UDC 66.094.2: 547.455
DOI: 10.15587/1729-4061.2024.311326

DEVELOPMENT OF A COMPLEX ANTIOXIDANT FOR STABILIZATION OF DRESSING ENRICHED WITH OMEGA-3 FATTY ACIDS

Serhii Stankevych
Corresponding author
PhD*
E-mail: art.intel.scientist@gmail.com
Nataliia Yakymenko-Tereshchenko
Doctor of Economic Sciences, Professor
Department of Tourism and Hospitality Business
National Technical University "Kharkiv Polytechnic Institute"
Kyrpychova str., 2, Kharkiv, Ukraine, 61002
Vladimir Panasenko
Doctor of Technical Sciences, Professor, Scientific Secretary
State Institution "State Research and Design Institute of Basic Chemistry"
Myronosytska str., 25, Kharkiv, Ukraine, 61002
Tatiana Gontar
PhD
Department of Restaurant, Hotel and Tourist Business
Ukrainian Engineering Pedagogics Academy
Universytets'ka str., 16, Kharkiv, Ukraine, 61003
Inna Zabrodina
PhD*
Oleg Kolontaievskyi
PhD
Department of Tourism and Hospitality***
Roman Voronov
PhD
Department of Electric Transport***
Maryna Ponomarova
PhD, Associate Professor
Department of UNESCO "Philosophy of Human Communication and Social and Humanitarian Disciplines"**
Viktoriia Novikova
PhD, Associate Professor
Department of Chemistry, Biochemistry, Microbiology and Food Hygiene**
Oleksandr Ashtaiev
Lecturer
Cyclical Commission of Food Technology and Hotel-Restaurant Business
A Separate Structural Unit "Kharkiv Trade and Economic Vocational College State University of Trade and Economics"
Otakara Yarosha lane, 8, Kharkiv, Ukraine, 61045
*Department of Zoology, Entomology, Phytopathology, Integrated Plant Protection and Quarantine B. M. Litvinova**
**State Biotechnological University
Alchevskykh str., 44, Kharkiv, Ukraine, 61002
***O. M. Beketov National University of Urban Economy in Kharkiv
Marshala Bazhanova str., 17, Kharkiv, Ukraine, 61002

The solution to the problem of developing a complex antioxidant for the oxidative stabilization of emulsion systems with a high content of ω-3 polyunsaturated fatty acids (PUFAs) is considered. The object of the study is the oxidative stabilization of dressing using a complex antioxidant of plant origin. The ratio of ω-3:ω-6 PUFAs in model samples of the emulsion system was 1:5.46 and 1:2.21. The reasonable range of antioxidant ratios in the complex was substantiated. The ratio of tocopherol extract, garlic and laurel essential oils in the complex antioxidant is 1:1:1, respectively. Over 30 days of storage of the emulsion system model samples stabilized with a complex antioxidant, there is a gradual accumulation of organic acids (from 0.73 % to 0.75 %). The content of primary oxidation products increases for sample No. 2 – from 0.7 to 1.9 mmol ½ O_2/kg, for sample No. 3 – from 0.4 to 1.2 mmol ½ O_2/kg. The obtained values of physicochemical parameters meet the requirements of regulatory documentation (DSTU 4561). The peculiarity of the obtained results is that the complex antioxidant showed a significant increase in the stability of the emulsion system of high nutritional value, in particular, slowed down the accumulation of organic acids and peroxides. From a practical point of view, the development can effectively stabilize food emulsion systems with a high content of oxidation-labile PUFAs. An applied aspect of the obtained scientific result is the possibility of modeling and developing new formulations of emulsion and individual fat systems with high nutritional value, containing high PUFA concentrations

Keywords: complex antioxidant, emulsion system, polyunsaturated fatty acids, oxidative stability, shelf life

Received date 05.07.2024
Accepted date 09.09.2024
Published date 30.10.2024

How to Cite: *Stankevych, S., Yakymenko-Tereshchenko, N., Panasenko, V., Gontar, T., Zabrodina, I., Kolontaievskyi, O., Voronov, R., Ponomarova, M., Novikova, V., Ashtaiev, O. (2024). Development of a complex antioxidant for stabilization of dressing enriched with omega-3 fatty acids. Eastern-European Journal of Enterprise Technologies, 5 (6 (131)), 6–14. https://doi.org/10.15587/1729-4061.2024.311326*

1. Introduction

Edible oils and fats are complex multicomponent systems, where a special place is occupied by polyunsaturated fatty acids (PUFAs). PUFAs are involved in the formation of both triglycerides and various physiologically active substances [1]. From a chemical point of view, the lack of PUFAs in the body leads to changes in the fatty acid composition of

cell membranes, which causes a violation of their functional stability, and is manifested in decreased resistance to harmful effects due to increased permeability. This ultimately leads to various diseases. PUFAs are essential, meaning they are not synthesized in the human body and must come with food [2]. Their biological action is most effective at a specific ratio of ω-3 and ω-6 PUFAs in fat systems, in particular emulsion ones. Individual vegetable oils do not meet current recommendations for the ratio of ω-6 and ω-3 fatty acids in the range of 1:2–1:10 [1, 3]. Therefore, it is important to obtain PUFA-containing fat systems with a given composition and properties. The components of these systems are unsaturated oils of the linoleic (sunflower, corn, sesame, pumpkin, safflower, etc.) and linolenic (linseed, camelina, hemp, chia, etc.) groups [4].

One of the main tasks in preserving the quality of fat systems is to protect their polyunsaturated component, the oxidation of which yields products that not only worsen the quality characteristics of foods, but are toxic [5]. There is a growing interest in using various bioactive substances of natural origin as antioxidants, since they not only meet safety requirements, but also have biological value, and are well combined with other components of fat systems. To inhibit oxidative deterioration, plant extracts containing a complex of antioxidants are used – flavonoids (quercetin, kaempferol, myricetin), catechins (carnosol, rosmanol, rosamiridiphenol), phenolic acids (carnosic, rosmarinic), etc. [6].

