflower oil in storage was compared in [8]. It was proved that the aqueous extract of melissa is more potent than the alcohol one. Melissa essential oil does not have a significant antioxidant effect. Antioxidant effect of essential oils of rosemary, cloves and cinnamon on nut and poppy oils has been proved [9].

Antioxidant effect of alcohol extract of pomegranate skin on quality of sunflower oil was assessed in work [10]. Since effectiveness of the proposed method has been experimentally established in heating to 80 °C, it cannot be recommended for oxidation stabilization of oils during their prolonged storage.

Accelerated storage of sunflower oil at a temperature of 60 °C during 24 days was also used in the study of antioxidant power of tropical rambutan fruit [11]. It was proved that the rambutan extract can be used as an alternative source of antioxidants for delaying oxidation of lipids. However, the use of rambutan is limited and economically unprofitable. Therefore, the proposed method is not universal as well.

It was proved for sunflower oil [12] that the oil extract of biomass of ripe aplanospores of Haematococcus pluvialis containing astaxanthin has the properties of an inhibitor of oxidative processes. It has been established that the induction period increased by 2.2 times due to the inhibitor introduction. Obtaining of astaxanthin from the aplanospores of Haematococcus pluvialis (both in natural conditions and in industrial growth) is a complex, long-term, and costly process. It is a significant disadvantage of the proposed method.

Effect of three natural antioxidants (extracts of rosemary, tea, bamboo) on quality of soybean and palm oil was investigated in [13]. It has been found that the extracts effectively reduced concentration of acid and peroxide numbers of fat. The highest inhibition was achieved with bamboo antioxidants.
Another study [14] highlights the effects of lighting conditions and relative inhibitory power of rosemary extract, tocopherol and ascorbic palmitate. The study has proved effectiveness of action of the rosemary extract on the oxidative stability of chia seed oil.

Work [15] studied the antioxidant activity of rosemary essential oil on oxidative stability of sunflower oil. The results of the study of oxidative stability have shown that residues (R1 and R4) and butylated hydroxytoluene have antioxidant activity higher than rosemary essential oil or distillate fractions. Fractions of essential rosemary oil can be used as natural antioxidants in the food industry.

The high inhibitory power of distilled water obtained in distillation of essential oil from aromatic herbs (basil, sage, rosemary) was proved in [16]. The authors recommended this by-product of ester and oil production as a natural functional food additive in the food industry. Also, a strong effect of alcohol rosemary extract on preservation of omega-3 fatty acids of linseed oil was experimentally proved in [17].

The study of 10 samples of corn oil has shown that herbal extracts of thyme, sage, peppermint and sumach facilitate inhibition of fat oxidation in storage [18]. According to the results, sumach extract has antioxidant activity higher than the sage extracts. Concerning the antioxidant activity of thyme and peppermint, a conclusion was made about their highest inhibitory ability and expediency of their use in the food industry.

An essential disadvantage of using the above-mentioned extracts of spicy and aromatic herbs is their intense taste and aromatic properties that can negatively affect organoleptic characteristics of oils.

The results obtained in studying the effect of citrus pectin on oxidation of fats of blended sunflower and linseed oils during two weeks of storage at 35 °C are presented in [19]. It has been established that low-molecular pectin exhibits an antioxidant capacity higher than high-molecular pectin. These results show the potential of structurally modified citrus pectin as a natural antioxidant in oil emulsions. Since effectiveness of the proposed antioxidant obtained from citrus pectin was recommended to improve oxidative stability of oil emulsions, it can be stated that this method is unacceptable for vegetable oils.

The method of obtaining antioxidants from peanut skin by extraction is proposed [20]. The best extraction conditions are at ethanol concentration of 73.9 % and temperature of 66.5 °C. Efficiency of the natural antioxidant obtained under these conditions was proved on a sample of soybean oil in conditions of accelerated oxidation (16 days at 60 °C). It should be pointed out that antioxidant production from peanut skin is complicated by the absence of significant volumes of this raw material.

