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ANTIOXIDANT ACTIVITY OF PLANTS EXTRACTS OF UKRAINIAN ORIGIN AND THEIR EFFECT ON THE OXIDATIVE STABILITY OF SUNFLOWER OIL

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Abstract. Today, more and more food manufacturers are abandoning the usage of synthetic antioxidants because of the negative impact they have on the human body. The main natural hydrophobic antioxidants such as tocopherols and carotenoids, are not cheap commercial products and are currently produced much less than fat industry requires. Therefore, obtaining other natural antioxidants from vegetable raw materials could be a solution. Among the potential sources of such raw materials were leaves and roots of herbs, bark and leaves of berry crops. 20 plants were studied. The purpose of the study was to obtain comparative data on the antioxidant activity of water-alcohol extracts of Ukrainian origin plants, as well as to study their influence on the stability of sunflower oil during its heat treatment. The induction periods of sunflower oil in the presence of antioxidants were determined, the antioxidant activity of plant extracts was determined based on the data obtained and compared with the antioxidant activity of synthetic butylhydroxyanisole, antioxidants were used in equal concentrations (200 ppm). The obtained plant extracts are arranged according to their antioxidant activity in a series (in order of decreasing activity): lemon balm grass > spirea grass > burdock root > bark of European guelder > blackberry leaves > blueberry shoots > thyme grass > raspberry leaves > calendula flowers > oak bark > mountain ash > leaves nettles > mountain ash > rosemary leaves > echinacea flowers > parsley > arugula > peppermint leaves > chamomile > dill. All deep-frying fats need protection from oxidative damage, especially unsaturated fats such as sunflower oil, which is currently widely used in deep-frying in the restaurant segment. From the results of the study, it can be concluded that the natural antioxidant (water-alcohol extract of bark of European guelder) was more effective than the synthetic antioxidant butylhydroxyanisole in inhibiting oxidative and hydrolytic processes during heat treatment of sunflower oil. During 5 days of heat treatment, the sample of sunflower oil with bark of European guelder extract was characterized by the lowest values of acid, peroxide and anisidine numbers.

Keywords: antioxidant, antioxidant activity, deep frying, sunflower oil.

Introduction. Formulation of the problem

Fat oxidation is a natural process that occurs between molecular oxygen and unsaturated fatty acids through a free radical chain mechanism. The primary oxidation products are always hydroperoxides. However, they are quite unstable and decompose to by-products, which include aldehydes, ketones, alcohols, epoxy compounds and acids. Secondary oxidation products cause unpleasant odors and tastes [1].

Hydroperoxides and, to an even greater extent, secondary oxidation products are substances dangerous to the human body that not only degrade the quality of fats, but also cause damage when consumed. Excessive formation of free radicals and reactive oxygen species can permanently damage cells and biomolecules with the subsequent accumulation of oxidatively modified products [2]. Mammals have a complex multi-step antioxidant system to regulate free radicals. The antioxidant system of the body contains enzymatic and non-enzymatic elements and includes endogenous and exogenous antioxidants [3]. Exogenous antioxidants are vital for the human body to function properly. Enriching food with antioxidants is one of the tasks of the food industry.

Antioxidant (AO) is a molecule that is able to neutralize the oxidative effects of free radicals. Antioxidants should promote two positive processes. The first is the inhibition of oxidation processes in dietary fats. The second is to reduce the risk of diseases associated with oxidative stress when used in combination with other foods.

Analysis of recent research and publications

Synthetic antioxidants are widely used in the industrial production of edible oils due to their low cost and high antioxidant activity. However, synthetic antioxidants have many disadvantages: they do not exhibit antioxidant properties in human tissues, cause liver damage and carcinogenesis, exhibit toxic effects during prolonged use and in high concentrations [4]. Due to various side effects, butylhydroxyanisole (BHA) and butylhydroxytoluene (BHT) are banned in the UK, Japan, and some European countries. Tret-butylhydroquinone (TBHQ) is banned in European countries, Canada and Japan. BHT, BHA and TBHQ show low antioxidant properties during frying because they evaporate during this process [5]. Therefore, the global food industry today is refocusing on the use of natural antioxidants, which are not only safe but also have biological activity, positively perceived by consumers.

The content of antioxidants in different foods can vary several thousand times. Spices, herbs contain the maximum concentration of antioxidants. Berries, fruits, nuts, chocolate, vegetables and their products are common foods high in antioxidants. In general, plant foods are significantly richer in AO than animal foods [6]. Antioxidants are secondary metabolites of plants - molecules that are not necessary for plant survival, but play an important role in the development, growth, reproduction and protection of plants [7]. Polyphenols, for example, can protect plants from the action of free radicals formed during photosynthesis [8]. The most well-known biologically active compounds that can inhibit the oxidation of lipids or other biomolecules are polyphenols (mainly phenolic acids and flavonoids) and terpenes (Fig. 1).

Vegetable fats contain significant amounts of natural antioxidants - tocopherols, carotenoids, etc. But in refined fats, their content is markedly reduced [9]. Under severe processing conditions - frying with oils, using them as frying fats, etc. fats are rapidly oxidized with the formation of toxic products of this process.

