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ELECTRICAL TREATMENT OF BIOLOGICAL OBJECTS AND FOODSTUFFS

The Influence of Natural Antioxidants on the Oxidative Stability of Iodine-Fortified Sunflower Oil in the Process of Storage

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Abstract—The task of obtaining oils with heightened antioxidative properties by incorporating natural antioxidative spice plant components into the receipt composition has been solved in order to decrease the intensity of possible oxidative reactions and increase the shelf life of iodine-fortified sunflower oil. It has been shown that natural antioxidants exert an effective influence on the stabilization of the investigated oils; i.e., the intensity of accumulation of primary and secondary oil oxidation products is inhibited.

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INTRODUCTION

The deficiency of iodine in food is one of the major problems of the world community, which is reflected in documents of the U.N.O. and in the governmental enactments of many countries [1–6].

About 13% of the world's population suffers from an iodine deficiency and 85% of the people living in the Republic of Moldavia are subject to the risk of development of iodine-deficient disorders (IDDs), as evidenced by the data of research conducted by specialists of UNICEF.

Taking into consideration that the creation of fortified foodstuffs is an urgent trend in eliminating the deficiency of iodine in food [11–17], we have developed technology for obtaining iodine-fortified sunflower oil and also investigated all its organoleptic and physicochemical indices.

To decrease the intensity of possible oxidative transformations and to increase the shelf life of the investigated oil, the task was posed to obtain iodine-fortified oil with increased antioxidant properties at the expense of incorporating into its composition natural antioxidants, namely, antioxidative spice plant components.

THE THEORETICAL ANALYSIS

Despite the fact that synthetic antioxidants are widely distributed in the world with the view of stabilizing vegetable oils, there are a number of works that testify to the inexpediency of their application [18, 19]. Taking into consideration the need for natural antioxidants, we have tried to use spice plants for this purpose.

The capability of antioxidants to hamper the oxidation process is determined by the fact that their composition includes weakly bound mobile hydrogen or functional groups that actively react with molecular oxygen or with free radicals that form in the oxidation process [20]. This condition is fulfilled in the case of phenols and aromatic amines [21, 22].

A new group of antioxidants that belong compositionally to aromatic diketones has recently been revealed [23]. The antioxidative action of this group of compounds is determined by the presence of a weekly bound hydrogen atom in the second position [24]. The literature lacks for data about the energy of the detachment of this hydrogen atom. Another requirement imposed on antioxidants is their high lipophility [25, 26].

The solubility of these components was investigated using the data of the literature with a view to determine the optimal conditions of their extraction (Table 1).