According to the published data, such inhibitors as leaves of sage, black currant, garlic and hips have a unique chemical composition and are known for their antioxidant properties. The antioxidant effect of salvia officinalis is primarily associated with rosemary and carnosol acids in its composition. Addition of salvia to fat-containing products gives a 15–17 times higher resistance to oxidation of fats [21].

Garlic is a natural store of antioxidants: selenium and allicin. Selenium is a part of many antioxidant enzymes that protect fats from peroxide oxidation. Among thioulates, allicin and its metabolites also exhibit anticarcinogenic, cardioprotective, bacteriostatic, antifungal, antithrombotic and insecticidal activity [22].

An antioxidant complex of blackcurrant leaves was investigated in [23]. It includes substances of phenolic and thiolic nature.

Extract of hips contains natural phytocomplex of vitamins (especially ascorbic acid), flavonoids represented by quercetin, isoquercitin, anthocyanins and catechins. These substances not only inhibit the process of oxidative damage to the product but also add biologically active substances to the blend that can enhance its functional effect on the body [24].

Extracts have strong antioxidant properties. They also contain tannic acids and phenolic compounds that are able to interact with allergens of peanut oils. As a result, deposition of major peanut allergens and formation of a digestive complex which does not interact with antibodies takes place. In this case, IgE bonding decreases in 10 to 16 times [25].

Thus, in order to increase oxidation resistance of vegetable oils, it was proposed to use numerous plant raw materials. It was recommended to use natural antioxidants in an amount from 0.05 % to 10 % to provide a sufficient stabilizing effect on the oxidative and hydrolytic processes in vegetable oils. This makes it possible to obtain products of a stable quality during production and extend their shelf life. However, there is no a universal inhibitor for all types of vegetable oils. This is explained by different chemical compositions of raw materials, the content of unsaturated fatty acids, parameters of production and conditions of product storage. Therefore, it is expedient to select a natural antioxidant specifically for the developed peanut and linseed blends.

3. The aim and objectives of the study

The study was conducted to establish the effect of natural antioxidants on in-storage quality of peanut and linseed oils.

To achieve this objective, the following tasks were solved:
- compare effect of plant antioxidants (oil extracts of leaves of sage and black currant, garlic and hips) on quality of blended peanut and linseed oils during a storage period of 14 months;
- determine effect of natural antioxidants on the change of acid and peroxide numbers of fat of blended peanut and linseed oils;
- study influence of natural antioxidants on the content of oleic, linoleic and linolenic fatty acids during storage of peanut and linseed oil blends;
- establish terms and conditions of storage of the developed oils.

4. The study materials and methods

New blended oils were taken as the study objects.

To prepare the blend, unrefined oil obtained from peanuts of the Krasnodar 14 variety was selected. It is also advisable to use peanuts of the following varieties: Krasnodar 15, Pink Large, Pale Pink 2, AR 1, AR 2 which have the highest fat content and are recommended for oil production. Linseed oil was used to obtain the blend as a source of linolenic acid. The following materials were also used: oil extracts from garlic, hips, leaves of blackcurrant and sage prepared by
Phitokhimfarm Co. Optimum concentration of 5% to the weight of oil was chosen for stabilization of the developed blends.

The methods of studying the blended oils are given in [26].

5. Results obtained in the study of the effect of natural antioxidants on in-storage quality of oils

To determine change of in-storage properties of blended peanut oils, samples of peanut and linseed seeds were studied without and with addition of experimental extracts. All samples were stored for 14 months in bottles of dark glass in a darkened room at a temperature not higher than 25 °C and relative humidity not higher than 85%. Changes in quality were controlled by organoleptic (appearance, color, taste and smell) and physical-chemical (peroxide number, acid number) indicators. Since linoleic, linolenic and olefinic fatty acids are the most important unsaturated acids in vegetable oils, it was also considered expedient to study changes in their content in the experimental peanut and linseed oil blends.

Table 1 gives data on the change of organoleptic indicators of peanut oil during storage.

