THE INFLUENCE OF *PETROSELINUM CRISPUM AND LEVISTICUM OFFICINALE* KOCH. EXTRACTS ON THE THERMAL STABILITY OF THE FUNCTIONAL MIXTURES OF VEGETABLE OILS

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Abstract: *In recent years there is a tendency to use the natural extract of herbs as stabilizators for the vegetable oils. This beneficial effect is due to the rich antioxidants content in these herbs. In this paper, as a source of natural antioxidants have been used oil extracts of parsley and lovage. The obtained extracts were injected into the mixture of oils of sunflower and grape seed, subsequently heated at a temperature of 160°C. Then, the samples of oils were examined for such quality indicators, as acid index, the content of dienes and trienes, refractive index, and were analyzed by UV/Vis spectra. Based on this data it was concluded that the natural extracts of parsley and lovage have an inhibiting effect on the thermal stability of the oil samples.*

Keywords: *antioxidants, natural plant extracts, parsley, lovage, sunflower oil, grape seed oil, free fatty acid content, thermal stability.*

1. Introduction

Vegetable oils and fats are recognized as important componenets 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 vitamines: vitamine A (Retinol), vitamine E (Tocopherols), vitamin K (2-methyl-1,4-naphthoquinone derivatives) and vitamin D (Secosteroids) and other biologically active compounds (Whitney Ellie *et al.*, 2008; Robert Goodhart *et al.*, 1980).

During storage and frying there is a negative effect happening to vegetable oils named oxidation. At the nutritional level, the oxidation of fatty constituents is the major chemical factor in the loss of food wholesomeness by deterioration of flavor and aroma, as well as in decay of nutritional and food safety qualities. (Valéria Ramalho *et al.*, 2008; Fritsch, 1981).

In order to retard or prevent the oxidative deterioration and extend the shelf-life of vegetable oils, antioxidants are incorporated into their composition. (Maryam Azizkhani *et al.*, 2009; Karpinska *et al.*, 2001). 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 (Prior, 2004; Hou, 2003; J. Pocorny *et al.*, 2001; Farag *et al.*, 1989). 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.

The obtained results show that tested extracts of parsley and lovage had strong antioxidant characteristics. The compounds responsible for parsley and lovage antioxidant activity are mainly phenolic acids (caffeic, ferulic, p-coumaric acids) and flavonoids such as flavonol aglycones (quercetin, kaempferol, and their glycosides) (Yıldız *et al.*, 2008; Kahkonen *et al.*, 1999; Larson, 1988).

The purpose of the current work was to describe the effect of added parsley and lovage extracts in the protection of sunflower and grape seed oils against the thermal oxidation process.

2. Materials and methods

2.1. Materials

Refined sunflower and grape seed oil was obtained from a local producer in the Republic of Moldova in April 2011. The oil samples were heated during 20 min at the temperature of 160 ^{0}C. After heat treatment the oil samples were used immediately in the experiment.

2.2. Chemicals

Ethanol (96%), potassium hydroxide (0,1n) and phenolphthalein were supplied by Eco-Chimie (Chisinau, Moldova). Chloroform was purchased from Sigma-Aldrich. All the chemicals used were of HPLC or analytical grade. Distilled water was used throughout.

2.3. Drying and Extraction

Herbs were dried at room temperature for 1 week. Dried leaves of parsley and lovage were ground before extraction. The dried powder of herbs was extracted with sunflower oil for 2h at 60^0C and liquid-to-solid ratio 10 ml per gram. The extracts of tasted herbs were filtered with paper filter and after were used in the experiments.

2.4. Sample preparation

Five oil samples were prepared: sunflower oil, grape seed oil, mixture of sunflower and grape seed oils, mixture of sunflower and grape seed oils with parsley extract and mixture of sunflower and grape seed oils with lovage extract. The content of herbs extract was 1ml Extract/100 ml Oil in every oil sample. The parsley and lovage extracts were added directly to the oils, followed by slow stirring until complete dissolution. Obtained oil samples were exposed to the thermal oxidation.

2.5. Thermal oxidation test

The test for thermal oxidation 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 20 min. The amount of primary oxidation products was determined through measuring of acid value (AV). These were determined according to AOAC Official Method (AOAC, 1999). Formation of secondary oxidation products was measured by dienes and trienes content (IUPAC, 1987). Oil samples exposed to the thermal oxidation test were analyzed using UV/Vis spectroscopy (Pretsch *et al.*, 2006).

2.6. Acid Value

Acid value was determined by potassium hydroxide titration as described in AOCS Official Method Cd 3d-63 (AOCS, 1999). The method was based on the number of milligrams of potassium hydroxide necessary to neutralize the free acids in 1 gram of oil sample. Results were expressed as milligram of potassium hydroxide per gram of walnut oil sample.

2.7. Refractive Index

The refractive index of walnut oil samples was measured following the process described in AOCS Official Method Cc 7-25 (AOCS, 1998). This index is related to degree of saturation but is affected by other factors such as acid value, oxidation, and heat treatment. Refractive index was determined using digital handheld refractometer Krüss Optronic DR 301-95 (Germany).