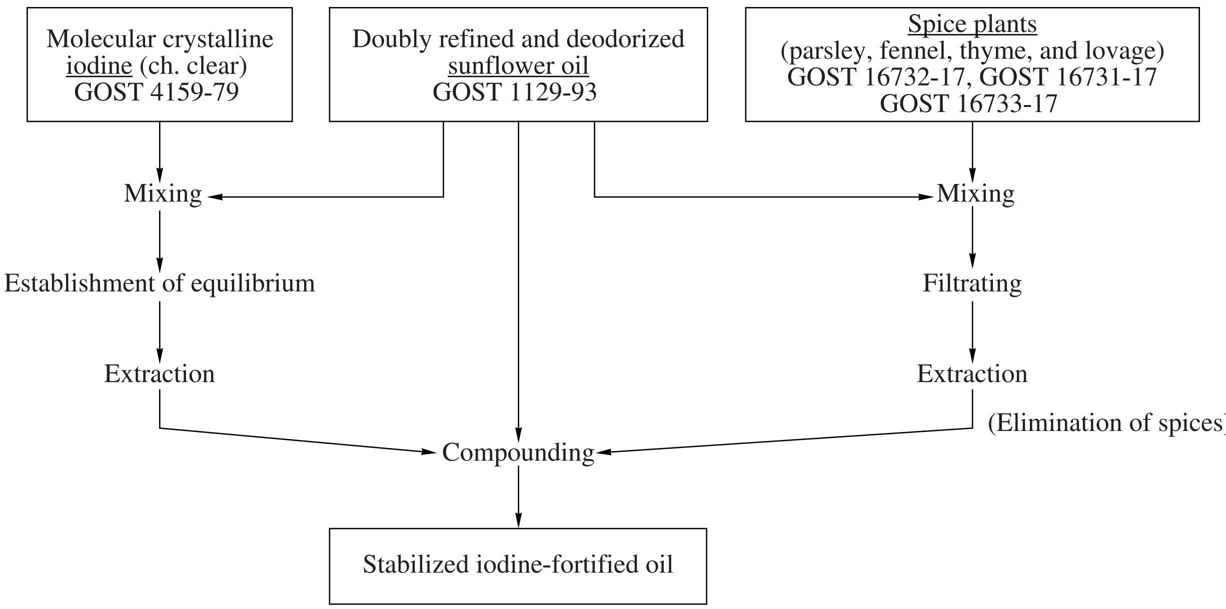
EXPERIMENTAL

The scheme shows the technological scheme for producing the iodine-fortified stabilized sunflower oil at the expense of spice plant extracts.

It was ascertained that the quantity of spice plants equal to 0.4–0.6 g/100 g is optimal for the iodine-fortified sunflower oil for achieving stable and minimal degrees of oxidation. Consequently, this concentration of the antioxidant permits the possible oxidative influence of iodine to be eliminated and allows the shelf life of the iodine-fortified sunflower oil to be prolonged.

The oxidative stability of the obtained iodine-fortified oils with spice plant extracts was investigated according to the value of the accumulation of primary and secondary oxidation products in the compared oil samples over 12 months at a temperature of 4–6°C.

The content of primary oxidation products was estimated using the peroxide values [28] and the quantity of hydroperoxides. Monohydroperoxides were



The scheme presents the main technological processes of producing stabilized iodine-fortified sunflower oil.

detected by a spectral method of analysis ($\lambda = 510$ nm) according to the procedure of Shanta and Decker [29].

The formation and intensity of the accumulation of the secondary oxidation products in the investigated oils were characterized by the *p*-anisidine [30] and tiobarbituric [31] values.

The reliability of the experimental data was estimated by methods of mathematical statistics with finding an average interval value from three parallel experiments at a confidence probability of 95% [32].

RESULTS AND DISCUSSION

Oxidative and hydrolytic decomposition is observed in the process of storing vegetable oils. The presence and depth of the process of oil oxidation and hydrolysis is characterized by the content of free fatty acids in oils, i.e., the acid value (AV).

The growth of the acid value or intensity in the formation of free fatty acids in the compared oils has a linear character (Fig. 1).

The presence of free fatty acids in fresh samples that did not undergo the storage process can be explained by the fact that fatty acids are normal intermediate metabolites of the adipose tissue.

The acid values of the sunflower oil samples without iodine and spice plant extracts and those of the oil samples with the iodine content of 1 μg I/ml do not essentially differ after 12 months of storage, averaging 0.316 mg KOH/g of oil. It should be noted that the acid value of these two investigated samples approached the limit of the admissible values (0.35 mg KOH/g of oil) stipulated by the GOST 1129-93 standard for sunflower oil.

Consequently, as has already been shown [33–35], molecular iodine incorporated into the composition of sunflower oil with the view of increasing its biological

Table 1. The solubility of antioxidative spice plant components

The name of the component	Solubility, g/100g		
	in water	in alcohol	in ethers
β-carotene	nonsoluble	easily soluble	easily soluble
Quercetin	0.006	0.029	1.419
Caffeic acid	soluble	easily soluble	easily soluble
Ferule acid	soluble	easily soluble	easily soluble
Terpenes:			
carvone	1.32	easily soluble	easily solubl
A-pinene	nonsoluble	easily soluble	easily soluble
Ascorbic acid	33.3	easily soluble	nonsoluble