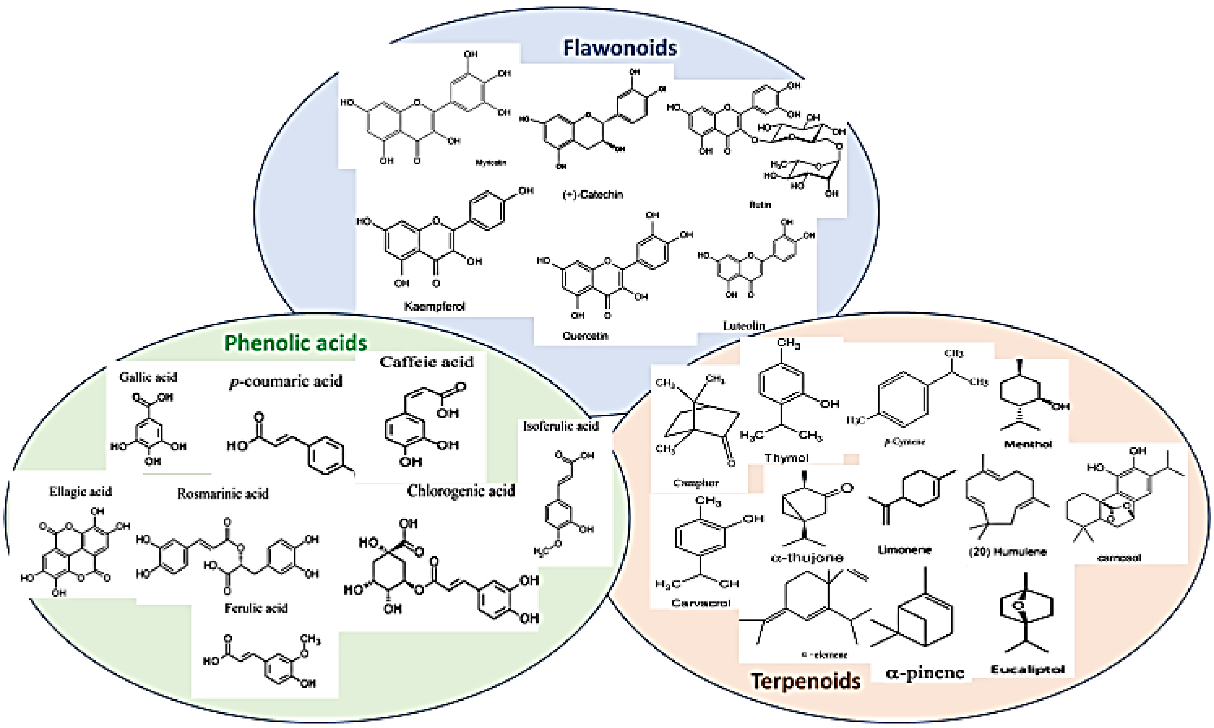

Fig. 1. The main antioxidants of plant origin

The simplest way to slow down the rate of oxidation is to introduce antioxidants into fats. In the production of edible fats, tocopherol concentrates, rosemary extracts, etc. are widely used. However, almost all of these imported additives are characterized by high cost, which is why their use in the same frying fats is not very common in Ukrainian food enterprises and especially in the restaurant industry. Therefore, food industry specialists are faced with the task of protecting fats in the simplest way using available antioxidants.

Due to the fact that the maximum amounts of AO are found in herbs and spices, the task of finding cheap, common and available raw materials for AO today, in our opinion, is to study and compare the antioxidant activity (AOA) of plants, including those grown on territory of Ukraine.

In most cases, antioxidants from plant raw materials are extracted with ethanol solvent, then the solvent is evaporated under reduced pressure or crystallized by freezing and added to oil [10]. Ethyl alcohol is a food solvent (biosolvent), safer than other organic solvents (acetone, chloroform, etc.), it has also been shown to give high yields of phenolic compounds [11], its extracts have maximum antioxidant activity compared to other solvents. Therefore, in the study it was decided to use only water-alcohol solvent, environmentally friendly and renewable (after distillation from the removed biologically active substances can be used again).

As frying fats, it is advisable to use oils of a saturated type because of their significantly greater resistance to oxidation. However, today there is the use of oils of various types (including polyunsaturated ones) for this purpose. Polyunsaturated oil (including sunflower oil) quickly accumulates toxic oxidation products under frying conditions [12], which means that protection is necessary through the use of antioxidants.

The purpose is to obtain comparative data on the antioxidant activity of water-alcohol extracts of plants, as well as to investigate their inhibition of oxidative damage to sunflower oil during its frying.

Objectives of the research:

1. Establish the effect of hydroalcoholic plant extracts on the kinetics of sunflower oil oxidation. The obtained data are compared with the antioxidant effect of the common antioxidant BHA.

2. To determine the effectiveness of the protection of sunflower oil subjected to heat treatment with the obtained antioxidant of plant origin. The obtained data are compared with the efficiency of a synthetic antioxidant.

3. Formulate conclusions on the prospects of using plant antioxidants to protect fats from oxidative damage.

Research materials and methods

Refined deodorized sunflower oil (TM "Oleyna") with a volume of 1 dm^3 was used as an oxidation model. The bottle of oil was opened before the start of the study and stored at -5°C without access to light for no more than 4 weeks.

Vegetable raw materials (peppermint leaves, echinacea flowers, calendula flowers, oak bark, viburnum bark, burdock roots, blackberry leaves, blueberry shoots, medicinal chamomile, thyme herb) were purchased in Ukrainian pharmacies. Dill, parsley, arugula were purchased from local stores. Rowan ordinary and chokeberry, Japanese spirea (Spiraea herba), bark of European guelder, raspberry leaves, nettle, melissa herb are collected on the territory of the Kharkiv region.

All plants were crushed and dried at 40°C. under a stream of air in a fume hood to a moisture content of ≤1%. Plant materials were ground using a laboratory mill (RRH-100 brand, Ukraine). The number of revolutions per minute is 28000, the power is 700 W. Next, the samples are sifted through a laboratory sieve with holes = 1 mm. Samples were stored at -5°C and used in the study for four weeks. Before extraction, all plant materials were ground in a mortar for 20s.

