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THE EFFECT OF BIOACTIVE COMPOUNDS FROM LOCAL BERRIES ON OXIDATIVE STABILITY OF VEGETABLE OILS

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Abstract. The oxidation of lipids in food is a complex process that is influenced by various factors such as: the chemical structure of the food; physical condition; the quantity and quality of substances with an antioxidant capacity in food matrix. Within this research was studied sea buckthorn, hawthorn and rosehips, which represent a natural concentrate of vitamins, carotenoids, folic acid etc. Were performed the evaluation of the antioxidant capacity of the enriched lipophilic extracts and the analysis of the impact of the bioactive compounds on the oxidative stability during storage. Local berries extracts are characterized by a rich complex of bioactive compounds, the use of which in obtaining functional food products will slow down oxidative processes and ensure food products with a longer shelf life.
Keywords: berries, bioactive compounds**,** oxidative stability, oils, fruit powder.

Lipid oxidation is one of the major causes of quality deterioration in natural and processed foods. Oxidative damage is a major economic concern in the food industry because it affects many quality characteristics such as flavor, color, texture, and nutritional value of foods, potentially toxic compounds.

Oxidative stability is the resistance of vegetable oils and fats to oxidation during processing and storage [4]. Oxidative resistance can be expressed as the period of time required to reach the critical oxidation point, regardless of whether it is a sensory change or a sudden acceleration of the oxidative process [16]. Oxidative stability is an important parameter to determine oil quality and shelf life [1] because low molecular weight compounds (LPP) are produced during oxidation.

Oxidation by-products make the oil less acceptable or unacceptable for consumers or for industrial use as a food ingredient. Oil oxidation also destroys essential fatty acids and produces toxic compounds and oxidized polymers. Oil oxidation is very important in terms of taste, nutritional quality and toxicity of edible oils.

High quality foods are obtained through complex processes, that both negatively and positively influence the finished product, which would lead to changes in their quality. The major cause of food spoilage is oxidation. The oxidation of lipids in food is a complex process that is influenced by various factors such as: the chemical structure of the food; physical condition; the quantity and quality of substances with an antioxidant role in food; how the food is processed, packaged and stored. One of the current strategies used in the food industry to inhibit the oxidation of lipids is the use of antioxidants. Berries are rich in antioxidants, vitamins and minerals. In order to analyze the bioactive profile of local berries powder were obtained lipophilic extracts according to Popovici V. et. al. [11]. The content of chlorophyll α and β, β-carotene, lycopene and zeaxanthin in the lipophilic extracts of rosehip (RLE), sea buckthorn (SBLE), hawthorn (HLE) was determined spectrophotometrically. The results obtained show that the lipophilic extracts are characterized by a rich carotenoid content. RLE contains an essential amount of β-carotene (17.04 mg/L), while RLE contains 1.6 times less and SBLE 2.6 times less. After 3 months storage, the β-carotene content decreased for RLE by 15%, SBLE by 5% and HLE by 30%. It can be observed that the amount of carotenoids changed non-essential due to storage conditions. Quantitative changes in carotenoids can occur due to oxidative

processes that occur along the way, but are slowed down if the extracts are stored in airtight containers to exclude access to oxygen, at low temperatures and in dark spaces.

In order to estimate the antioxidant potential of the lipophilic extracts from the studied plant sources, the analysis of the antioxidant activity was carried out with the help of the DPPH free radical, and the results obtained are presented in Figure 1.

Some studies have shown that the antioxidant activity of horticultural extracts is correlated with total phenolic substances rather than with the individual phenolic compound [18]. It is important to mention that different phenols develop different activities, depending on their chemical structure and the free radical scavenging capacity of these classes of compounds differ.

