INCORPORATION OF SWEET PEPPER EXTRACTS TO IMPROVE THERMAL STABILITY OF VEGETABLE OIL MIXTURES

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Abstract: *Sweet pepper is known not only for taste, aroma and flavor, but also for antioxidant effects and properties. Sweet pepper contains phenolic substances such as phenolic acids, flavonoids, phenolic diterpenes and volatile oils. Phenolic compounds in these vegetable materials are closely associated with their antioxidant activity and also play an important role in stabilizing lipid peroxidation. Efficacy of sweet pepper extracts in stabilizing sunflower and grape seeds oils in thermal oxidation conditions has been studied. Extracts were prepared in water/ethanol and oil solutions, total polyphenol content (TPC) was in the range of 25.3-59.4 mg/ml for extracts on the basis of oil and in the range of 50.01-267.2 mg/ml for extracts on the basis of EtOH/H_2O and antioxidant activity range in the extracts was 20-74,29%. Being highest in TPC and antioxidant potential of sweet pepper extracts were added to vegetable oil mixtures. Obtained samples of oils with extracts were heated at 160^{0}C. The oxidation of the oil samples was evaluated by means of free fatty acids content, peroxide and p-anisidine value. The results of UV/Vis spectroscopy confirm stabilization effect on thermal oxidation of the tested oils. This study demonstrates that natural vegetable extract such as sweet peppers can effectively inhibit the lipid oxidation of sunflower and grape seeds oil mixture in thermal oxidation conditions.*

Keywords: *total polyphenol content, scavenging activity DPPH•, antioxidants, natural vegetable extracts , green and red sweet pepper, sunflower oil, grape seed oil, free fatty acid content, peroxide value, p-anisidine value, thermal stability.*

1. Introduction

The current development trend of the food industry is to obtain natural antioxidants, extracted from the raw materials of vegetable origin [1]. Later received natural antioxidants are used to purpose of obtaining a new food products resistant to oxidation processing's during the storage. This new and promising direction in catering is specifically created to improve nutrition and health structure and to prevent disease spread in society [2].

Vegetable oils and fats are recognized as important components of our diet. They provide essential fatty acids such as α-Linolenic acid (ω−3 fatty acid) and Linoleic acid (ω−6 fatty acid), fat-soluble vitamins: vitamin A (Retinol), vitamin E (Tocopherols), vitamin K (2-methyl-1,4-naphthoquinone derivatives) and vitamin D (Secosteroids) and other biologically active compounds [3, 4].

During storage and frying of oils, fats and fatty foods, lipid oxidation is one of the main causes of quality deterioration. It leads to losses of nutritional value of food as well as to changes in color, texture, sensory and other physiological properties [5, 6].

In order to retard or prevent the oxidative deterioration and extend the self-life of vegetable oils, the addition of antioxidants is necessary [7, 8]. In spite of high effectiveness of synthetic antioxidants such as tert-butylhydroquinon (TBHQ), their

application is restricted in several countries because of their possible toxicity and carcinogenic effects [9-12].

Due to these safety concerns, there is an increasing trend among food scientists to replace these synthetic antioxidants with natural ones, which in general, are supposed to be safer.

It is known that sweet pepper is characterized by biological and nutritional value due to its contents of antioxidants, including ascorbic acid, tocopherol, β-carotene, flavonoids, and phenolic acids. The highest antioxidant activity is shown by flavonoids, because their molecules contain many hydroxyl groups, which are held by neutralizing free radicals by hydrogen separation [13, 14].

The purpose of the present work was to investigate the optimum conditions of drying for sweet peppers, for which the maximum safety of polyphenols is held, and according to high scavenging activity. Further on the work studied the possibility of extracts obtained from dried pepper samples and their introduction into vegetable oil in order to give thermal oxidation stability.

2. Materials and methods

2.1. Materials

The refined and deodorized sunflower and refined grape seed oils free from antioxidant additions were purchased from a local producer in the Republic of Moldova.