To obtain extracts, the prepared raw material was soaked in a mixture of ethyl alcohol - water (ratio 70:30, respectively) in a glass sausage to swell the raw material. Duration of soaking – 1 hour. It was then heated to 60°C with a magnetic stirrer heating element (RIVA – 04.4, RIVA-STAL, Ukraine) and extracted for 4 hours with constant stirring. Hydromodule 1:5 (w/v). Temperature control was performed by thermocouple. The flask was also connected to an air reflux condenser. The obtained extracts were filtered off from plant material (Whatman № 42). The filtrate was then heated in a rotary evaporator at 40°C under pressure to remove the solvent. The obtained concentrates were stored at -5°C in closed glass boxes without access to light for no more than 4 weeks and were used in the study of oxidation kinetics.

The antioxidant activity (AOA) of the extracts was studied by the volumetric method in the presence of an inert octane solvent manometric unit by oxidation of sunflower oil. A manometric setup measures the absorption of small amounts of oxygen by a sample. The unit consists of a reaction cell with a volume of 5 cm^3, a thermostatically controlled manometer, a system of connecting glass tubes and valves connected to a source of pure (99.9%) oxygen and a vacuum pump, as well as a thermostat. Work with the unit includes the following stages: 1) preparatory: by connecting to a vacuum pump (through a two-way valve lubricated with vacuum grease), the air mixture is extracted from the system of glass tubes of the unit; by connecting to a source of pure oxygen (a two-way valve), the system is filled with pure oxygen. Such sequential operations are performed 5–8 times; 2) working: measurement of the volume of oxygen absorbed by the sample in mm3 over a certain time by monitoring the change in the level of the column of colored liquid attached to the oil sample. By determining the constants of the reaction vessels of the installation, the obtained data on the kinetics of oxidation of the samples in mm^3/min are listed in mol/s.

The volume of oxygen in mol/dm^3 was calculated by expression:

$$V(O_2) = \Delta V \times 10^{-6} \times 10^3/(22,4 \times V_{sample}), \text{ mol/dm}^3$$

where 10^{-6} – the conversion factor of the volume of oxygen in dm^3,

22,4 – volume of 1 mole of gas,

$10^3/V_{sample}$ – the conversion factor of the amount of absorbed oxygen per 1 liter of substrate.

The study was performed under conditions of initiated oxidation, ie due to thermal decomposition of the AIBN solution (2,2-azo-bis-iso-butyronitrile). Purification of AIBN was performed before a series of experiments. To do this, it was recrystallized from anhydrous ethanol, then acetone, then benzene. A constant rate of initiation was achieved by the introduction of the same number of AIBN. The study was performed at a temperature of 70ºC (±0.1°C). Concentration [AIBN]= $2 \cdot 10^{-3}$ mol/l for all samples. AIBN was dissolved in o-xylene (non-oxidizing solvent). The graphical method [13] determined the value of the induction period (τi) as a segment of the abscissa axis cut off by the perpendicular from the point of intersection of the tangents with the kinetic.

In studies of the kinetics of sunflower oil oxidation, 200 ppm (0.2 g/kg of oil) butylhydroxyanisole or a concentrate obtained from extraction from plants was used.

The efficiency of inhibition of the process of sunflower oil oxidation was determined by a set of inhibitor reactions and was designated as antioxidant activity, quantitatively calculated by the formula

$$AOA = \tau_i / \tau_s,$$

where τ_i and τ_s are the periods of induction of sunflower oil oxidation with and without antioxidant, respectively.

The AOA of the studied antioxidants was compared with the AOA of the standard antioxidant, for which butylhydroxyanisole was taken in an amount of 200 ppm relative to the oil.

Deep frying. Refined deodorized sunflower oil (TM Oleina) with a volume of 2 L was placed in a fryer (Clatronic FR 3586, Germany Tefal FZ 7000 France) heated to 180±5°C. Oil at a temperature of 180±5°C [14] was kept in a deep fryer every day during the experiment for 2 hours. Also, every day, three batches of potatoes, 200 g each, were fried for 10 minutes.

The oil was stored at 5°C until the next frying cycle. Frying was carried out for 5 days.

Fresh potatoes were peeled, cut to a uniform thickness (0.5×0.5×8.0 mm) with a mechanical slicer, weighed 200 g and immediately used for frying.

AO extracts were added to sunflower oil for deep frying as follows. Used viburnum bark extract in the amount of 0.2 g/kg or 1 g/kg. Initially, the nanoemulsion concentrate was prepared by ultrasonic mixing: 500 cm3 of sunflower oil and AO extract in the amount of 0.8 g/kg or 4 g/kg were placed in an ultrasonic bath (Jeken PS-06A, Poland), operating parameters – 50 W, 40000 Hz. Similarly, to reduce the errors of the study was made butylhydroxyanisole in the amount of 0.2 g/kg. After stirring for 1080 s under sonication conditions, the obtained AO concentrate was diluted in 1500 cm3 of sunflower oil, mixed thoroughly and transferred to a deep fryer.

Acid value (AV), peroxide value (POV) and p-anisidine (p-AnV) values were determined according to official AOCS methods 3d-63, Cd 8-53 and Cd18-90, respectively.

Each experiment was performed twice, the article shows the average values between the two studies. The root mean square error of the determination did not exceed 5%.

Results of the research and their discussion

Obtained by various methods (DPPH • radical method, ABTS • etc.) AOA values of plant extracts do not always correspond to their effectiveness as antioxidants when introduced into fats [15]. The possible reason for this effect is the presence or absence of synergism between the AO of one plant. Therefore, we chose the method of determining the AOA of plant extracts by their direct introduction into fats, namely – sunflower oil.