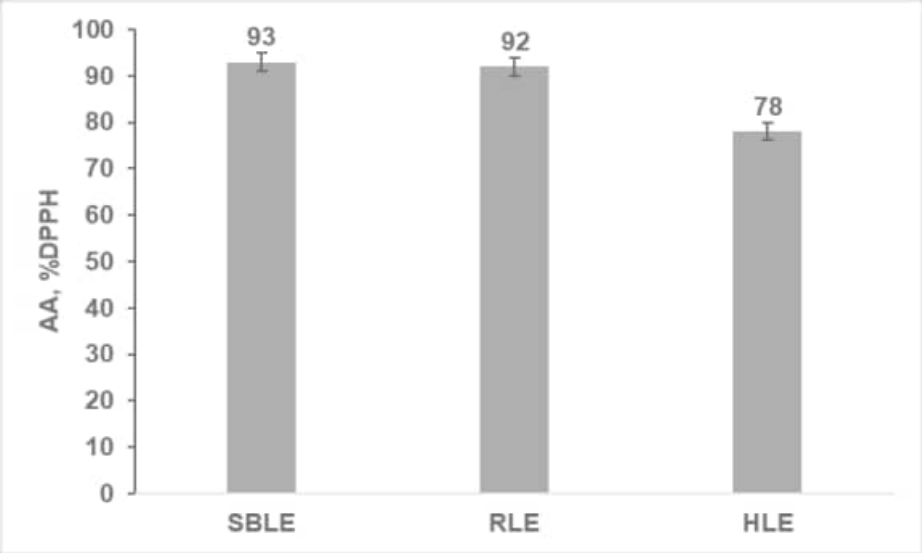

Figure 1. Antioxidant activity of lipophilic extracts

Following the results in Figure 1, it was established that the lipophilic extracts from rose hips, sea buckthorn and hawthorn powders are characterized by high antioxidant capacity, namely that the DPPH free radical inhibition capacity value varies from 72.05±1.90% to at 90.84±1.90%. This fact is explained by the rich content of biologically active compounds with an antioxidant character in the analyzed extracts and directly in the plant powders from indigenous berry fruits [12,14]. The use of local berries powder in obtaining functional food products will slow down oxidative processes and ensure food products with a longer shelf life.

Oxidative processes can be evaluated based on lipid quality parameters, which characterize the quality of oils and fats. For this reason, it is important to study the evolution of the physico-chemical and quality parameters of oil with lipophilic extracts during storage for 3 months. For this reason, some quality parameters were analyzed including: acidity value, peroxide value, conjugated dienes and trienes content. The stability of vegetable oil with lipophilic extract enriched with berry powder added in the amount of 10% was studied.

The acidity value (AV) for CS is within the permissible limits (0.6 mg KOH/g) for vegetable oil. In the case of oil with RLE (0.17±0.01 mg KOH/g) and SBLE (0.21±0.01 mg KOH/g), the acidity value exceeds the CS value, and for oil with HLE (0.13 ±0.01 mg KOH/g) a non-essential decrease is attested. This variation is due to the accumulation of free fatty acids in the pulp of sea buckthorn, hawthorn and rose hips. After a period of 3 months of storage, an increase in AV values is attested for all investigated samples of oil and lipophilic extracts, but which do not exceed the maximum value of 0.6 mg KOH/g oil, provided according to the technical regulations in force for vegetable oil of sunflower [8–10].

The first oxidation products of lipids are peroxides, which later split into secondary oxidation products: aldehydes, ketones, oxidized organic acids and hydrocarbons. Also, peroxides generate the appearance of free radicals (extremely offensive particles that endanger the health of the consumer). It is well known that free radicals cause autoxidation of unsaturated lipids in oils. Antioxidant

molecules prevent or inhibit these harmful reactions [17]. Since peroxides are the first substances formed during the degradation of lipids, determining their quantity is the method used to determine the degree of oxidation of fatty matter [5].

The peroxide value (PV) for CS is within the permissible limits (max. 10 m_{echiv} O_2/kg). In oils enriched with extracts, the PV is considerably lower – in the case of RLE - by 0.5 m_{echiv} O_2/kg, and in the case of SBLE and HLE – by approximately 1.0 m_{echiv} O_2/kg in relation to the peroxide value for CS.

It was established that when obtaining lipophilic extracts from horticultural sources, they are characterized by a lower PV value compared to the PV of vegetable oil CS, which indicates that the biologically active compounds from horticultural sources considerably slow down the formation of peroxides, respectively it takes place slowing down the oxidation process of the researched product. The oil with SBLE shows the lowest value of PV (3.66±0.13 m_{echiv} O_2/kg), the oils with HLE and RLE also show a low value compared to the control sample, which proves that it shows a slowing down activity of oxidation [13].

After a storage period of 3 months, it is observed that the PV values for the oils with HLE, SBLE and RLE are lower compared to CS. For oils with lipophilic extracts, PV increased for RLE by 40%; for SBLE with 35%; for HLE by 46% and for CS by 49%.