So, research aimed at substantiating the composition of a complex antioxidant for fat systems enriched with ω-3 PUFAs will allow expanding the range of useful emulsion products based on valuable unrefined vegetable oils. The research results will make it possible to increase the stability and nutritional value of enriched fat systems during storage, and inhibit ω-3 PUFA oxidation, which will contribute to preserving quality parameters and organoleptic properties during storage. The obtained scientific results are relevant for the oil-fat and food industries, and restaurant business, as there is a need to expand the range and increase the nutritional value of emulsion fat systems and prolong their shelf life.

2. Literature review and problem statement

In [7], the antioxidant content and the oxidation induction time of the emulsion system lipid component under simulated conditions were investigated. The solution to the problem of developing compositions of oxidation-stable emulsion systems based on nutritionally valuable oils, in particular hemp, by adding natural antioxidants is considered. The peculiarity of the work lies in determining the effect of the composition of hemp oil emulsion systems on free radical oxidation during storage. The composition of stabilizers in the hemp oil emulsion system (lecithin – 0.8–1.0 %; xanthan gum – 0.0–0.1 %) is proposed, which is effective in inhibiting oxidative deterioration. The content range of β-carotene in model emulsion systems (0.012 %) is outlined, which increases the oxidation induction time of lipids by 1.58...2.08 times. The disadvantage of the study is the lack of data on the microbiological stability of the emulsion system over the specified time period. An attempt to overcome this drawback was somewhat made in [8], considering the specifics of developing emulsion systems with a high content of phospholipids and ω-3 PUFAs based on fish oil. Flavored sunflower oil (13.8–18.5 %) was used as an additional recipe component. Sunflower oil was pre-flavored with allspice CO_2 extract. To reduce the activity of oxidative, hydrolytic and microbial processes, an additive was used – a dry birch bark extract, the main component of which is pentacyclic triterpene alcohol. The pronounced antioxidant and antimicrobial effects of the extract in fatty systems were proved. But the issue of increasing the solubility of this component in water, as well as in oils and fats, where it forms a suspension, remained unresolved.

This drawback was not found in [9], devoted to solving the problem of oxidative stabilization of the fat system while preserving its nutritional value. The peculiarity of the work lies in developing the composition of a complex antioxidant – a flavored oil composition with high oxidative stability (essential oils of coriander, basil and thyme). The consumer properties of this mixture are: the oxidation induction time (at 80 °C) is 4.0 hours, the content of α-linolenic fatty acid is 10.6 % of the total amount of fatty acids. The ratio of essential oils in the complex antioxidant was determined, with which the oxidation induction time of the fat system exceeds that in the control sample by 3.75 times. The disadvantage of the study is the lack of data on the shelf life of the developed oil composition and flavored oil composition. In turn, the study [10] considers the solution to the problem of oxidative stabilization of the labile lipid component of an emulsion system enriched with ω-3 PUFAs due to fat-soluble essential antioxidants. The reasonable range of component ratios in the lipid system (unrefined linseed, corn, and sesame oils) stabilized against oxidative deterioration due to natural antioxidants (tocopherols, sesamol, sesamolin) was substantiated. The ratio of linseed, corn and sesame oils is 1:2:1, respectively. There is also a study examining the oxidation induction time of oil solutions of fat-soluble dyes chlorophyll and beta-carotene [11]. The effect of the content of fat-soluble antioxidants with chromophoric groups on the oxidation induction time of their solutions in refined sunflower oil was investigated. The non-additive effect of chlorophyll A and β-carotene on the oxidative deterioration of lipids was found. In particular, the content of 0.10 g/l beta-carotene and 0.05 g/l chlorophyll A in the fat system leads to a decrease in the oxidation induction time by 8.4 % compared to an oil solution of 0.10 g/l beta-carotene without chlorophyll A. The obtained data are explained by a compensatory effect of the antioxidant β-carotene on the pro-oxidant effect of chlorophyll A in the oil solution. The study also did not consider the effect of tocopherols on the oxidative stability of chlorophyll A and beta-carotene oil solutions. In addition, the drawback of [10, 11] can be considered the lack of data on the oxidation induction time of model fat systems of fat-soluble dyes at storage temperatures of such products, namely 0...+20 °C. This issue was somewhat resolved in [12], investigating the oxidative stability of biotechnologically transesterified fatty systems containing no trans-isomers of antioxidant-stabilized fatty acids. The results allow developing biotechnologically transesterified three-component fat systems enriched with PUFAs to produce milk fat substitutes. The shortcoming of the study is the lack of considering the effect of emulsion systems on the oxidative stability of transesterified fat systems. This is the approach used in [13], using non-traditional oils (from guava seeds) in an emulsion system as a substitute (from 10 to 50 %) of refined olive oil in salad dressings. The results showed that up to 20 % guava seed oil substitution in salad dressing re-

sulted in better organoleptic parameters compared to higher levels. The composition of the model emulsion systems showed an increase in the total content of phenols (5.85–8.23 %) and carotenoids (58.45–61.12 %), which also increased oxidative stability. Studies of 3-month storage showed better quality parameters and oxidative stability of the developed emulsion system compared to the control one. In addition, the composition of the avocado emulsion system enriched with ω-6 PUFAs is known [14], including chopped avocado, whey protein and mint extract. Mint extract is reported to have improved physical stability, as well as oxidative and microbiological stability. The issue of determining the interaction mechanism of the mint extract active components with polyunsaturated fatty acids and proteins of the emulsion system remains unresolved. It is also important to determine rational conditions for maximizing the antioxidant activity of biologically active mint substances.

The study [15] revealed the interaction mechanism of the ether component with triglyceride components and synthetic antioxidants. This was done within the composition characteristics of the complex antioxidant for the ω-3 PUFA concentrate (a mixture of tert-butylhydroquinone (0.04 %), ascorbic acid (0.004 %), dill essential oil (0.8 %). It was proved that the introduction of dill essential oil to the complex antioxidant can increase the efficiency of oxidative stabilization of PUFA ethyl esters and, accordingly, preserve the biological value of the concentrate during storage.