The sweet peppers of red and green color were harvested in late June 2010 in the central part of Moldova. The fresh and healthy vegetables were washed, cleaned, sliced, crushed to powder, dried and used in analyses.

2.2. Chemicals

1,1-Diphenyl-2-picrylhydrazyl (DPPH$^{\bullet}$) as free radical form (90% purity), Folin-Ciocalteu's phenolic reagent, sodium carbonate and gallic acid were supplied by Sigma-Aldrich. Methanol (99,8%), ethanol (99,9%), chloroform, para-anithidine, izo-octane, potassium hydroxide and phenolphthalein were provided by Eco-Chemistry (Kishinev, Republic of Moldova). All reagents were of analytical grade. Distilled water was used throughout.

2.3. Drying

Super-high frequency and convection drying were used for vegetable drying. The SHF drying was performed at 30% and 50% of magnetic intensive. The convection drying was made at 60^0C and 80^0C.

2.4. Extraction

Dried sweet peppers were ground before extraction. The dried powder of vegetables was extracted with 70% EtOH/H2O and sunflower oil for 2 h at 60^0C and liquid-to-solid ratio 10 ml per gram. The extracts of tasted vegetables were filtered with peppers filter and then they were used in the experiments. The extracts obtained were analyzed for the scavenging activity DPPH$^{\bullet}$ [15] and total polyphenol content [16] assays. Absorbance measurements were recorded on a UV/Vis spectrophotometer HACH-LANGE DR-5000 (Germany).

2.5. Sample preparation

We prepared the following oil samples: sunflower oil, grape seed oil, mixture of sunflower and grape seed oils, mixture of sunflower and grape seed oils with red and green peppers extract on the basis of oil / EtOH/H2O. The content of vegetable extract was 1ml Extract/100 ml Oil in each oil sample. The sweet peppers extracts were added directly to oils, followed by slow stirring until complete dissolution. The oil samples obtained were further exposed to the thermal oxidation test.

2.6. Thermal oxidation test

The test for oxidation processes was performed on the oven SPT – 200 Vacuum drier (Germany). The oil samples were transferred in beakers, containing 30 ml of

sample. The temperature was set at 160 ^{0}C. Heating was carried out continuously for 25 min. The amount of primary oxidation products was determined through measuring of peroxide value (PV) and acid value (AV). These were determined according to AOAC Official Method [17]. Formation of secondary oxidation products was measured as p-anisidine value [18]. The oil samples exposed to the oxidation test were analyzed using UV/Vis spectroscopy [19].

2.7. Statistical analysis

Experimental results were means ± SD (standard deviation) of three parallel measurements and processed statistically by the method of those small squares with application of coefficient Student and determination of interval of investigation [20].

3. Results and discussion

3.1. Total polyphenol content and antioxidant activity DPPH of sweet peppers extracts

The antioxidant activity expressed as the DPPH values of sweet peppers extracts tested as well as the amount of total polyphenol content of these extracts are investigated and the results obtained are shown in figure 1-4.

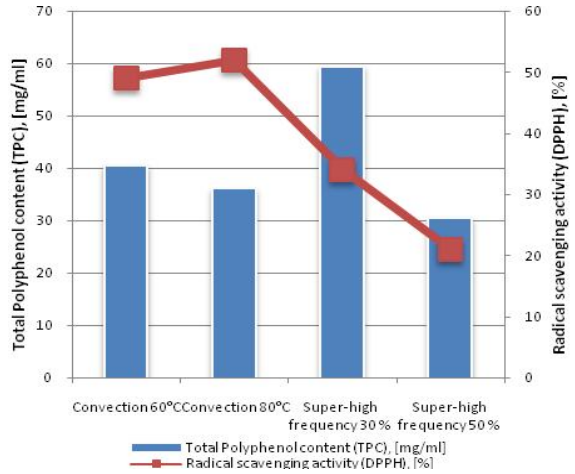

Fig.1. Comparison of DPPH and Folin-Ciocalteu assays of red sweet peppers extract on the basis of oil