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Oil storage period, months</th>
<th>0–8</th>
<th>9–12</th>
<th>13–14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>peanut and linseed oil with no addition of extracts (the control sample)</td>
<td>Clear homogeneous oily liquid without sediment and foreign inclusions</td>
<td>Oily liquid with a slight sediment</td>
<td>Oily liquid with a slight opacity over sediment</td>
</tr>
<tr>
<td>Color</td>
<td>Light yellow with a greenish hue</td>
<td>Pale, with a yellowish hue</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taste and smell</td>
<td>Peculiar to the blend components, without foreign smell, flavor and bitterness</td>
<td>Bitter flavor, slight musty smell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance</td>
<td>peanut and linseed oil with garlic extract</td>
<td>Clear homogeneous oily liquid without sediment and foreign inclusions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>Light yellow with a greenish hue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taste and smell</td>
<td>Peculiar to the blend components, with a pronounced pungent and strong taste and smell peculiar to the blend components, without foreign smell, off-flavor and bitterness</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance</td>
<td>peanut and linseed oil with hip extract</td>
<td>Clear homogeneous oily liquid without sediment and foreign inclusions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>Light orange with a yellowish hue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taste and smell</td>
<td>Peculiar to the blend components, with a pronounced fragrant scent and sweet-sour taste, without foreign smell, off-flavor and bitterness</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance</td>
<td>peanut and linseed oil with sage leaf extract</td>
<td>Clear homogeneous oily liquid without sediment and foreign inclusions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>Light green with a yellowish hue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taste and smell</td>
<td>Peculiar to the blend components, with a pronounced fragrant, slightly styptic taste, without foreign smell, of-flavor and bitterness</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance</td>
<td>peanut and linseed oil with black current leaf extract</td>
<td>Clear homogeneous oily liquid without sediment and foreign inclusions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>Light green with a yellowish hue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taste and smell</td>
<td>Peculiar to the blend components, with a rather pronounced fragrant smell and sweet-sour spicy and slight styptic taste without foreign smell, of-flavor and bitterness</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6. Discussion of results obtained in the study of the effect of natural antioxidants on the in-storage quality of oils

The study of organoleptic characteristics indicates that the blended oil with extracts right after bottling and after 12 months of storage had characteristics peculiar to the blend components. It has been established that the samples of oil blends did not have foreign smell, off-flavor and bitterness and their color was light yellow with a greenish hue. The blend with a hip extract had an orange hue. In oils stored for 9 to 12 months, there was slight sediment which is not a rejection factor. Appearance of slight sediment is the result of deposition of smallest particles of waxy substances that may remain in oil during production. Oils without addition of extracts stored for more than 12 months acquired a faint musty smell and slight bitterness caused by the rancid-
technology process in them. Peanut and linseed oil with the extract of sage leaves did not change its taste and smell from beginning to end of storage and only a barely noticeable taste of bitterness peculiar just to the added extract has appeared.

Color of oils without extracts has become a bit lighter. Discoloration of oil is usually explained by decomposition of carotenoids during prolonged storage. According to these data, there was a slight opacity over the sediment in oils without extracts stored for more than 12 months, which may be the cause of oil self-hydration in a prolonged storage. The oil without extracts retained its high organoleptic properties for eight months and subsequently began to spoil while the oils with extracts had high organoleptic characteristics throughout their shelf life.

It was shown that an increase in the acid number to the critical limit in the oil without addition of extracts was observed at the end of the tenth month of storage while this indicator in all oils with extracts did not exceed the standard value after 12 months of storage. Increase in the acid number is mainly caused by hydrolysis of triglycerides as a result of biological oxidation of unsaturated fatty acids of glycerides under the influence of lipoxigenases.

Peroxides in oils appeared earlier than the bitter taste which was confirmed by organoleptic studies. For example, increase in the peroxide number was observed in the blends without addition of plant extracts after 10 months of storage and its level was at the upper standard limit. In the oil blends with addition of natural antioxidants, peroxide compounds exceeded their level only after 12 months of storage, except for the blend with the extract of sage leaves which reached the upper limit only in the fourteenth month of storage: 10.2 % O mmol/kg.