Thus, spicy-aromatic extracts are a scientifically interesting natural complex of biologically active compounds. They contain substances that exhibit antioxidant and antimicrobial properties, acting on emulsion systems more gently than compounds of similar action, but of synthetic origin. Phytoextracts are natural compositions of non-lipid (volatile low molecular weight hydrocarbons, carbonyl and phenolic compounds, higher alcohols, etc.) and lipid (fatty acids, sterols, tocopherols, carotenoids, organophosphorus compounds) fractions [6]. Antioxidant properties were found in 32 types of spices [16]. Adding 0.2 % extract of anise, cardamom, coriander, ginger, dill, fennel, and marjoram increases the oxidative stability of fats by 2–3 times, and adding rosemary and sage – by 15–17 times [17].

So, natural antioxidants (vitamins, essential oils, etc.) are widely used to inhibit oxidative processes in emulsion systems [6, 9, 15]. At the same time, essential oils having a pleasant smell can also act as flavors. The studies [7] showed that the introduction of tocopherols or essential oils into emulsion systems decreases the content of oxidation products in them during storage and slows down their accumulation during heat treatment.

Summarizing the above data, it can be noted that emulsion systems, in particular sauces (dressings), are products with high fat content, and developing their new types enriched with ω-3 PUFAs is a certain problem. Therefore, there is a need to justify the use of antioxidants in new fat systems in order to increase their stability and nutritional value during storage by inhibiting PUFA oxidation. Given the above, it is appropriate to conduct a study on developing a complex antioxidant composition based on natural components for stabilizing ω-*3 PUFAs in an emulsion fat system (dressing)*. As the fat base of the emulsion system, it is of interest to use a blend of cold-pressed pumpkin seed and camelina oils, and as components of a complex antioxidant – tocopherol extract and essential oils of garlic and laurel. Tocopherols interrupt oxidation chain reactions, converting free radicals into more stable forms. Garlic essential oil contains allicin and a number of organosulfur compounds with high antioxidant activity, and also has antimicrobial properties, which helps to extend the shelf life of the product. Laurel essential oil is rich in eugenol and other phenolic compounds [6, 15]. Using garlic and laurel essential oils not only increases the ω-3 PUFA stability, but also gives the dressing a unique flavor. This will increase the oxidative stability of the created oil base of the emulsion system, which is valuable from a physiological and economic point of view.

3. The aim and objectives of the study

The aim of the study is to develop the composition of a complex antioxidant for an emulsion system (dressing) enriched with ω-3 PUFAs. The results obtained will allow increasing the stability and nutritional value of the dressing during storage by reducing the level of ω-3 PUFA oxidation, which will preserve its quality parameters and organoleptic properties.

To achieve the aim, the following objectives were accomplished:

– to study the oxidation dynamics of the oil base of the emulsion system (dressing) based on unrefined cold-pressed oils with different ω-3:ω-6 PUFA ratios;

– to substantiate the composition of a complex antioxidant for the oxidative stabilization of emulsion system (dressing) samples enriched with ω-3 PUFAs;

– to study the quality parameters of the emulsion system (dressing) with high nutritional value, stabilized against oxidation by a complex antioxidant.

4. Materials and methods

4. 1. Object and hypothesis of the study

The object of the study is the oxidative stability of an emulsion system (dressing) enriched with ω-3 PUFAs under the influence of various antioxidant complexes.

The main hypotheses of the study are:

– the possibility of effectively inhibiting the oxidative deterioration of the dressing oil base (pumpkin seed and camelina oils) using a complex antioxidant, including tocopherol extract, garlic and laurel essential oils;

– the dressing enriched with ω-3 PUFAs and stabilized with a complex antioxidant will have a high nutritional value compared to traditional ones.

The study adopted the following assumptions:

– tocopherol extract, garlic and laurel essential oils retain their antioxidant properties throughout the dressing's shelf life;

– the oxidation induction time of the oil base of dressing samples is proportional to their oxidation induction time under recommended storage conditions (without light access at temperatures from 0 °C to +20 °C).

The study made the following simplification: fresh samples of unrefined cold-pressed oils from different batches or different manufacturers have almost the same fatty acid and antioxidant composition, physicochemical properties, and similar oxidative stability.

4. 2. Materials used in the experiment

The following materials were used in the study:

– unrefined pumpkin seed oil (produced in Ukraine), according to CAS 8016-49-7;

– unrefined camelina oil (produced in Ukraine), according to CAS 8001-20-5;

– tocopherol extract (produced in Ukraine), according to CAS 1406-66-2;

– garlic essential oil (produced in Ukraine), according to CAS 8000-78-0;

– laurel essential oil (produced in Ukraine), according to CAS 8007-48-5.

4. 3. Methods of studying the quality parameters of oil raw materials and oil base of dressings

The peroxide value of oils and their mixtures was determined according to EN ISO 3960:2017, IDT. The fatty acid composition of the oil samples was determined according to ISO 5508:1990, IDT.

4. 4. Method of preparing dressing samples

Dressing preparation is carried out at room temperature. Dressing samples were prepared with different proportions of unrefined pumpkin seed and camelina oils to obtain the specified ω-3:ω-6 PUFA ratios. To obtain 100.0 g of the finished product, citric acid (0.5 g), sugar (2.0 g), salt (0.5 g), sodium benzoate (0.1 g), xanthan gum (0.3 g) are successively dissolved in prepared water (80 ml). Then, Dijon mustard (1.7 g) and a mixture of oils (15.0 g) are gradually added with thorough mixing, and the system is subjected to homogenization (1,000 rpm) for 4–6 minutes.

4. 5. Method of studying the oxidation induction time of the oil base of dressings under different storage conditions

Dressing samples with different ω-3:ω-6 PUFA ratios were stored in a dark place at 20 °C for 12 weeks. Samples were periodically taken to determine the peroxide value. The induction time of the oil component of the dressing samples was determined graphically after analyzing the peroxide value increase dynamics.

The oxidation induction time of dressing samples stabilized with antioxidants was determined by an accelerated method based on the exposure of dressing samples, through the volume of which air is bubbled, at a constant elevated temperature (80±1 °C).

4. 6. Methods of determining the organoleptic and physicochemical parameters of the developed dressing

The organoleptic and physicochemical parameters of the finished product were determined according to DSTU 4487:2015. The oil component of the dressing was obtained by the extraction method.