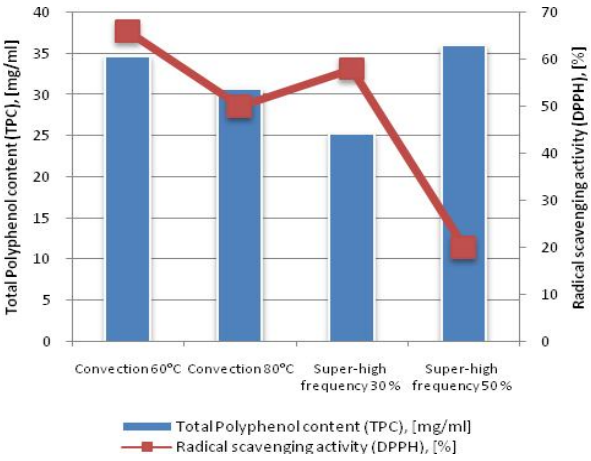

Fig. 2. Comparison of DPPH and Folin-Ciocalteu assays of green sweet peppers extract on the basis of oil

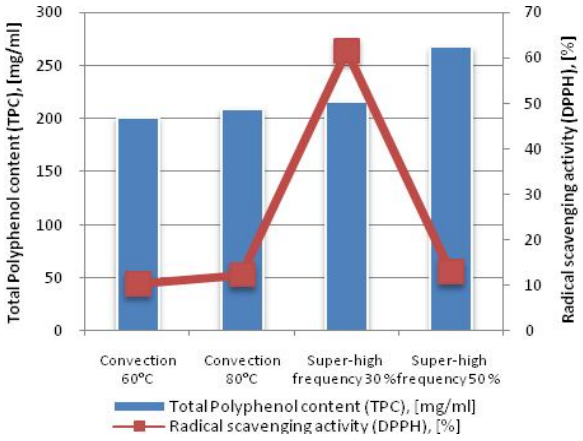

Fig. 3. Comparison of DPPH and Folin-Ciocalteu assays of red sweet peppers extract on the basis of EtOH/H2O

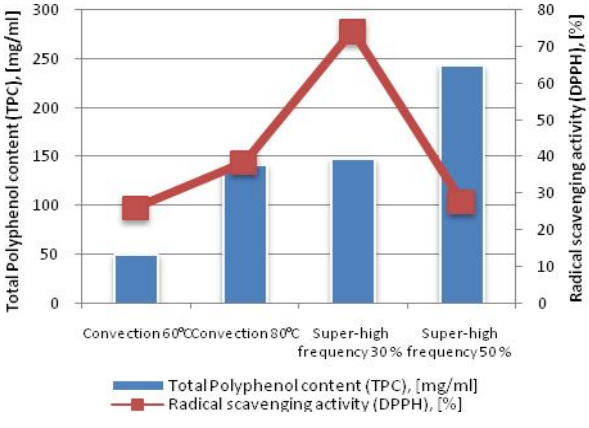

Fig. 4. Comparison of DPPH and Folin-Ciocalteu assays of green sweet peppers extract on the basis of EtOH/H2O

The total polyphenol content in sweet peppers extracts was in the range of 25.3-59.4 mg/ml for oil –based extracts and in the range of 50.01-267.2 mg/ml for EtOH/H2O- based extracts. The highest content of total polyphenols was in accordance with the results of antioxidant function determination found in extracts of sweet peppers pre-dried by SHF with magnetic intensive 50%. The lowest total polyphenol content was recorded in sweet peppers extracts dried by convection at 60 ^{0}C and 80 ^{0}C corresponding to their low antioxidant function.

Using the DPPH assay we obtained a hierarchy of antioxidant activity ranging from 74, 29% to 20%. Interestingly, the highest antioxidant function was found in the extracts of vegetable samples dried by convection at the temperature of 80 ^{0}C and by super-high frequency (SHF) drying with magnetic intensive 30%.