At the initial stage of fat storage, oxygen is practically not absorbed and the oxidation of the product is very slow. This period, called the period of induction, ends with the beginning of the rapid accumulation in the product of hydroperoxides, which, depending on storage conditions, are converted at different rates into aldehydes, ketones, hydroxy acids and other secondary oxidation products. The taste and smell of the obtained volatile substances make the food product unpleasant, and its composition is unacceptable for use in food purposes. Thus, the period of time, which is defined as the period of induction, and is the period of storage of fat. It is most appropriate to determine the period of induction by accelerated means, ie at elevated temperature (we conducted research at 70ºC) and in the presence of a substance that accelerates oxidation (we used AIBN). According to the obtained kinetic curves of the amount of oxygen absorbed by the oil sample at a certain time (Fig. 2), it is possible to draw a conclusion about the significant effect on the stability of sunflower oil for oxidation of the introduced AO.

The induction period for sunflower oil oxidation without the addition of antioxidants was 1420 ± 40 s (Fig. 2), the introduction of dill AO extended the induction period to 2010 ± 50 s, and burdock roots AO to 3870 ± 70 s. Butylated hydroxyanisole (BHA) was used as a positive control. It was administered in the concentration allowed by the regulatory documents - 200 ppm. The same concentration was used to study the effectiveness of all other AOs. The period of sunflower oil oxidation in the presence of BHA was 2400±50 s.

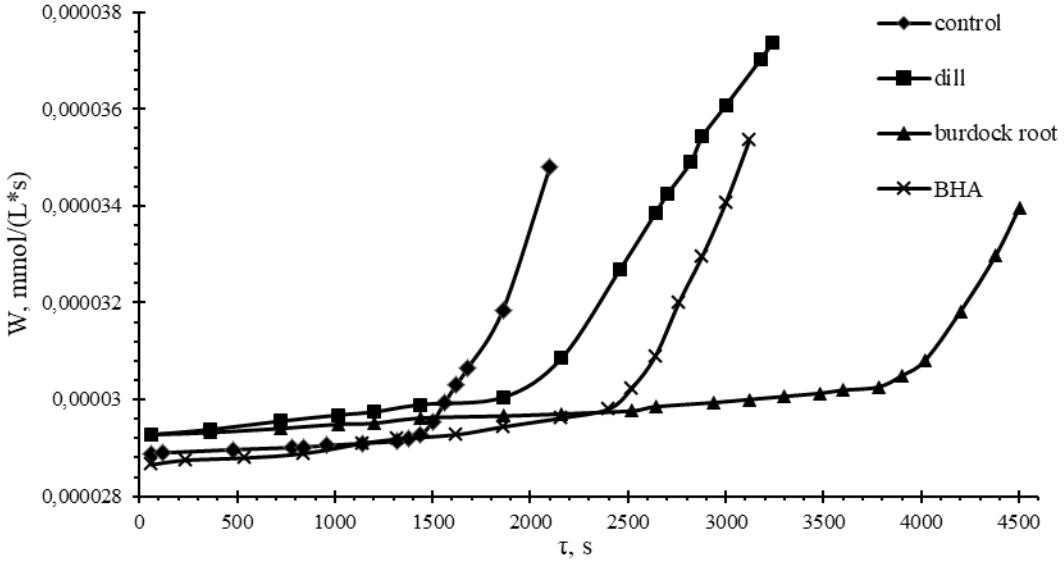

Fig. 2. Kinetics of accelerated oxidation of sunflower oil at 70 ºC in the presence of 2·10^{-3} mol/l AIBN

The results of studies to establish the duration of the period of induction of sunflower oil oxidation in the presence of AO from other plants, as well as the calculated values of the antioxidant activity of the obtained AO are presented in Table.

Table – Periods of induction of sunflower oil oxidation in the presence of AO

The name of the antioxidant	*The period of induction of oxidation of sunflower oil in the presence of plant extracts, s*	*Antioxidant activity (AOA)*
Peppermint leaves	2130 ± 60	1,50
Echinacea flowers	2400 ± 50	1,69
Calendula flowers	2760 ± 70	1,73
Burdock roots	3870 ± 70	2,72
Oak bark	2790 ± 50	1,96
Bark of European guelder	3600 ± 70	2,53
Raspberry leaves	2850 ± 60	2,01
Blackberry leaves	3360 ± 70	2,37
Dill	2010 ± 50	1,41
Parsley	2370 ± 40	1,67
Arugula	2340 ± 40	1,65
Rowan ordinary	2520 ± 50	1,77
Rowan chokeberry	2670 ± 40	1,88
Blueberry shoots	3120 ± 80	2,20
Nettle leaves	2520 ± 70	1,77
Medicinal chamomile	2100 ± 40	1,48
Rosemary leaves	2490 ± 40	1,75
Thyme herb	3000 ± 60	2,11
Japanese spirea leaves and flowers	3900 ± 80	2,75
Melissa herb	4140 ± 80	2,91
Butylhydroxyanisole	2400 ± 50	1,69

Butylhydroxyanisole (E 320, BHA) prolongs the period of induction of sunflower oil by 1.7 times. Such antioxidant activity will be established as sufficient to determine the prospects for the use of aqueous-alcoholic solution of a particular plant as an antioxidant. Above the BHA AOA showed melissa herb, spirea grass, burdock roots, viburnum bark, blackberry leaves, blueberry shoots, thyme herb, raspberry leaves, oak bark, calendula flowers, rowan chokeberry, nettle leaves, rowan ordinary, rosemary leaves, echinacea flowers

Mint leaf extract prolongs the period of sunflower oil induction by 1.5 times. This result is less than the AOA of butylhydroxyanisole by 13%. Peppermint is a known source of antioxidants. All parts of the plant, including wood, seeds, bark, stem, pod, leaf, fruit, root, contain a variety of AO. The leaves are characterized by high levels of ferulic acid, caffeic acid and catechin [7]. However, according to our research, mint extracts are not strong AOs.