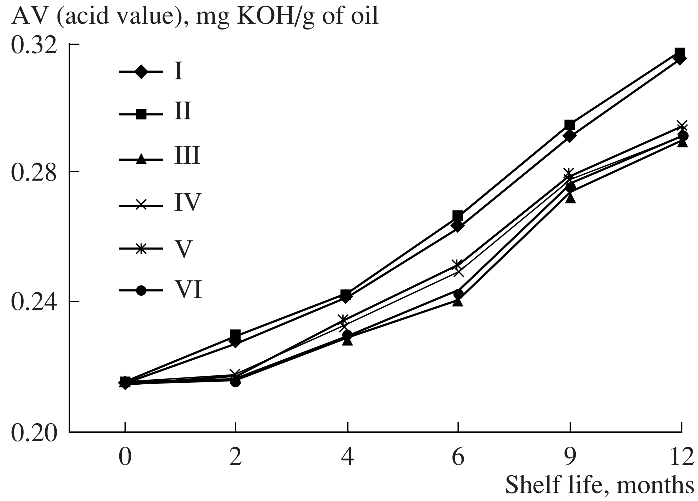


Fig. 1. The change in the AV of the compared oil samples in the course of storage. I—oil without iodine and spice plant extracts; II—oil with an iodine content (1 μg I/ml); and III, IV, V, and VI—oils with an iodine content (1 μg I/ml) and with spice plant extracts (parsley, fennel, thyme, and lovage, respectively).

value is fixed by the double bonds of oil fatty acids with the formation of stable π complexes.

The π-complexes formed between iodine and the double bonds of triglyceride fatty acids slow down the processes of oxidation and hydrolysis that take place in the investigated oils in the course of storage.

When comparing the acid values of the oil group with the iodine content of 1 μg I/ml and with the spice plant extracts, one can note that free fatty acids accumulate to a lesser extent in a sample containing a parsley extract as an antioxidative component and that the acid values are within the range of 0.215–0.291 mg KOH/g of oil. Meanwhile, the acid value of a sample with a fennel extract already amounted to 0.294 mg KOH/g of oil after 12 months of storage. This being the case, the acid value remained within the limits of the above-indicated GOST standard in all the samples investigated.

According to the theory of N.N. Semenov, the oxidation of oil must be considered as a chain reaction that develops through the formation and conversion of free radicals. The essence of the chain reaction mechanism is that chain reactions appear and develop through the formation and inactivation of free radicals. Free radicals are fatty acid molecules. One of the atoms of which has a free valence; therefore, they are chemically active and easily attach oxygen. Moreover, they attach oxygen to the place of the free valence of a radical with the formation of peroxides, rather than to the double bonds of fatty acids (as the theory of Bakh–Engler states). The formed free peroxide radical is subsequently a leading component in the oxidation chain, since all the remaining oxidation products are formed through it.

The presence and quantity of peroxides and hydroperoxides in vegetable oils are known to determine the level of the oil storage stability. Table 2 shows the dynamics of the accumulation of these compounds in the compared oil samples during storage.

As the presented data show, the summary rate of oxidative reactions that lead to the formation of peroxides and hydroperoxides in the course of storage for 12 months is lower for the group of stable oils with the iodine concentration of 1 μg I/ml and with extracts of spice plant components (it varies from 7.8 to 9.2 mEq/kg of oil for peroxides and from 0.071 to 0.116 mM for hydroperoxides) than in the initial oil (from 8.4 to 9.9 mEq/kg of oil for peroxides and from 0.079 to 0.128 mM for hydroperoxides).

When comparing the oil samples without and with the iodine content (1 μg I/ml), one should note that the degree of the accumulation of the primary oxidation products in these oils does not depend on the presence of iodine in the composition of the investigated oil or is within the same limits, varying from 8.4 mEq/kg of oil before storage to approximately 10.0 mEq/kg after 12 months of storage and from 0.079 to 0.128–0.129 mM for peroxides and hydroperoxides, respectively.

Figure 2 visually illustrates the intensity of the processes of the formation of the primary oxidation products (peroxides and hydroperoxides) in the investigated oils depending on the duration of storage.

The shelf life of the oil samples is plotted on the abscissa. The height of each column corresponds to the quantitative expression of the peroxide accumulation for a concrete sample at a given index of shelf life.