The use of vegetable powders with an antioxidant potential when obtaining lipophilic extracts will show antioxidant activity (AA). Thus, AA was determined under the conditions of gastric and intestinal digestion *in vitro*. Gastric and intestinal digestion was simulated *in vitro* for 2h. During the simulation, aliquots of 2h of digestion were extracted, which were later subjected to research and AA determination through the reaction with the DPPH free radical, and the obtained results are shown in Figures 2 and 3.

The evaluation of the antioxidant activity following induced gastric digestion (acidic environment) attests an essential increase for the oils with lipophilic extracts of sea buckthorn, hawthorn and rose hips compared to CS whose values constitute 17.58%. For oils enriched with lipophilic extracts, the values are: for SBLE – 46.43%; for RLE - 37.08% for HLE - 39.29%.

The high values of antioxidant activity for oils with lipophilic extracts compared to CS after 2 hours of digestion are explained by the gradual release of bioactive compounds in the process of gastric digestion. Another important factor would be the influence of the pH in the solution and the enzymatic interactions in the researched product. Following the research [2], it was established that changes in the content of bioactive compounds with an antioxidant capacity, including polyphenols, flavonoids, can increase the antioxidant capacity of the analyzed samples. This fact explains the essential variation of the activity of the samples enriched with lipophilic extracts with fruit powder compared to the vegetable oil (CS) sample. This phenomenon is explained by the presence in the researched extracts of other substances that increase the antioxidant capacity of the product following the *in vitro* digestion process of the studied product. These bioactive compounds such as amino acids, peptides are released during digestion or have undergone changes that can subsequently affect the ability to capture free radicals. Another hypothesis could be the loss of volatile substances during gastric digestion due to the increased antioxidant capacity in the product.

The study shows that gastric digestion does not essentially change the qualitative and quantitative composition of the bioactive compounds with an antioxidant capacity in the analyzed product. This fact suggests that these compounds show high stability in low pH conditions (pH=2.0±0.1). The acidic environment together with digestive enzymes favors the release of bioactive compounds, respectively what influences the increasing antioxidant capacity of the products with the addition of plant powders of sea buckthorn, hawthorn and rose hips [8].

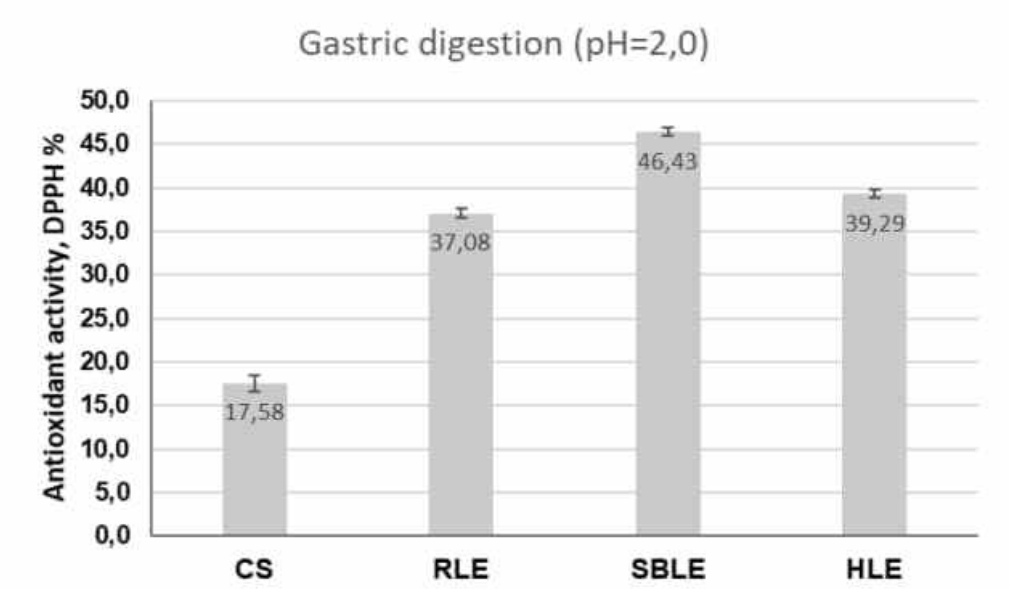

Figure 2. Antioxidant activity *in vitro* (gastric digestion): CS – control sample; SBLE – sea buckthorn lipophilic extract; RLE – rosehip lipophilic extract; HLE – hawthorn lipophilic extract

In continuation of the gastrointestinal digestion process, the simulation of the induced intestinal digestion phase was carried out by incubating the samples in an alkaline medium (pH=8.2±0.1) and determining the antioxidant activity after 2 hours of digestion.