Thyme is an aromatic plant that is a rich source of polyphenols with rosmarinic acid (51.7 mg/g dry extract), apigenin (7.6 mg/g dry extract) and luteolin (4.1 mg/g dry extract). Total antioxidant activity by DPPH (2,2-diphenyl-1-picrylhydrazyl) method from 40 to 73 mg TE/g Dry Extract [8]. The obtained value of thyme AOA is 2.11, which is 20% more than BHA.

Common phenols, common flavonoids and caffeic acid derivatives were found in burdock root. Phenolic acids (mainly chlorogenic, caffeic and p-coumaric acids) are contained in burdock root in significant quantities [16]. All this indicates the potential high antioxidant activity of aqueous-alcoholic extracts of the roots of this plant, especially given the high degree of extraction of flavonoids by ethyl alcohol. The obtained value of AOA = 2.72. Burdock roots are one of the strongest AOs studied (efficiency compared to BHA is 38% higher). Prolongation of the period of induction of sunflower oil by almost 3 times is an excellent result, which indicates the need for further studies of the antioxidant efficiency of burdock root.

Bark of European guelder according to a study [17] is characterized by a higher content of flavanols (especially catechins) than other parts of this plant, more acids that exhibit AO properties and flavonols contain flowers. Catechin and chlorogenic acid are the main phenols of this plant. AOA according to the ORAC method for bark was 108 mM TE / 100 g, while this value for fruit - 10.9, flowers - 61.8 mM TE / 100 g. According to our study, the AOA of bark of European guelder is 2.53 (efficiency in inhibiting oxidation compared to BHA is 33% higher), which confirms the high AO potential of this waste of berry production.

It is known that oak bark accumulates a large number of polyphenolic compounds, resulting in a wide range of biological effects, including antioxidant, antibacterial and anti-inflammatory activity [18]. Study [19] showed a higher extractivity of the aqueous-ethanol solvent compared to the aqueous one in terms of AO extraction from oak bark and a higher AOA of the obtained extracts compared to butylhydroxybutanol. In our study, we found a higher value of AOA of oak bark extract compared to VNA – by 14%. AOA of oak bark = 1.96, which corresponds to high efficiency in inhibiting fat oxidation.

Rowanberry is a popular ornamental plant in Europe containing many polyphenolic compounds, including quercetin, isoquercetin, hyperin, rutin, catechin, epicatechin, and chlorogenic acid [20]. The obtained value of AOA for rowan ordinary is 1.77 (4.8% higher than BHA), rowan chokeberry is 1.88 (10% higher than BHA). Thus, it is advisable to use mountain ash as an AO in the food industry.

Echinacea flowers contain the following phenolic AO: kaftaric acid, chlorogenic acid, caffeic acid, echinacoside (the main phenolic component of echinacea), ferulic acid, verbascoside, chicory acid, 3,4-di-o-caffeoylquinic acid, 3,5 -caffeoylquinic acid, etc. [21]. The total antioxidant activity by the method of absorption of free radicals DPPH ranged from 15 to 80 mg TE / g depending on the method of extraction of AO. According to our study, the AOA of echinacea was 1.69, which is equal to this value for BHA. Thus, echinacea, although not a strong AO, is a good substitute for synthetic AO.

Calendula flowers showed AOA of 1.73 (13% higher than BHA). Another study of the absorption of free radicals by DPPH showed that the ethanolic extract of C. suffruticosa is characterized by high antioxidant activity higher than butylhydroxytoluene [22]. The biologically active substances of calendula are represented by the following substances: carotenoids and lycopene, phenolic acids (protocatechuic, vanillin, syringic acids), hydroxycinnamic acids (p-coumaric, caffeic, chlorogenic acids), flavonoids and their glyceside, isocytin rutin), coumarins (scopoletin, umbelliferone, esculetin), also contains essential oil with terpenoids and terpenoid esters. The total content of flavonoids is from 455 ± 29 ÷ 1350 ± 86 mg of rutin.eq./100 g dw. The combination and concentration of these compounds makes calendula a promising source of effective AO.

Japanese spirea is an ornamental plant common in Ukraine, native to China and Japan. Despite the lack of literature on the content of polyphenols in it, it is one of the most effective AO of the studied plants. Spiraea AOA is 2.75 (38% higher than BHA efficiency). Thus, given the availability of spirea, its high antioxidant potential, there is a need for additional studies of the AO composition of spirea and its use as a food ingredient that can effectively inhibit oxidation.

Blackberries, raspberries, blueberries are of great economic importance. Their leaves are a by-product of berry growing and can be used as an alternative source of biologically active compounds.

Raspberry leaves are rich in tannins, flavonoids, quercetin, phenolic acids, triterpenes, mineral salts, and vitamin C, respectively, the antioxidant potential is high [1]. The established AOA of raspberry leaves is equal to 2.01 (16% higher than the value for BHA).

Blackberry leaves showed some of the best antioxidant properties of all studied plants (AOA = 2.37). According to other studies, the high content of phenolic compounds, mainly derivatives of quercetin, syringic and chlorogenic acids in blackberry leaves show the potential for specific phenolic compounds [23].

Thus, the leaves of blackberries and raspberries are characterized by high antioxidant potential. The use of raspberry and blackberry leaves to extract AO will not only expand the range of domestic biologically active substances, but also increase the profitability of production of these berries.