2.8. Conjugated dienes and trienes

The experiment was carried out according to the AOCS Official method Ti la 64 (AOCS, 1993) with minor modifications. Approximately 0,02 g of oil was placed into a 25 ml volumetric flask. The sample was dissolved in 2,2,4-trimethylpentane, brought to volume and mixed thoroughly. Absorbance of the dissolved oil was measured in UV/Vis spectrophotometer HACH-LANGE DR-5000 (Germany) at 236 nm and 273 nm using quartz cuvette 10×10 mm. The CD and CT values were calculated using the following equations:

$$C_{CD/CT} = A_{236/273} / (\square \times l) \text{ and } CD/CT_{value} = [C_{CD/CT} \times (2.5 \times 10^4)] / W$$

where $C_{CD/CT}$ is the CD/CT concentration in mmol/ml (i.e., the molar concentration), $A_{236/273}$ is the absorbance of the oil solutions at 236 nm and 273 nm, $\square$ is the molar absorptivity (i.e., the extinction coefficient) of linoleic acid hydroperoxide (2.525×10^4 $M^{-1} \cdot cm^{-1}$), l is the path length of the cuvette in cm (1 cm), 2.5×10^4 is a factor that encompasses the volume of 2,2,4-trimethylpentane (25 ml) used to dissolve the oil sample as well as a unit conversion (1000 μmol/mmol) so that the content of CDs and CTs can be expressed in μmol, and W is the weight of the oil in gram. Results were expressed in micromole conjugated dienes and trienes per gram of oil.

2.9. Statistical analysis

Variance analysis of the results was carried out by least square method with application of coefficient Student and Microsoft Office Excel program version 2007. Differences were considered statistically significant if probability was greater than 95% (p-value <0.05). All assays were performed by triplicate at room temperature 20 ± 1 ^{0}C. Experimental results are expressed as average ± SD (standard deviation) (Snedecor *et al.*, 1989).

3. Results and discussions

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).

In this paper were evaluated several physical-chemical indices: acid value, refractive index, dienes and trienes content. The obtained data are presented in Table 1.

Tabel 1

The evolution of the physical-chemical indices of the studied samples.

Nr.of sampl.	*Sample name*	*Temperature, °C*	*Acid value*	*Refractive index*	*Conjugated dienes content*	*Conjugated trienes content*
1	Sunflower oil	20	1,088	1,4743	15,8696	7,0078
		160	1,262	1,4743	28,0418	13,9965
2	Grape seed oil	20	1,111	1,4743	17,8961	8,1548
		160	1,277	1,4743	25,1166	14,8133
3	Mixture (80% sunflower+ 20% grape seed oil)	20	1,094	1,4745	12,4434	5,0869
		160	1,262	1,4743	18,7134	5,3122
4	Mixture + oil extract of parsley	20	1,111	1,4745	13,9394	5,9598
		160	1,144	1,4746	23,1993	9,2439
5	Mixture + oil extract of lovage	20	1,027	1,4744	13,7797	5,6523
		160	1,116	1,4745	15,1199	5,2649

According to the data presented above in the table, we can observe the following evolution: the acid value decreases in the samples enriched with the natural extracts of parsley and lovage. This value varies from 1,015 to 1,111 for the samples kept at 20°C, and from 1,094 to 1,277 – for the samples heated up to 160°C. The decreasing of the acid value shows an inhibition of the oxidative process, due to the antioxidants present in the natural extracts of parsley and lovage. The same evolution was observed for the rest of physical-chemical indices (refractive index, the content of conjugated dienes and trienes). This thing confirm the fact that the natural extract of herb have a benefic effect on the inhibition of the accumulation of the primary oxidation products during thermal oxidation process.

Figure 1 shows UV/Vis spectra of tested sunflower and grape seed oils, their mixture with/without extracts.

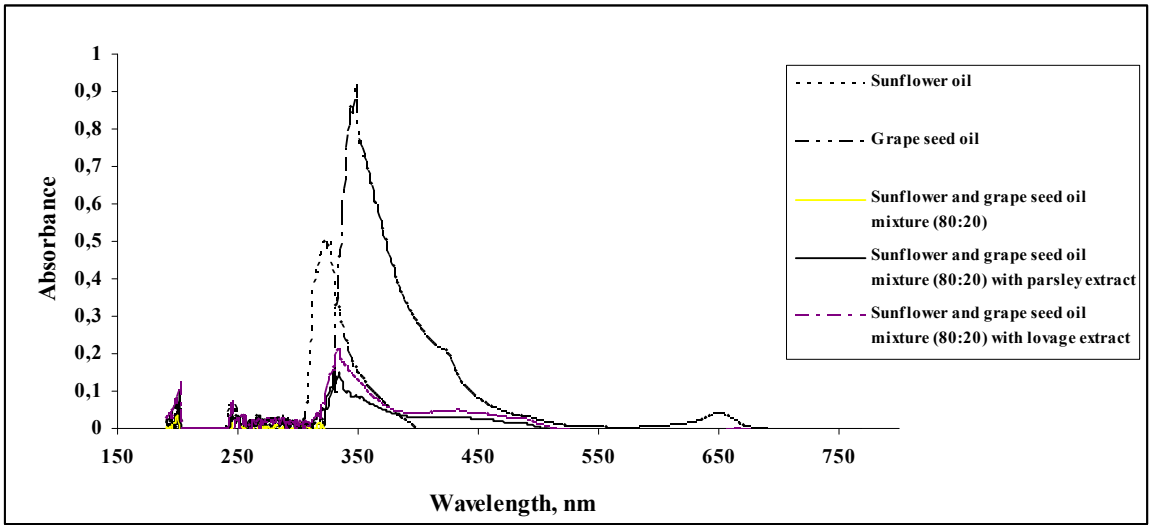

Figure 1. UV/Vis spectra of tested vegetables oils with/without parsley and lovage extracts.

4. Conclusions

The incorporation of the natural plant extracts into the composition of the mixture of sunflower and grape seed oils exerts an effective influence on the processes of stabilization of the tested oils; i.e., it inhibits the intensity of the accumulation of the primary and secondary oxidation products during thermal oxidation process.

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