4. 7. Method of analyzing the economic feasibility of using the proposed raw components

Economic effect ($E_{c.r.}$) represents a cost reduction of products, comparing the use of components of extruded protein-fat systems in the production with a commercial analog, and is calculated by formula (1):

$$E_e = \sum_{i=1}^{n} P_i \cdot C_i - \sum_{j=1}^{m} P_j \cdot C_j, \quad (1)$$

where P_i, P_j is the cost of the components of extruded protein-fat systems in the composition of the commercial analog and the proposed ones, respectively, $/kg; C_i, C_j is the content of the components of extruded protein-fat systems in the composition of the commercial analog and the proposed ones, respectively, kg/t.

4. 8. Research planning and statistical processing of results

The research was carried out three times. To determine the dependencies for the dynamics of the peroxide value of the emulsion system samples during storage, as well as the physicochemical parameters of the emulsion system samples stabilized with a complex antioxidant, one-factor experiments were used.

To determine the dependence of the oxidation induction time of the dressing oil base model samples on the complex antioxidant component ratio, three-factor experiments were used. To process the obtained experimental data, statistical methods using the Microsoft Excel (USA) and Stat Soft Statistica (USA) software packages were applied. Statistical models for the dependencies of the oxidation induction time of the dressing oil base model samples on the complex antioxidant component ratio (2) and (3) were determined by approximating the experimental results by constructing a trend line. The completeness of the effect of the complex antioxidant component ratio on the oxidation induction time of the dressing oil base model samples (dependencies (2) and (3)) was assessed using the coefficient of determination R^2.

The significance test of the equation coefficients of approximation dependencies (2) and (3) was carried out by the least squares method. The significance of the equations of dependencies (2) and (3) was defined by calculating the Fisher's test and comparing it with the table value.

5. Results of research on developing a complex antioxidant for stabilizing the dressing enriched with ω-3 polyunsaturated fatty acids

5. 1. Study of the oxidation dynamics of the dressing oil base with different ratios of polyunsaturated fatty acids

Pumpkin seed oil and camelina oil have different PUFA profiles, in particular the ω-3 and ω-6 groups. Since individual vegetable oils do not provide the recommended PUFA ratio, it is important to obtain fat systems with a given ω-3 and ω-6 ratio to realize their biological effect. Therefore, it was decided to investigate the oxidative stability of model samples of the emulsion system with different oil and, accordingly, PUFA ratios. The selected ratios are technologically reasonable due to simplified dosage calculation. Samples of the dressing oil base with different component ratios are given in Table 1.

Table 1

ω-3 and ω-6 PUFA ratios of the dressing oil base with different component ratios

Sample No.	Pumpkin seed oil and camelina oil ratio	ω3–:ω6– PUFA ratio
1	1:0	1:518.00
2	3:1	1:5.46
3	1:1	1:2.21
4	1:3	1:1.12
5	0:1	1:0.57

The peroxide value dynamics of dressing samples of the specified composition (Table 1) during storage for 12 months are shown in Fig. 1.

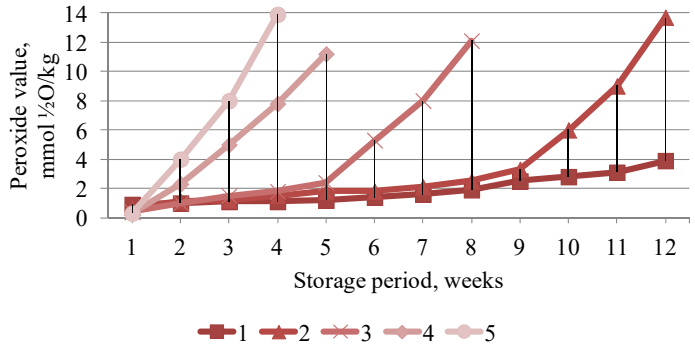

Fig. 1. Peroxide value dynamics of the emulsion system samples during storage

The most oxidation-stable is sample 1, containing only pumpkin seed oil with a high ω-6 PUFA content (51.8 %). Within 12 weeks of storage, its peroxide value increased to only 3.90 mmol ½O/kg, indicating a relatively low oxidation level. The least stable was sample 5, containing only camelina oil with a high ω-3 PUFA content (31.5 %). The peroxide value of this sample increased sharply to 13.90 mmol ½O/kg already after 4 weeks of storage, indicating intensive oxidation.

In addition, samples with a higher ω-3 PUFA content (No. 2–5) showed a much higher oxidation rate during the specified storage period. In particular, samples 3 and 4 were unstable after 4 weeks of storage, when the peroxide value increased to 12.10 and 7.80, respectively. Sample 2 containing 3:1 pumpkin seed oil and camelina oil showed moderate oxidative stability with a peroxide value of 13.70 after 12 weeks of storage.

To develop emulsion systems (dressings) enriched with ω-3 PUFAs, it is worth paying attention to complex antioxidants that can protect these PUFAs from oxidation. Samples 3 and 2 (ω-3:ω-6 PUFA ratio of 1:2.21...5.46) showed moderate stability (the oxidation induction time of 5 and 9 weeks, respectively), and using them as a dressing oil base may be appropriate, provided that they are additionally stabilized with antioxidants.

5. 2. Substantiation of the composition of a complex antioxidant for stabilizing the dressing enriched with ω-3 polyunsaturated fatty acids

To substantiate the composition of the complex antioxidant for the oxidative stabilization of the emulsion system oil base, three main components were chosen: tocopherol extract, garlic and laurel essential oils. The choice of these components is based on their antioxidant properties, as well as the potential non-additive effect on oxidation inhibition.