Rosemary leaves extended the period of induction of sunflower oil by 1.75 times, which is approximately equal to the results of BHA. Chamomile flowers were not very effective AO (efficiency 14% lower than BHA).

Blueberry shoots have not previously been studied for antioxidant efficacy. Blueberry leaves are characterized by a high content of phenols with a predominant presence of quercetin derivatives, chlorogenic acid and halocatechin [23]. The AOA of blueberry shoots is 2.2, which is 23% higher than the result of BHA. Incl. blueberry shoots – a promising material for natural AO.

Dill, parsley and arugula are edible herbs widely used in cooking. Some studies [24] indicate a high content of AO. These herbs in our study were slightly less effective than BHA. Dill is 19% less effective than BHA. Although AOAs of butylhydroxyanisole (1.69), extracts of parsley (1.67) and arugula (1.65) are almost the same and these herbs can be recommended for effective AOs and in general for culinary use to combat oxidative stress.

Melissa was the most effective AO of the studied. It inhibited the oxidation of sunflower oil 42% more effectively than BHA. AOA melissa = 2.91, which indicates the high AO potential of this plant and the prospects for its widespread use in various sectors of the food industry not only due to pleasant organoleptic characteristics, biological activity of its components, but also due to excellent AO properties.

The resulting plant extracts for their effectiveness in inhibiting the oxidation of sunflower oil should be arranged in a row: melissa herb > spirea herb > burdock root > bark of European guelder > blackberry leaves> blueberry shoots> thyme herb> raspberry leaves> oak bark > calendula flowers > rowan chokeberry> nettle leaves > rowan ordinary > rosemary leaves> echinacea flowers > parsley > arugula> mint pepper leaves> chamomile > dill.

Obtained AO from melissa herb, spirea, burdock roots, bark of European guelder can be considered a rich food source of powerful antioxidants.

As already mentioned, the use of vegetable oils as frying fats is one of the most traumatic ways for their oils to be used. The deep frying process is usually carried out in the range of 150–190°C, which leads to oxidation, hydrolysis and polymerization of fats. These dangerous processes can be monitored with indicators such as total polar compounds (TPC), peroxide and acid values [14]. Using these methods, it is necessary to establish the effect of the most effective of the obtained AO on maintaining the quality of sunflower oil during deep frying.

The obtained extracts belong to hydrophilic substances and do not dissolve in fats, that is, except for systems in which intensive mixing takes place, they are not able to perform their function of inhibiting oxidation. In recent decades, many methods of introducing water-soluble antioxidants into fats have been developed. In most cases, antioxidants from vegetable raw materials are extracted with an ethanol solvent, the solvent is evaporated under reduced pressure or it is crystallized by freezing and added to the oil [10]. The obtained extracts belong to hydrophilic substances and are insoluble in fats, ie, except for systems in which intensive mixing takes place, they are not able to perform their function of inhibiting oxidation. However, the introduction of hydrophobic substances into fats is possible under conditions of formation of nanoemulsions. Nanoemulsions today are attracting a lot of attention from scientists, especially as drug delivery systems. This type of use improves the stability, solubility, and bioavailability of bioactive compounds in the body, as well as protects them from adverse environmental conditions (pH, light, humidity, temperature, etc.) [25]. Using ultrasound, stable nanoemulsions of bark of European guelder extract and refined deodorized sunflower oil were obtained. The emulsions did not delaminate after 1 month of storage.

Sunflower oil was used for deep frying of potato chips. Parameters such as acid value (AV), peroxide value (POV) and p-anisidine value (p-AnV) were set during 8 days of frying. The results are shown in Fig. 3-5. The results were compared with sunflower oil, which was introduced using ultrasound 0.2 g/kg of extracted substances of bark of European guelder. As a positive control, sunflower oil with the allowed amount (0.2 g/kg) of BHA was used (see Fig. 3-5).

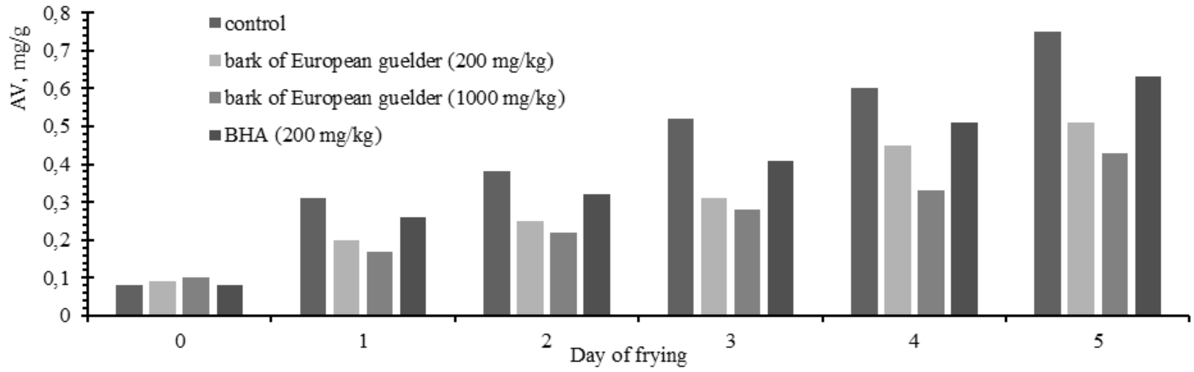

Fig. 3. Kinetics of acid value of sunflower oil without / with antioxidants in the process of deep frying