As one can note from Fig. 2, the dependence between the content of peroxides and the shelf life has an autoaccelerated character. The growth of the peroxide accumulation takes place at the first stage, and, at the second stage, the accumulation has a constant value. The duration of the first stage characterizes the persistence of the oxidized system, which is apparently

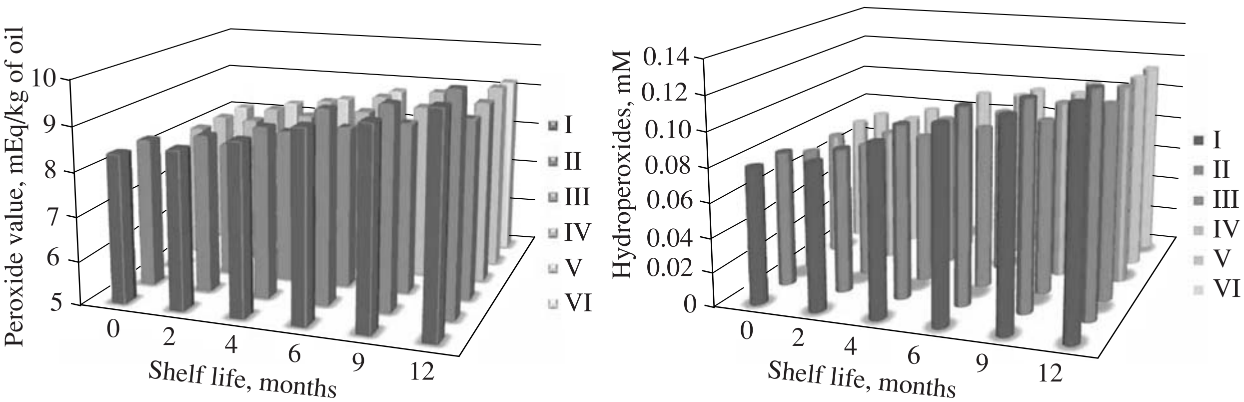


Fig. 2. The dynamics of the accumulation of peroxides and hydroperoxides in the compared oil samples during storage. I—oil without iodine and spice plant extracts; II—oil with an iodine content (1 μg I/ml); and III, IV, V, and VI—oils with an iodine content (1 μg I/ml) and with spice plant extracts (parsley, fennel, thyme, and lovage, respectively).

determined by the properties of the system itself and also by the presence of various spice plant components that slow down the processes of oxidative oil destruction.

Since the samples from the oil group with an iodine content (1 μg I/ml) and with spice plant extracts differ from the oil samples without and with an iodine content (1 μg I/ml) only by containing the antioxidative spice plant components, the difference in the time necessary to achieve a constant value of the peroxide accumulation in the investigated samples is determined to a greater extent by this factor. It is probable that a greater part of the antioxidative spice plant components contained in the oils with spice plant extracts is spent within 6 months of storage, after which these samples are oxidized analogously to the oil samples without spice plant extracts.

It was ascertained based on the obtained results that the increase in the shelf life of the oil group with the iodine content (1 μg I/ml) and with the spice plant extracts was achieved due to the lower rate of the accumulation of peroxides and hydroperoxides in the investigated oils in the first months of storage.

Peroxide and hydroperoxide compounds are known to be unstable. They decompose in the storage process with the formation of the secondary products of vegetable oil oxidation, more stable carbonyl compounds—aldehydes, ketones, and their derivatives with carbonic chains of various lengths.

Table 2. The dynamics of the accumulation of peroxides and hydroperoxides in the compared oil samples