After analyzing all the aspects and factors, particularly those responsible for maximum preservation of scavenging activity of polyphenol in vegetable matter, in further research we used the SHF mode of drying of sweet peppers with magnetic intensive 30%.

Figures 5-8 show UV/Vis spectra of experimental extracts of sweet peppers. It was established, that spectra of extracts is characterized by peaks at 325 nm, which is specific to polyphenol compounds.

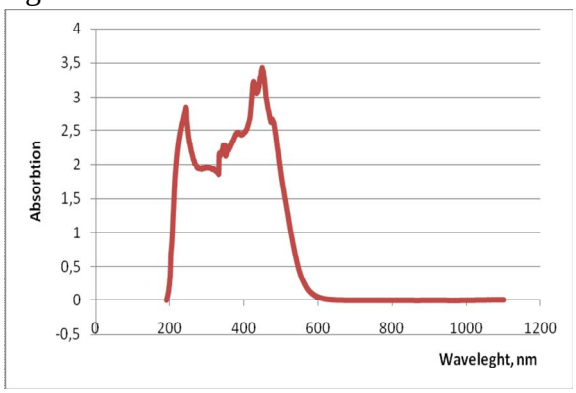

Fig. 5. UV/Vis spectra of red sweet peppers extract on the basis of EtOH/H2O

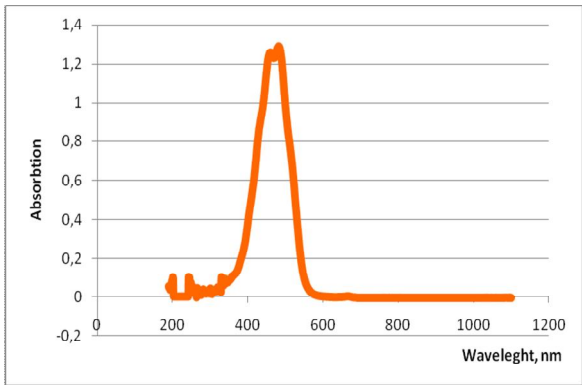

Fig. 6. UV/Vis spectra of red sweet peppers extract on the basis of oil

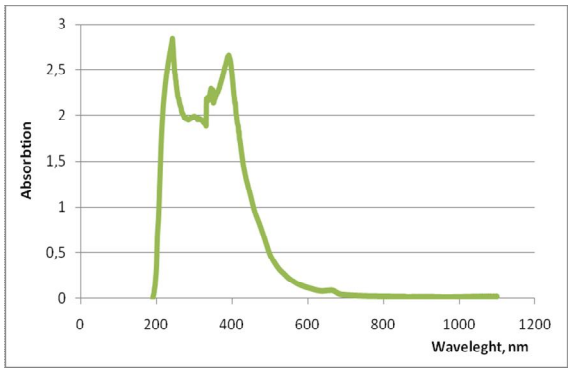

Fig. 7. UV/Vis spectra of green sweet peppers extract on the basis of EtOH/H2O

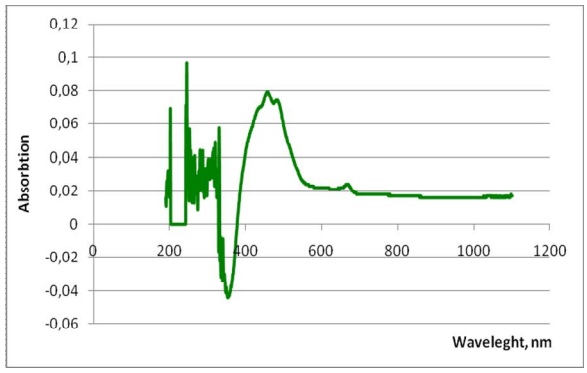

Fig. 8. UV/Vis spectra of green sweet peppers extract on the basis of oil

3.2. Oxidative stability of sunflower and grape seed oils with addition of extracts

Oxidative and hydrolytic decomposition is observed in the heating process of 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 (table 1). When comparing the acid values of the oil group with added sweet peppers extracts, one can notice that free fatty acids are accumulated to a lesser extent in a sample containing oil-based red sweet peppers extract as an antioxidizing component and that the acid values are 0,546 mg KOH/g oil.