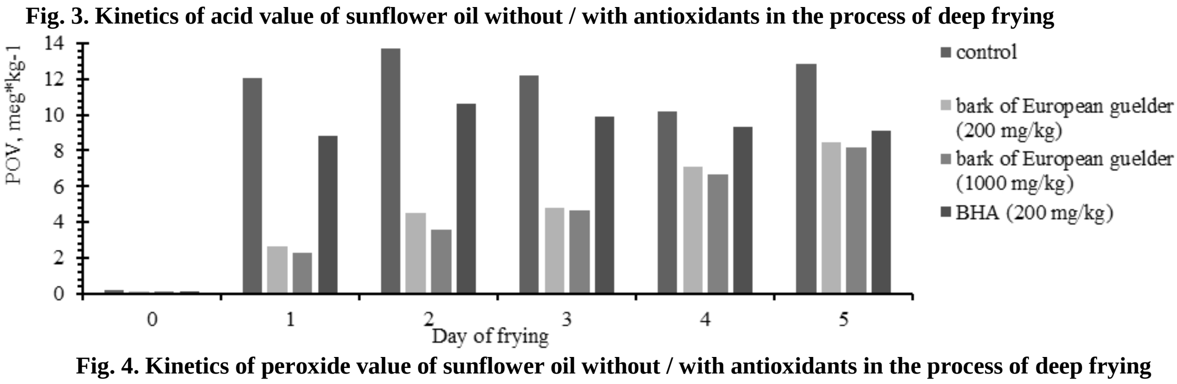

Fig. 4. Kinetics of peroxide value of sunflower oil without / with antioxidants in the process of deep frying

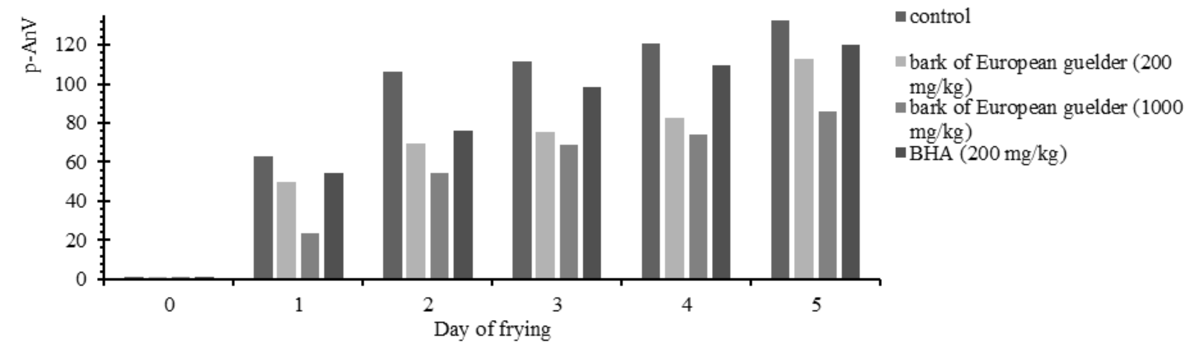

Fig. 5. Kinetics of anisidine value of sunflower oil without / with antioxidants during deep frying

The acid number of all oil samples increases with each new frying cycle. Bark of European guelder extract in amounts of 200 and 1000 ppm effectively protected sunflower oil from hydrolysis during all frying days. Its inhibitory effect was significantly higher than the effective ness of BHA. The lowest acid number at the end of frying was a sample of sunflower oil with 1000 ppm of bark of European guelder extract - 0.43 mg/kg, which is 43% less than in the control (sample without AO).

The results of research (Fig. 4) show that monitoring the qualitative changes in sunflower oil during frying by using peroxide numbers is incorrect – the value of this indicator changes quite chaotically. This pattern is observed due to the rapid destruction under the influence of high frying temperature (180°C) hydroperoxides with the formation of secondary oxidation products. It is more expedient to use data on the indicator of anisidine value (Fig. 5). However, it should be noted that during the first two or three days of frying, bark of European guelder successfully stabilized oils for the formation of hydroperoxides in contrast to BHA. Even after 5 days of frying, the oil enriched with antioxidants meets the requirements of regulatory documents on the value of the peroxide value.

The samples gradually accumulated carbonyl compounds during frying (Fig. 5). All antioxidants markedly inhibited the formation of non-volatile carbonyl compounds during deep frying (Fig. 5). The lowest value of anisidine value was characterized by a sample of sunflower oil with 1000 ppm of bark of European guelder extract – 85.6, which is 35.3% less than in the control (sample without AO). Presumably, BHA with a molecular weight of 180.24 g/mol evaporates faster during frying [5] compared to the AO complex of bark of European guelder. Thus, the molecular weight of catechin – the main flavonoid of bark of European guelder is 458.37 g/mol. Catechin also contains five active hydroxyl groups that are responsible for the antioxidant activity of this molecule. The number of hydroxyl groups of BHA is one. The phenomenon of synergism between different AOs of the complex AO of European guelder is also possible. All this may explain the greater efficiency of extracted from the bark of European guelder AO compared to synthetic BHA.