The obtained data (Figure 3) show us that the antioxidant activity of the oil with lipophilic extracts of sea buckthorn, hawthorn and rose hips is higher compared to CS. The AA of CS sunflower oil is 4.26%, while for oils enriched with lipophilic extracts, the AA values are: for SHLE – 8.09%; for RLE – 7.06 % for HLE 4.56 %. Following intestinal digestion, a gradual decrease in antioxidant activity is observed within 2 hours both for the samples with the addition of lipophilic extract and for CS. This fact can be explained by the low stability of the biologically active compounds in the conditions of the alkaline environment (pH=8.2±0.1) and the formation of metabolites that inhibit the antioxidant activity of the biologically active compounds in the studied products.

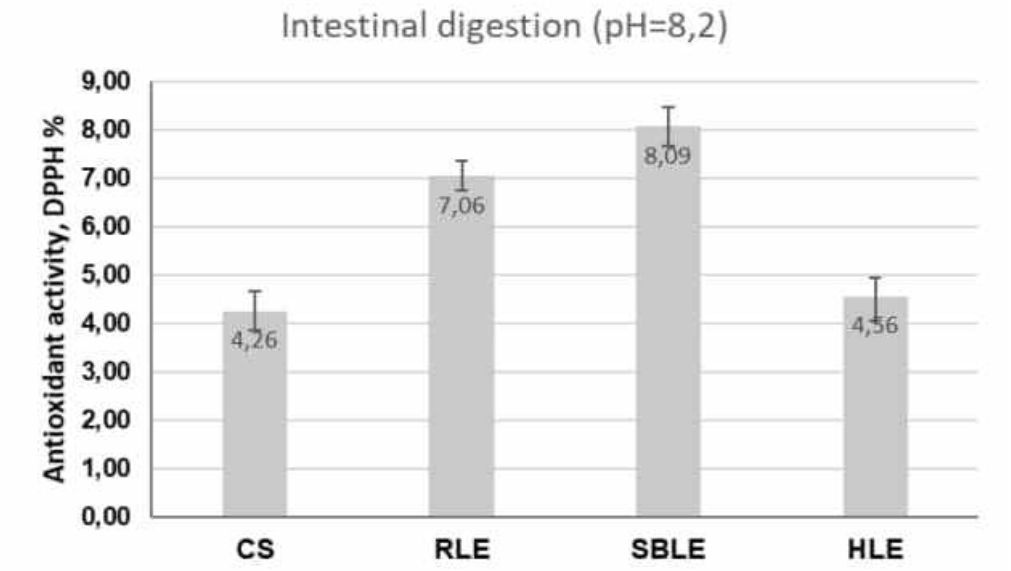

Figure 3. Antioxidant activity *in vitro* (intestinal digestion): CS – control sample; SBLE – sea buckthorn lipophilic extract; RLE – rosehip lipophilic extract; HLE – hawthorn lipophilic extract

The berries of sea buckthorn, hawthorn and rose hips are characterized by a rich complex of biologically active compounds, the use of which in obtaining lipophilic extracts or food products with increased lipid content will allow slowing down oxidative processes and respectively ensuring food products with an extended shelf life. The results of the analysis of the physico-chemical quality parameters of the lipophilic extracts of sea buckthorn, hawthorn and rose hips in relation to the control sample of vegetable oil show that the oxidation process is slowed down considerably, both initially and during the storage of them. The obtained results show that the lipophilic extracts of hawthorn and rose hips contain red, yellow and orange pigments, especially *β*-carotene, lycopene and zeaxanthin [3, 6, 15].

Conclusions

This study carried out the analysis of the oxidative stability of edible oils and the impact of plant sources with antioxidant potential on slowing down the oxidative processes of food products allowed the following conclusions to be drawn:

- ✓ The manufacture of safe, harmless food products rich in nutrients and mineral substances is one of the main concerns of companies in the field and studies.
- ✓ The use of local raw materials represents a particular advantage to considerably reduce production prices, so that the market price of the finished product is also affordable.
- ✓ The oxidation process is one of the most widespread causes of deterioration of food products, especially those with increased lipid content. The process can be slowed down with the help of bioactive compounds with an antioxidant character, which are found in abundance in local fruits and berries.
- ✓ The possibility of developing the technology to obtain lipophilic extracts from vegetable powders with antioxidant capacity represents a good possibility to replace synthetic additives with natural ones in order to obtain safe complex food products with an increased shelf life.

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