Shelf life, months	Oil without iodine and spice plant extracts		Oil with an iodine content (1 μg I/ml)		Oil with an iodine content (1 μg I/ml) and parsley extract		Oil with an iodine content (1 μg I/ml) and fennel extract		Oil with an iodine content (1 μg I/ml) and thyme extract		Oil with an iodine content (1 μg I/ml) and lovage extract	
	Peroxides, mEq/kg of oil	Hydroperoxides, mM	Peroxides, mEq/kg of oil	Hydroperoxides, mM	Peroxides, mEq/kg of oil	Hydroperoxides, mM	Peroxides, mEq/kg of oil	Hydroperoxides, mM	Peroxides, mEq/kg of oil	Hydroperoxides, mM	Peroxides, mEq/kg of oil	Hydroperoxides, mM
0	8.4 ± 0.1	0.079 ± 0.004	8.4 ± 0.1	0.079 ± 0.003	7.8 ± 0.2	0.071 ± 0.004	8.1 ± 0.1	0.073 ± 0.003	8.1 ± 0.1	0.074 ± 0.005	8.1 ± 0.1	0.072 ± 0.003
2	8.6 ± 0.2	0.085 ± 0.003	8.6 ± 0.2	0.084 ± 0.006	8.1 ± 0.2	0.078 ± 0.003	8.4 ± 0.1	0.078 ± 0.005	8.4 ± 0.1	0.079 ± 0.003	8.3 ± 0.1	0.078 ± 0.004
4	8.9 ± 0.1	0.099 ± 0.007	8.9 ± 0.2	0.101 ± 0.004	8.5 ± 0.1	0.086 ± 0.006	8.6 ± 0.1	0.089 ± 0.004	8.7 ± 0.1	0.088 ± 0.008	8.5 ± 0.1	0.091 ± 0.005
6	9.3 ± 0.1	0.112 ± 0.004	9.4 ± 0.1	0.114 ± 0.005	8.7 ± 0.1	0.094 ± 0.005	8.8 ± 0.1	0.096 ± 0.006	8.9 ± 0.2	0.099 ± 0.009	8.8 ± 0.2	0.096 ± 0.004
9	9.5 ± 0.1	0.119 ± 0.005	9.6 ± 0.1	0.121 ± 0.003	8.9 ± 0.1	0.101 ± 0.003	9.0 ± 0.2	0.104 ± 0.004	9.1 ± 0.2	0.103 ± 0.003	9.0 ± 0.1	0.103 ± 0.005
12	9.9 ± 0.2	0.128 ± 0.007	10.0 ± 0.1	0.129 ± 0.003	9.1 ± 0.2	0.113 ± 0.003	9.2 ± 0.2	0.116 ± 0.004	9.3 ± 0.2	0.115 ± 0.006	9.2 ± 0.1	0.114 ± 0.006

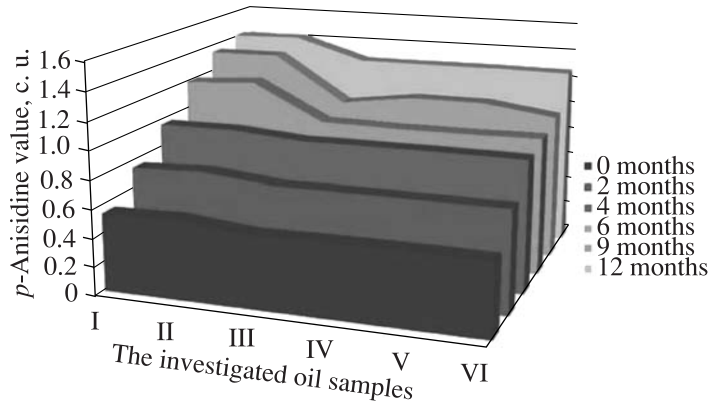
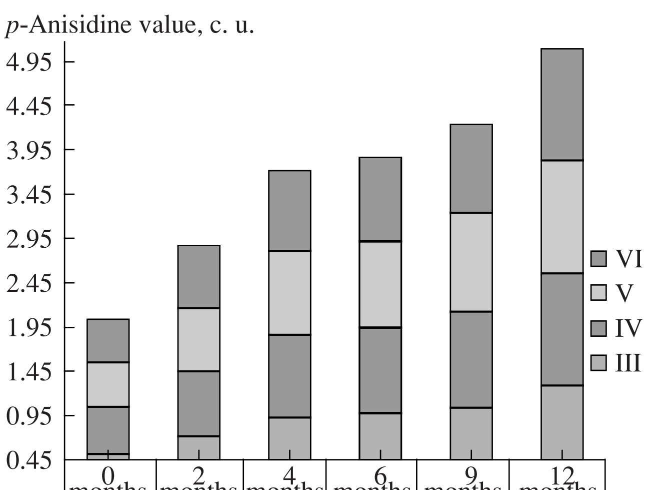


Fig. 3. The change of the *p*-anisidine value in the compared oil samples during storage. I—oil without iodine and spice plant extracts; II—oil with an iodine content (1 μg I/ml); and III, IV, V, and VI—oils with an iodine content (1 μg I/ml) and with spice plant extracts (parsley, fennel, thyme, and lovage, respectively).