These study results were confirmed by changes in the fatty acid composition of oils, especially olefinic, linoleic and linolenic acids, which are unsaturated and therefore easily hydrolyzed and oxidized. These processes proceed faster in blends without antioxidants. For example, the content of oleic acid in it was 32 % smaller in 10 months of storage. The respective figures were 50 % for linolenic acid and 25 % for linoleic acid. However, these changes were not critical. This is due to the fact that peanut oil contains many natural antioxidants (tocopherols, carotenoids, phenols).

The processes of hydrolysis and self-oxidation took place more slowly in the blends with addition of plant extracts. The content of oleic acid decreased as follows: by 26.5 % in the blend with the garlic extract, by 23 % in the blend with the hip extract, by 21.1 % in the blend with the sage leaf extract and by 26 % in the blend with the black currant leaf extract. The content of linolenic acid in oilseed blends decreased somewhat slower: by 24.3 % with the garlic extract, by 19 % with the hip extract, by 18 % with the sage leaf extract and by 19.5 % with the black currant leaf extract. Linoleic acid was the least stable. Its content in the blends was reduced as follows: by 31 %, with the garlic extract, by 28.3 % with the hip extract, by 27 % with the sage leaf extract and by 28.9 % with the black currant leaf extract. High antioxidant activity of the extracts of sage leaves, hips, black currant leaves and garlic is explained primarily by the content of phenolic groups in them which have low dissociation energy and are potent hydrogen donors. The presence of tocopherol, carotenoids and ascorbic acid in oil blends also effectively inhibits formation of free radicals due to their ability to give their hydrogen to peroxyl, alleoxy and alkyl radicals. In addition, combination of tocopherol with phenolic compounds gives the effect of synergy resulting in a decrease in the rate of oil oxidation by destroying free radicals, formation of chelate compounds with metal prooxidants, inhibition of oxygen and inactivation of lipoxigenase.

The positive effect of antioxidants on stability of oil blends was confirmed by several experiments. At the same time, depending on their influence on the blend stability, extracts can be ranked as follows: leaves of sage > hips > leaves of black currant > garlic.

The results of above experiments coincide with changes in organoleptic characteristics of oil blends during storage and changes in acid and peroxide numbers of fat.

Ratios of polyunsaturated fatty acids ω-6/ω-3 in all samples remained at the level of ratios of these acids in fresh blends, namely, 4:1 which corresponds to the principles of “healthy nutrition”.

The conducted studies are a fragment of a comprehensive work plan on assessment of the effect of plant antioxidants on quality of blended peanut and linseed oils. The further studies will include consideration of alcohol extracts of leaves of sage, hips, leaves of black currant and garlic as a source of antioxidants to preserve quality of vegetable oils. It is also supposed to carry out experiments to establish the induction period for oxidation of the developed peanut and linseed oil blends and the constants of chain breakage which will also allow us to confirm effectiveness of the use of plant extracts as inhibitors of oxidation processes.

7. Conclusions

1. Based on the results of organoleptic evaluation, characteristics of the qualitative indicators of blended oils during their storage were established. It was found that the oil blends with extracts had smell and taste peculiar to the blend components, with no foreign smell, flavor or bitterness right after bottling and after 12 months of storage. They had light yellow color with a greenish hue. The blend with the hip extract had an orange hue.

2. Resistance of blended peanut oils to oxidative processes has been proved. Acid and peroxide numbers in oils blended with natural antioxidants exceeded the standard level only after 12 months of storage. It can be stated that the oil extracts of leaves of sage, hips, leaves of black currant and garlic had an inhibitory effect. For example, their introduction in an amount of 5 % promoted increase in oxidative stability of peanut and linseed oil blends in 1.2–1.7 times and preserving the content of polyunsaturated fatty oleic, linoleic and linolenic acids.

3. It has been confirmed that the use of natural antioxidants slows down the processes of hydrolysis and self-oxidation in the developed peanut and linseed oil blends. The use of plant extracts in formulations of new oil blends preserved 69.0–73.0 % of linolenic acid, 73.5–78.9 % of oleic acid and up to 82 % of linolenic acid from their initial content in the product.

4. Conditions and guaranteed storage life were established: no more than 12 months in bottles of dark glass in a darkened room at a temperature not higher than 25 °C and relative humidity not more than 85 %.
References