The ability of the complex antioxidant to inhibit the oxidative destruction of the emulsion system oil base was investigated, depending on the ratio of components. Model samples No. 2 and No. 3 were subjected to oxidative stabilization (the composition is described in Table 1). The oxidation induction time of the specified samples without an antioxidant is 6.5 and 2.2 hours, respectively. The content of the complex antioxidant added was 0.2 %. Approximation equations describing the dependence of the peroxide value of the oxidation induction time of the oil base of dressing samples No. 2 and No. 3 on the complex antioxidant component ratio are presented using equations (2) and (3), respectively:

$$IT_2(c_t, c_g, c_l)=13.5386\cdot c_t+8.6171\cdot c_g+ +9.9636\cdot c_l+7.3125\cdot c_t\cdot c_g+12.3268\cdot c_t\cdot c_l+ +11.7000\cdot c_g\cdot c_l; \quad (2)$$

$$IT_3(c_t, c_g, c_l)=4.5823\cdot c_t+2.9166\cdot c_g+ +3.3723\cdot c_l+2.4750\cdot c_t\cdot c_g+4.1721\cdot c_t\cdot c_l+ +3.9600\cdot c_g\cdot c_l, \quad (3)$$

where $IT_2(c_t,c_g,c_l)$ – oxidation induction time of sample No. 2, hours;

$IT_3(c_t,c_g,c_l)$ – oxidation induction time of sample No. 3, hours;

c_t – content of tocopherol extract, mass fraction;

c_g – content of garlic essential oil, mass fraction;

c_l – content of laurel essential oil, mass fraction.

The values R^2=0.957 for dependence (2) and R^2=0.981 for dependence (3) indicate a high effect of variations in the complex antioxidant component ratio on variations in the oxidation induction time of the dressing oil base model samples. The calculated Fisher's test values of 18.527 for dependence (2) and 11.73 for dependence (3) are greater than its critical table value $F_{tab}(3, 6)$=4.76 at the significance level p=0.05. Therefore, the test results allow with a probability of 95 % recognizing the values of the coefficients of determination R^2=0.957 for dependence (2) and R^2=0.981 for dependence (3) as significant, and the equations of dependencies (2) and (3) as significant.

Graphic dependencies of the oxidation induction time of the dressing oil base model samples with different ω-3 PUFA contents are shown in Fig. 2.

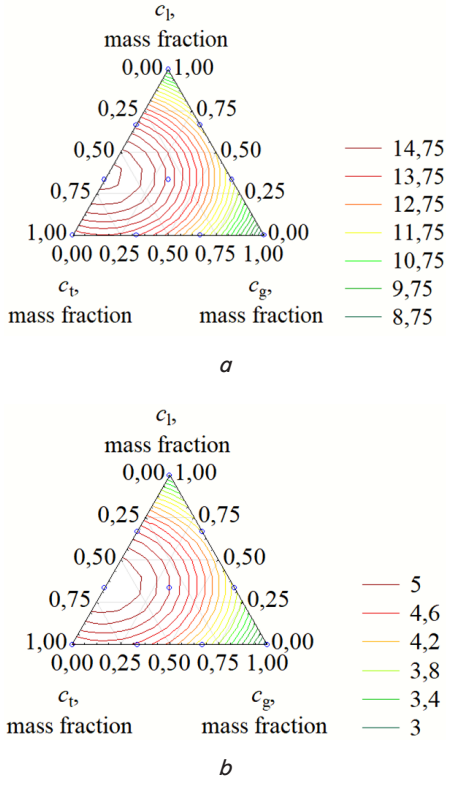

Fig. 2. Dependence of the oxidation induction time of the dressing oil base model samples on the complex antioxidant component ratio (c_t – tocopherol extract content; c_g – garlic essential oil content; c_l – laurel essential oil content): *a* – sample No. 2; *b* – sample No. 3

Analyzing the results of the study, it can be determined that when using an individual tocopherol extract as an antioxidant, the induction time for sample No. 2 is 13.65 hours, and for sample No. 3 – 4.62 hours. Using only individual essential oils as antioxidants, the induction time is significantly reduced: for sample No. 2 – 9.1-and 10.4 hours (garlic and laurel essential oils), respectively, and for sample No. 3 – 3.08 and 3.0 hours, respectively. Mixed combinations of antioxidants show quite interesting results in inhibiting lipid oxidation. For example, with a ratio of 66 % tocopherol extract and 33 % garlic essential oil in the complex antioxidant, the induction time for sample No. 2 is 13.3 hours, and for sample No. 3 – 4.5 hours. Similarly, with a ratio of 66 % tocopherol extract and 33 % garlic essential oil in the complex antioxidant, the induction time for sample No. 2 increases to 15.0 hours, and for sample No. 3 – to 5.0 hours. The longest induction time for model samples is observed in the model system where all three components are included in the complex antioxidant. This indirectly indicates a non-additive effect of combining the selected components of the complex antioxidant.

5. 3. Study of the characteristics of the dressing stabilized against oxidation with a complex antioxidant

By organoleptic characteristics, the obtained model samples of the emulsion system (dressing) remain stable for 30 days of storage at a temperature of 5±1 °C. The emulsions have no flakes and films on the surface and are characterized by a harmonious aroma of unrefined oils with light hints of garlic and laurel leaves. The taste of the emulsions is well balanced, slightly salty, moderately sour, without foreign or unusual flavors. The product color is beige-cream, corresponds to the color of the components, and the texture is uniform.

The quality parameters of model samples of the emulsion system with different ω-3 PUFA contents on the day of manufacture and over 30 days of storage were studied. As quality parameters, the titratable acidity and peroxide value of the samples were investigated (Fig. 3).

The graphic dependencies show that over 30 days of storage, in model samples of the emulsion system stabilized with a complex antioxidant, there is a gradual accumulation of organic acids and primary oxidation products. For samples No. 2 and No. 3, the titratable acidity in terms of acetic acid increases from 0.73 % to 0.75 %.

The peroxide value, reflecting the content of peroxides and hydroperoxides in the fat component, also increases during storage. In sample No. 2, the peroxide value increases from 0.7 to 1.9 mmol ½O_2/kg. For sample No. 3 – from 0.4 to 1.2 mmol ½O_2/kg, indicating a lower oxidation rate compared to sample No. 2. The obtained titratable acidity and peroxide values meet the requirements of regulatory documentation (DSTU 4561, EU Regulation No. 852/2004): not higher than 0.9 % and 10 mmol ½O_2/kg, respectively.

The calculation results confirm that the cost of the proposed product, consisting of tocopherol extract, garlic and laurel essential oils, is $19.23/kg, while the cost of the comparative product (a mixture of natural tocopherols in sunflower oil) is $25.0/kg. The cost ratio of these products shows that the proposed product is 1.3 times cheaper than the comparison product. This confirms the economic feasibility of producing a complex antioxidant with the proposed composition.