Conclusion

1. As a result of research to obtain comparative data on the antioxidant activity of water-alcohol extracts of plants of Ukrainian origin. The obtained plant extracts on their effectiveness in inhibiting the oxidation of sunflower oil should be arranged in a row: melissa herb> spirea herb> burdock root> bark of European guelder > blackberry leaves> blueberry shoots> thyme herb> raspberry leaves> calendula flowers> oak bark> rowan chokeberry> nettle leaves> rowan ordinary > rosemary leaves> echinacea flowers> parsley> arugula> mint pepper leaves> chamomile> dill. Melissa herb, spirea herb, burdock roots, bark of European guelder, blackberry leaves, blueberry shoots, thyme herb, raspberry leaves, oak bark, calendula flowers, rowan chokeberry, nettle leaves, rowan ordinary, rosemary leaves, echinacea flowers showed higher antioxidant activity than BHA. Of particular interest are the data obtained regarding the high antioxidant efficiency of spirea, burdock roots, bark of European guelder, blackberry leaves, blueberry shoots due to the small number of known studies. Antioxidant effect of spirea extracts and blueberry shoots studied for the first time. The following are among the most promising sources of antioxidants from the studied plants: melissa grass, spirea grass, burdock roots, viburnum bark, blackberry leaves, blueberry shoots, thyme grass, raspberry leaves, marigold flowers. The antioxidant activity of the burdock root extract was 2.72 (it prolongs the induction period of sunflower oil by 2.72 times, which is 38% higher than the result when using BHA). The antioxidant activity of bark of European guelder is 2.53 (the effectiveness of inhibiting the oxidation of sunflower oil is 33% higher compared to BHA). Japanese spirea is an ornamental plant widespread in Ukraine. Despite the lack of literature data on the content of antioxidants in it, its water-alcohol extract turned out to be one of the most powerful antioxidants from the studied plants. The antioxidant activity of spirea is 2.75 (38% higher than the effectiveness of BHA). Blueberry shoots have also not been previously studied as antioxidants. The

antioxidant activity of blueberry shoots is equal to 2.2, which is 23% higher than the result of BHA. Melissa turned out to be the most effective antioxidant among those tested. It inhibited the oxidation of sunflower oil by 42% more effectively than BHA. The antioxidant activity of lemon balm is 2.91, which indicates the high antioxidant potential of this plant and the prospect of its wide application in various branches of the food industry, not only due to its pleasant organoleptic characteristics, biological activity of its components, but also due to its excellent antioxidant properties.

2. All frying fats, especially unsaturated ones, such as sunflower oil, which is widely used in deep-frying in the restaurant segment, need protection against oxidative damage. From the results of the study we can conclude that the natural antioxidant (bark of European guelder) was more effective than the synthetic antioxidant BHA in inhibiting oxidative and hydrolytic processes during the frying of sunflower oil. During 5 days of frying, the bark of European guelder extract protected sunflower oil from hydrolytic processes more effectively than BHA (the lowest values of the acid number after each day of heat treatment). Also, bark of European guelder extract best inhibited the formation of non-volatile carbonyl compounds (the lowest anisidine number values after each day of heat treatment). It is incorrect to use the value of peroxide numbers to characterize the state of the oil during heat treatment due to the instability of hydroperoxides at high temperatures.

3. According to our research, the bark, roots and leaves of plants are characterized by the maximum values of antioxidant activity. These data make it possible to recommend the use of these plant wastes for the production of antioxidants that can inhibit the oxidation of fats. The most promising raw materials for the production of antioxidants include the following parts of plants: lemon balm herb, spirea herb, burdock roots, bark of European guelder, blackberry leaves, blueberry shoots, thyme herb, raspberry leaves, oak bark, marigold flowers, mountain ash, nettle leaves, mountain ash, rosemary leaves, echinacea flowers. These plants more effectively inhibited the oxidation of sunflower oil compared to a synthetic antioxidant.

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АНТИОКСИДАНТНА АКТИВНІСТЬ ЕКСТРАКТІВ З РОСЛИН УКРАЇНСЬКОГО ПОХОДЖЕННЯ ТА ЇХ ВПЛИВ НА ОКИСНУ СТІЙКІСТЬ СОНЯШНИКОВОЇ ОЛІЇ

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Анотація. Сьогодні все більше виробників харчової продукції відмовляються від використання синтетичних антиоксидантів через негативний вплив, який вони оказують на організм людини. Основні природні гідрофобні антиоксиданти – токофероли і каротиноїди, є недешевими товарними продуктами і зараз їх виробляють значно менше за потреби жирової індустрії. Тому існує потреба в одержанні інших натуральних антиоксидантів з рослинної сировини. Серед потенційних джерел такої сировини розглядались листя та коріння трав, кора та листя ягідних культур. Було досліджено 20 рослин. Метою дослідження було отримання порівняльних даних щодо антиоксидантної активності водно-спиртових екстрактів рослин українського походження, а також дослідження їх впливу на стабільність соняшникової олії під час її термічного оброблення. Визначали періоди індукції соняшникової олії в присутності антиоксидантів, за одержаними даними визначали антиоксиданту активність екстрактів рослин і порівнювали з антиоксидантною активністю синтетичного бутилгідроксианізолу, антиоксиданти використовували у рівних концентраціях (200 ppm). Отримані рослинні екстракти за їх антиоксидантною активністю розташовуються в ряд (за зниженням активності): трава меліси > трава спіреї > корінь лопуха > кора калини > листя ожини > пагони чорниці > трава чебрецю > листя малини > квіти календули > кора дубу > горобина чорноплідна> листя кропиви> горобина звичайна > листя розмарину > квіти ехінацеї > петрушка > рукола > листя м'яти перцевої > ромашка > кріп. Захисту щодо окиснювального псування потребують всі фритюрні жири, а особливо – ненасиченого типу, такі як соняшникова олія, яка на сьогоднішній день широко застосовується під час смаження у фритюрі в ресторанному сегменті. З результатів дослідження можна зробити висновок, що природний антиоксидант (водно-спиртовий екстракт кори калини) виявився більш ефективним за синтетичний антиоксидант бутилгідроксианізол щодо гальмування окисних і гідролітичних процесів в ході термічної обробки соняшникової олії. Впродовж 5 днів термічної обробки зразок соняшникової олії з екстрактом кори калини характеризувався найменшими значеннями кислотних, пероксидних та анізидинових чисел.

Ключові слова: антиоксидант, антиоксидантна активність, фритюрне смаження, соняшникова олія.