Table 1.
Quality indices of sunflower and grape seed oils with/without addition of extracts

No	Name of oil samples	Quality indices of oils tested					
		Acid Value [mg KOH/g oil]		Peroxide Value [mEq/kg oil]		p-Anisidine Value [c.u.]	
		20 ± 2^0C	160 ± 2^0C	20 ± 2^0C	160 ± 2^0C	20 ± 2^0C	160 ± 2^0C
1.	Refined and deodorized sunflower oil	**0.183±0.002**	**0.756±0.003**	**8.22±0.1**	**20.43±0.3**	**0.5294±0.0005**	**1.2274±0.0007**
2.	Refined grape seed oil	**0.211±0.001**	**0.873±0.005**	**8.40±0.2**	**20.87±0.1**	**0.6441±0.0003**	**1.4814±0.0003**
3.	Mixture of sunflower and grape seed oils	**0.192±0.001**	**0.774±0.002**	**8.27±0.1**	**20.57±0.3**	**0.5764±0.0005**	**1.3207±0.0003**
4.	Mixture of sunflower and grape seed oils with addition of EtOH/H2O-based red sweet peppers extract	**0.178±0.002**	**0.722±0.003**	**8.02±0.1**	**19.76±0.7**	**0.4767±0.0005**	**1.3324±0.0003**
5.	Mixture of sunflower and grape seed oils with addition of oil-based red sweet peppers extract	**0.159±0.005**	**0.546±0.002**	**7.82±0.3**	**19.75±0.9**	**0.4024±0.0003**	**1.3125±0.0009**
6.	Mixture of sunflower and grape seed oils with addition of EtOH/H2O-based green sweet peppers extract	**0.177±0.001**	**0.917±0.005**	**7.92±0.2**	**19.95±0.5**	**0.4951±0.0005**	**1.3107±0.0008**
7.	Mixture of sunflower and grape seed oils with addition of oil-based green sweet peppers extract	**0.159±0.007**	**0.740±0.002**	**7.82±0.4**	**19.78±0.3**	**0.4327±0.0007**	**1.2796±0.0007**

Table 1 illustrates the intensity of the formation processes of the primary oxidation products (peroxides) in the oils tested depending on heating temperature. Peroxide compounds are known to be unstable. They decompose in the heating process with the formation of the secondary products of vegetable oil oxidation, more stable carbonyl compounds.

The change in the intensity of accumulating such aldehydes like 2, 4-decadienal and 2-octenal, is compared with vegetable oils', being expressed by the amount of the *p*-anisidine value. The incorporation of sweet peppers extracts in the composition of oil mixture exerts an effective influence on the processes of stabilization of the oils tested. Thus, the *p*-anisidine value of the oil mixture without extracts reached 1,4814 c. u. after heating process, and this value of oils added by parsley and lovage extracts decreased and varied from 1,2796 to 1,3324c.u. respectively.

4. Conclusions

The results of this study indicate that the antioxidant activity of vegetable extracts depends on various factors: vegetable species, method and conditions of drying. It was established that SHF mode of drying sweet peppers with magnetic intensive 30% is the most optimal from the point of view of the maximum preservation of

scavenging activity of polyphenol in vegetable matter. Red sweet peppers extract were the most abundant source of polyphenol compounds and showed the highest value of antioxidant activity in the group of the extracts studied.

The incorporation of natural vegetable extracts into the composition of mixtures of sunflower and grape seed oils exerts an effective influence on the processes of stabilization of the oils tested; for example, it inhibits the intensity of accumulating primary and secondary oxidation products during thermal oxidation process.

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