6. Discussion of the results of developing a complex antioxidant for the stabilization of dressing with ω-3 polyunsaturated fatty acids

The oxidative stability of model samples of the emulsion system with different pumpkin seed and camelina oil ratios was studied (Table 1, Fig. 1). The results show that the ratio of ω-3 and ω-6 PUFAs in the fat component of the emulsion system significantly affects its oxidative stability. Oil with a high ω-6 PUFA content was more oxidation-stable, while oil with a high ω-3 PUFA content was less stable. Blended oils showed intermediate oxidative stability. The ω-3 and ω-6 ratio in such mixtures significantly affected the oxidation rate. This may be due to several factors. First, ω-6 PUFA molecules have a more linear structure, making them less prone to free radical formation and further oxidation. In addition, pumpkin seed oil contains a significant amount of natural antioxidants (tocopherols, carotenoids) [9], effectively protecting unsaturated fatty acids from oxidation. The decrease in oxidative stability in samples with a high ω-3 PUFA content may be due to the increased oxidation susceptibility of these acids, while the higher stability of samples with ω-6 PUFAs and blended oils may be related to a more favorable structure of ω-6 PUFA molecules and the presence of antioxidants in pumpkin seed oil.

The composition of a complex antioxidant for the oxidative stabilization of an emulsion system enriched with ω-3 PUFAs was substantiated (using the examples of model samples No. 2 (ω-3:ω-6 PUFAs 1:5.46)

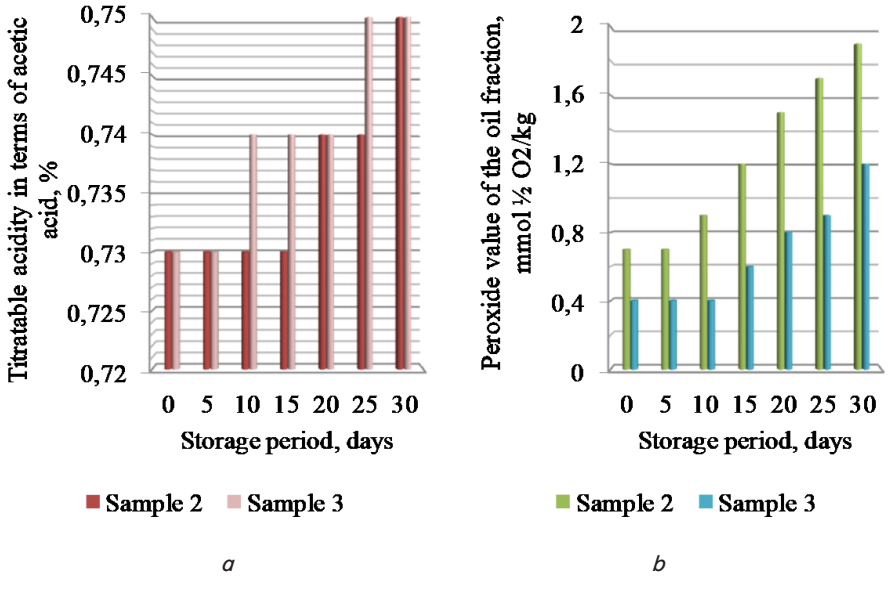

Fig. 3. Dependence of the physicochemical parameters of emulsion system samples 2 and 3 stabilized with a complex antioxidant: *a* — titratable acidity in terms of acetic acid; *b* — peroxide value of the oil fraction

and No. 3 (ω-3:ω-6 PUFAs 1:2.21)). It was proved (Fig. 2, dependencies (1) and (2)) that adding essential oils in combination with tocopherols to the emulsion system fat base increases the antioxidant activity of the latter, which is manifested in a much longer inhibition of lipid oxidative destruction. This result indicates the importance of a comprehensive approach to selecting antioxidants for the stabilization of emulsion systems enriched with ω-3 PUFAs, and can be used in developing new formulations with components labile to free radical oxidation. The reasonable ratio of the complex antioxidant components was substantiated, which is: tocopherol extract: garlic essential oil: laurel essential oil 1:1:1, respectively. At this ratio, the oxidation induction time for sample No. 2 is 16.25 hours and sample No. 3 – 5.50 hours. The results obtained (Fig. 2, dependencies (1) and (2)) indicate the prospects for using a complex antioxidant based on tocopherol extract, garlic and laurel essential oils to stabilize fat systems, including emulsions enriched with ω-3 PUFAs. This approach can be used to develop new, more stable foods with a high PUFA content. The research results can be explained by the synergistic effect of the complex antioxidant components, including tocopherol extract, garlic and laurel essential oils. Tocopherols effectively interrupt oxidation chain reactions, while essential oils enhance this effect due to their antioxidant properties. The reasonably selected ratio of components ensures maximum stability of the emulsion system enriched with ω-3 PUFAs and significantly extends the oxidation induction time. This emphasizes the importance of an integrated approach to stabilizing such systems.

The results of the stability study of the emulsion system model samples with the addition of a complex antioxidant for 30 days were analyzed. The dressing retains its organoleptic properties (taste, aroma, consistency) for 30 days of storage, indicating the effectiveness of the complex antioxidant used. There is also no flaking, filming or foreign flavors, which are typical signs of lipid oxidation. The titratable acidity (Fig. 3, *a*) and peroxide value (Fig. 3, *b*) of the fat component of both model samples slightly increase during the specified storage period, indicating slow processes of lipid oxidation and hydrolysis. The obtained titratable acidity and peroxide values meet the requirements of regulatory documentation. Thus, using a complex antioxidant helps to inhibit lipid oxidation processes, preserving the organoleptic properties and, accordingly, extending the shelf life of emulsion systems enriched with ω-3 PUFAs. Analysis of the economic feasibility of using a complex antioxidant proved the priority of using the selected raw components compared to the raw components of a similar natural commercial product.