If peroxides and hydroperoxides do not exert an influence on the change in the organoleptic indices of oils, aldehydes and ketones that form at the following stages of oxidation are carriers of an unpleasant taste and smell of oxidized vegetable oil.

Figure 3 shows the kinetics of the change in the intensity of the accumulation of such aldehydes as 2,4-decadienal and 2-octenal in the compared vegetable oils, which is expressed by the amount of the *p*-anisidine value.

It was ascertained that the quantity of aldehydes that accumulated in the first four months of storage did not essentially differ for all the investigated samples from the corresponding indices of the compared samples, varying from 0.5123 to 0.5492 c. u. (in fresh samples) and from 0.9331 to 0.9714 c. u. (after four months of storage). It is probable that the processes of the formation and accumulation of the secondary oxidation products (aldehydes) in the vegetable oil samples did not take place intensively in the first months of their storage, which is likely to be determined by the properties of the system itself.



	0 months	2 months	4 months	6 months	9 months	12 months
VI	0.5179	0.9343	1.0353	1.7241	0.9793	1.2791
V	0.5219	0.9371	1.1043	1.7251	0.9723	1.2834
IV	0.5203	0.9359	1.1021	1.7261	0.9704	1.2807
III	0.5123	0.9331	1.0341	1.7232	0.9786	1.2786

Fig. 4. The influence of antioxidative spice plant components on the storage stability of the compared oils with an iodine content (1 μg I/ml): III—parsley; IV—fennel; V—thyme; VI—lovage.

The incorporation of the spice plant extracts in the composition of the oils with the iodine content of 1 μg I/ml exerts an effective influence on the processes of stabilization of the investigated oils. Thus, the *p*-anisidine value of the oil without iodine and spice plant extracts came to 1.4216 c. u. after 12 months of its storage, and this value of the oils with the iodine content and spice plant extracts decreased and varied from 1.2786 to 1.2834 c. u.

When comparing the antioxidative properties of the spice plant extracts (parsley, fennel, thyme, and lovage) incorporated into the oil samples, one should note that the antioxidative components of the parsley and lovage extracts exert the greatest influence on inhibiting the processes of oil oxidation (Fig. 4).

This regularity is also traced for the acid and peroxide values of the corresponding oil samples. The greater stability of the oils with the parsley and lovage spice plant extracts can be explained by the more effective stabilizing action of the antioxidative components of these spice plants.

CONCLUSIONS

1. The technology has been developed for obtaining iodine-fortified oil with antioxidative properties that are due to the antioxidative spice plant components contained in this oil. The stable iodine-fortified oil with the prophylactic action can be used as a salad dressing

with the view of imparting a pleasant specific aroma of spice plants to various cold courses and snacks.

2. The processes have been studied of the formation and accumulation of the primary oxidation products in the investigated oil samples. The following has been ascertained:

—The accumulation of free fatty acids in the oil group with the iodine content (1 μg I/ml) and with spice plant extracts runs less intensively after 12 months of storage, being within the range of 0.291–0.294 mg KOH/g of oil; meanwhile, the acid value of the oil sample without iodine came to 0.315 mg KOH/g of oil.

—The summary rate of the oxidative reactions that lead to the formation of peroxides and hydroperoxides during storage is lower for the stable oil group with the iodine content (1 μg I/ml) than for the oil without the iodine and spice plant extracts and the oil group with the iodine content (1 μg I/ml) and without the spice plant extracts.

3. The incorporation of the spice plant extracts into the composition of the oils with the iodine content (1 μg I/ml) exerts an effective influence on the processes of stabilization of the investigated oils; i.e., it inhibits the intensity of the accumulation of the secondary oxidation products in the compared oil samples.

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