The results of the stability study of the emulsion system model samples with the addition of a complex antioxidant for 30 days demonstrate the effectiveness of antioxidant protection of the lipid component. Preserved organoleptic properties of the dressing, such as taste, aroma and consistency, indicate the maximum inhibition of lipid oxidation processes. The absence of flaking, filming and foreign flavors confirms that the complex antioxidant used effectively inhibits reactions characteristic of autocatalytic lipid oxidation. A slight increase in titratable acidity and peroxide value indicates slow hydrolysis processes and initial stages of lipid oxidation, which are expected during long-term storage, but these indicators remain within the limits of regulatory documentation. Thus, the complex antioxidant not only prevents the rapid development of oxidation processes, but also helps to extend the shelf life of the product, especially given the emulsion system enrichment with ω-3 PUFAs, which are vulnerable to oxidation.

The advantages of this study are due to the use of a complex antioxidant, providing effective protection of the emulsion system lipid component from oxidation. This solution can not only preserve the organoleptic properties of the product during long-term storage, but also minimize the hydrolysis and oxidation processes of ω-3 polyunsaturated fatty acids, which are vulnerable to destructive reactions. Compared to similar studies, the proposed approach demonstrates higher system stability, reduced titratable acidity and peroxide value, confirming a longer shelf life and improved quality of the final product. The research results have potential applications in the food industry, in particular the production of foods with high ω-3 and ω-6 PUFA contents. They can be used to create new, more stable foods such as salad dressings, sauces, margarines, mayonnaises, etc. Since ω-3 PUFAs are important for human health, but are rather oxidation-unstable, using a complex antioxidant with the composition substantiated in the study can improve the quality parameters of the given emulsion systems during storage. Thus, the effect of implementing the research results lies in expanding the range of emulsion products for health purposes. The research results can be used in the food industry, especially in the oil and fat sector.

The results of the study differ from [7] in placing emphasis on the effect of the ω-3 and ω-6 PUFA ratio in the fat component on the oxidative stability of emulsion systems, and not only on the antioxidant content. The difference from [8] is that the study focuses on the stabilization of emulsion systems with ω-3 PUFAs using essential oils and tocopherols, while [8] uses fat-soluble antioxidants to stabilize fat with a high content of phospholipids. The study also differs from [9] in developing not just a flavored oil composition, but a complex antioxidant ensuring longer stability of emulsion systems with ω-3 PUFAs. In contrast to [10, 11], the study focused on using essential oils in combination with tocopherols for ω-3 PUFA stabilization, and not only on traditional fat-soluble antioxidants. In addition, the study considers the inhibition of lipid oxidation processes in emulsion systems, and not in fat systems without taking into account emulsification, as in [12]. The difference of the study compared to [14] is the focus on the use of a complex antioxidant containing more than one ether component, while [14] considers the stabilization of the emulsion system by adding an individual mint extract, without taking into account the complex antioxidant approach. Thus, developing the composition of a complex antioxidant for stabilizing emulsion systems with PUFAs is interesting both scientifically and practically. The results of the studies (Fig. 1–3 and dependencies (1), (2)) allow visualizing the dependencies of the oxidation induction time of model samples of the emulsion system oil base depending on the complex antioxidant component ratio. The obtained data were used to substantiate the rational composition of a complex antioxidant.

The obtained solutions completely cover the identified problem part due to a comprehensive approach to the development of methods for inhibiting the oxidation processes of the lipid component of stable emulsion systems enriched with ω-3 PUFAs. A complex antioxidant based on natural components, such as tocopherols, garlic and laurel essential oils, can effectively inhibit oxidation processes and stabilize the lipid component. This ensures high stability of the emulsion system during storage, preserving the organoleptic

properties of the product. This solution also avoids the typical problems, such as flaking or loss of flavor, often seen in similar products. Thus, the developed measures significantly increase the stability and nutritional value of the emulsion system, which fully meets the goals set and confirms the feasibility of using the proposed approach.

A limitation is that the results of the study may not meet the regulatory requirements for emulsion systems in some regions or countries, which limits their application at the international level. In particular, 21 CFR Part 169 – Requirements for Specific Standardized Food Dressings in the USA are more extensive and additional product research is needed. In addition, the results of the study should take into account the microbiological stability of the product, which may also limit its shelf life and require additional measures to ensure the product safety. Accordingly, the drawback of the studies is the lack of research on the microbiological aspects of storing emulsion systems, which are critical for food safety.

It is advisable to expand the use of the developed complex antioxidant to other types of emulsion and fat systems, in particular products with other vegetable oils or blends. This may allow creating new products with high oxidative stability. In addition, since microbiological stability is a critical aspect of food products, it is worth investigating the effect of the developed antioxidants on the microbiological stability of emulsion systems.

7. Conclusions

1. The oxidation dynamics of the oil base of the emulsion system (dressing) based on pumpkin seed and camelina oils with different ω-3:ω-6 PUFA ratios was analyzed. It was found that samples with a higher ω-3 PUFA content show an increased tendency to oxidative spoilage, manifested as a sharp increase in the peroxide value during storage. Sample 1 (pumpkin seed oil) was the most oxidation-stable, while sample 5 (camelina oil) showed the highest oxidation rate. This indicates the need for additional stabilization of ω-3 PUFAs with antioxidants in systems with a high content of these acids.

2. The expediency of using a mixture of tocopherol extract, garlic and laurel essential oils in a 1:1:1 ratio to stabilize the dressing enriched with ω-3 PUFAs was substantiated. The effectiveness of this combination is explained by the synergistic effect of the components, enhancing antioxidant activity and inhibiting oxidation processes. Using such a mixture, the oxidation induction time of samples with an ω-3:ω-6 PUFA ratio of 1.00:5.46 and 1.00:2.21 significantly increases, confirming the stabilizing effect of the developed antioxidant complex.

3. The study of the quality parameters of the emulsion system samples stabilized against oxidation with a complex antioxidant confirmed the effectiveness of the developed composition in ensuring long-term product stability. Dressing samples retain their organoleptic characteristics, as well as the titratable acidity and peroxide value of the lipid component for 30 days of storage. This indicates the high effectiveness of the used antioxidant complex in preventing oxidation. The increased shelf life and stability of the product without filming or foreign flavors are important achievements, testifying to the prospects for introducing such antioxidant systems to industrial production. At the end of the studied storage period, both samples met the requirements of regulatory documentation (DSTU 4561, EU Regulation No. 852/2004), confirming their compliance with established quality standards.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship, or otherwise, that could affect the research and its results presented in this paper.

Financing

The study was conducted without financial support.

Data availability

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

References

1. Osaili, T. M., Hasan, F., Al-Nabulsi, A. A., Olaimat, A. N., Ayyash, M., Obaid, R. S., Holley, R. (2023). A worldwide review of illness outbreaks involving mixed salads/dressings and factors influencing product safety and shelf life. Food Microbiology, 112, 104238. https://doi.org/10.1016/j.fm.2023.104238
2. Wu, Z., Tan, B., Liu, Y., Dunn, J., Martorell Guerola, P., Tortajada, M. et al. (2019). Chemical Composition and Antioxidant Properties of Essential Oils from Peppermint, Native Spearmint and Scotch Spearmint. Molecules, 24 (15), 2825. https://doi.org/10.3390/molecules24152825
3. Norazlina, M. R., Jahurul, M. H. A., Hasmadi, M., Mansoor, A. H., Norliza, J., Patricia, M. et al. (2021). Trends in blending vegetable fats and oils for cocoa butter alternative application: A review. Trends in Food Science & Technology, 116, 102–114. https://doi.org/10.1016/j.tifs.2021.07.016
4. Belinska, A., Bliznjuk, O., Shcherbak, O., Masalitina, N., Myronenko, L., Varankina, O. et al. (2022). Improvement of fatty systems biotechnological interesterification with immobilized enzyme preparation usage. Eastern-European Journal of Enterprise Technologies, 6 (6 (120)), 6–13. https://doi.org/10.15587/1729-4061.2022.268373

5. Lakshmayya, N. S. V., Mishra, A. K., Mohanta, Y. K., Panda, J., Naik, B., Mishra, B., Varma, R. S. (2023). Essential oils-based nano-emulsion system for food safety and preservation: Current status and future prospects. Biocatalysis and Agricultural Biotechnology, 53, 102897. https://doi.org/10.1016/j.bcab.2023.102897
6. Demydova, A., *Aksonova*, O., Yevlash, V., Tkachenko, O Kameneva, N. (2022). Antioxidant activity of plants extracts of Ukrainian origin and their effect on the oxidative stability of sunflower oil. Food Science and Technology, 16 (3). https://doi.org/10.15673/fst.v16i3.2514
7. Kunitsia, E., Popov, M., Gontar, T., Stankevych, S., Zabrodina, I., Stepankova, G. et al. (2024). Determination of the influence of hemp oil-based emulsion systems composition on the oxidation products content during storage. Technology Organic and Inorganic Substances, 3 (6 (129)), 6–13. https://doi.org/10.15587/1729-4061.2024.304466
8. Felix-Sagaste, K. G., Garcia-Carrasco, M., Picos-Corrales, L. A., Gonzalez-Ruelas, T., Rodriguez-Mercado, J. A. (2023). Plant-animal extracts and biocompatible polymers forming oil-in-water emulsions: Formulations for food and pharmaceutical industries. Hybrid Advances, 3, 100072. https://doi.org/10.1016/j.hybadv.2023.100072
9. Kunitsia, E., Kalyna, V., Haliasnyi, I., Siedykh, K., Kotliar, O., Dikhtyar, A. et al. (2023). Development of a flavored oil composition based on hemp oil with increased resistance to oxidation. Eastern-European Journal of Enterprise Technologies, 5 (11 (125)), 26–33. https://doi.org/10.15587/1729-4061.2023.287436
10. Kalyna, V., Stankevych, S., Zabrodina, I., Shubina, L., Chuiko, M., Mikheeva, O. et al. (2024). Development of the composition of anoxidation-stable dressing with high nutritional value. Eastern-European Journal of Enterprise Technologies, 1 (11 (127)), 29–37. https://doi.org/10.15587/1729-4061.2024.296621
11. Petik, P., Stankevych, S., Zabrodina, I., Zhulinska, O., Mezentseva, I., Haliasnyi, I. et al. (2023). Determination of fat-soluble dyes influence on the oxidation induction period of their oil solutions. Eastern-European Journal of Enterprise Technologies, 3 (6 (123)), 13–21. LOCKSS. https://doi.org/10.15587/1729-4061.2023.279619
12. Belinska, A., Bliznjuk, O., Masalitina, N., Bielykh, I., Zviahintseva, O., Gontar, T. et al. (2023). Development of biotechnologically transesterified three-component fat systems stable to oxidation. Eastern-European Journal of Enterprise Technologies, 5 (6 (125)), 21–28. https://doi.org/10.15587/1729-4061.2023.287326
13. Joshi, T., Kapoor, S., Rana, S., Bala, M., Singh, A., Mahajan, B. V. C. (2024). Valorization of guava seed oil as a functional ingredient in salad dressing: implications on quality characteristics, rheological behaviour, morphology, oxidative stability and shelf life. Journal of Food Measurement and Characterization, 18 (8), 6698–6710. https://doi.org/10.1007/s11694-024-02683-8
14. Mooliani, H., Nouri, M. (2021). Optimization of oxidative, physical stability and microbial characteristics of salad dressing emulsions based on avocado and whey protein combined with mint (Mentha spicata L) extract. Journal of Food Measurement and Characterization, 15 (6), 5713–5724. https://doi.org/10.1007/s11694-021-01131-1
15. Mikołajczak, N., Tańska, M., Ogrodowska, D. (2021). Phenolic compounds in plant oils: A review of composition, analytical methods, and effect on oxidative stability. Trends in Food Science & Technology, 113, 110–138. https://doi.org/10.1016/j.tifs.2021.04.046
16. Serra, J. J., Mura, J., Fagoaga, C., Castellano, G. (2023). Oxidative Stability of Margarine is Improved by Adding Natural Antioxidants from Herbs and Spices. https://doi.org/10.20944/preprints202305.1445.v1
17. Ali, M. A., Chew, S. C. (2022). Efficacy of exogenous natural antioxidants in stability of polyunsaturated oils under frying temperature. Journal of Food Measurement and Characterization, 17 (1), 408–429. https://doi.org/10.1007/s11694-022-01601-0