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BLENDING OF SUNFLOWER OIL WITH GRAPE SEED OIL: IMPACT ON PHYSICO-CHEMICAL PARAMETERS AND RADICAL SCAVENGING ACTIVITY

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Abstract: *Sunflower oil (SFO) was blended with grape seed oil (GSO) in order to improve its quality. If sunflower oil is a traditional one on Romania market the grape seed oil is a non-conventional one which has a high content in unsaturated fatty acids like oleic and linoleic ones and a large amount of tannins like the oligomeric proanthocyanosides. Also, grape seed oil is rich in bioactive compounds like phenolic components, tocopherols, e.g. thus making it a valuable source in order to improve the nutritional quality of the blended oils. The main goal of the present work was to compare and correlate the physical-chemical and radical scavenging activity of the SFO blended with GSO in different proportions: 10:0, 9:1, 8:2, 7:3 and 0:10, w/w. The physical-chemical properties analyzed in this study were refractive index, iodine value, peroxide value, saponification value and acid value. The radical scavenging activity was measured by the 1,1-diphenyl-2-picrylhydrazyl (DPPH) method. The results showed that by increasing the proportion of GSO in SFO, the physico-chemical parameters values decreased, while the radical scavenging activity increased. Oxidative stability of oil blends was improved with the level increase of GSO. This study showed that the quality of sunflower oil may be improved with the addition of grape seed oil.*

Key words: *oil blends, sunflower oil, grape seed oil*

1. Introduction

Vegetable oils from seed sources are of important interest in different food and application industries. One of these vegetable oils, well known worldwide due to its functional properties, is the grape seed oil. This oil is obtained from the seed of grapes (*Vitis vinifera L.*), a by-product of the winemaking industry, which makes up to 15% of the solid waste produced in wine industries [1]. Various extraction methods like solvent extraction, hydraulic pressing, supercritical carbon dioxide [2, 3, 4] e.g., are used to recover the grape seed oil. The oil content of the grape seeds range between 12-20% of its dry weight [5, 6] depending on the pressing condition [7] used. Grape variety, degree of ripening, soil quality, climate and the technological procedure of grape processing are some of the factors that influence the grape seed oil yield [8].

Grape seed oil is a valuable source of dietary fat due to its high content in unsaturated fatty acids (85–90%) [1], which has many benefits such as the prevention of thrombosis, dilation of blood vessels, inhabitation of cardiovascular diseases, reduction of cholesterol in serum and the oxidation of low-density lipoproteins e.g.

[9]. Due to its compounds that have beneficial health effects, grape-seed oil has a high potential to be used in pharmaceutical and food applications [10, 11]. Its content is high in unsaturated fatty acids, oleic and linoleic acids [12] that are very important for the stability of oils due to the chemical reactions in the double bonds. The rates of those oxidation reactions depend on the number of double bonds in the carbon chain [13]. Grape seed oil contains a large amount of tannins, like the oligomeric proanthocyanosides (OPCs), in a higher level than in the other seed oils [14]. Also, grape seed oil is rich in bioactive compounds like phenolic components that are known for their antioxidant properties [15]. Also, it contains tocopherols, especially α-tocopherols [13] that have the highest vitamin E activity [16], thus making it important for human health and biological activity [17]. Grape seed oil has a high antioxidant potential, Fernandes et al. (2013) reporting that DPPH radical scavenging activities varied between 38.68 and 69.89% depending on grape genotype. Due to its content, grape seed oil can be used in blends with other vegetable oils, especially in the cases when a high level of antioxidant protection is needed. Therefore, considering the above mentioned, this study was focused on grape seed oil and also due to the fact that this oil has a high content of unsaturated fatty acids such as linoleic acid (72–76%, w/w), which exceeds those from the sunflower oil (60–62%) accordingly to C. Ghisalberti, PCT Int. Appl. WO 2001018161 A2 (15 March, 2001). In addition, grape seed oil has, unlike the sunflower one, low levels of linolenic acid [20] which is desired in edible oils because it improves the oxidative stability [21]. Having three double bonds on its hydrocarbon chain, the linolenic acid is readily oxidized and therefore, the stability of an oil rich in linolenic acid would be too short [22].

Sunflower oil is a vegetable oil with poor oxidative stability which is prone to flavor degradation due to its high proportion of polyunsaturated fatty acids [23]. This oxidation process of unsaturated fatty acids represents one of the major causes which determine the development of off-flavor compounds and decrease the nutritional value of the food products [24]. Lipid oxidation changes the physicochemical parameters of the oil, thus influencing directly the quality of the vegetable oil and has harmful effects on food quality and human health [25]. Sunflower oil is not quite suitable at high temperature (e.g. for frying) due to the higher magnitude of oxidation [26]. One way to improve the oxidative stability of this oil is by blending it with oils that have high antioxidant levels, like grape seed oil. The blending of these oils changes the functional properties without any chemical or biological process [27].

Various studies have been reported on the blending of vegetable oils with different physicochemical properties in order to improve some quality parameters such as, peroxide value, oxidative stability, e.g. [25, 28]. Although the quality of the above mentioned vegetable oils, such as sunflower oil and grape seed oil has been evaluated by many researchers, to our knowledge, their quality parameters, in different blends have not been extensively studied.

The objective of the present study was to investigate the effects of grape seed oil with sunflower oil in different blends proportion on the some physical-chemical values like refractive index (RI), iodine value (IV), acid value (AV), peroxide value (PV) and radical scavenging activity by means of the DPPH method. This study may be useful in the development of healthy blended oils with an improved quality.

2. Materials and methods

2.1. Materials

Sunflower oil and grape seed oil was purchased from the local market (Suceava, Romania). Sunflower oil (SFO) was blended with grape seed oil (GSO) at the following SFO:GSO mixing ratios: 10:0; 9:1, 8:2, 7:3 and 0:10 (w/w). All reagents and chemicals that were used in this work were of analytical grade.

2.2. Methods of analysis

The analysis of the physical and chemical parameters was carried out according to the methods described in the Romanian or international standard methods. All tests were performed in duplicate.

The *refractive index* (RI) of the oil samples at room temperature was determined according to the SR EN ISO 6320:2002/AC:2006 by using an a *Abbé* refractometer (Leica Plus). The RI is a factor by which the wavelength and the velocity of the radiation are reduced with respect to their vacuum values [29].

The *iodine value* (IV), expressed as grams of I_2 absorbed by 100 g oil (SR EN ISO 3961:2013), was determined using the Hanus method.

Saponification value (SV) is expressed as mg KOH required for the saponification of the free fatty acids and esterified from 1 g of oil sample and it was determined according to the SR EN ISO 3657:2013.

Acid value (AV) was determined according to the SR EN ISO 660:2009 and is expressed in mg KOH required to neutralize the free fatty acids present in 1 g vegetable oil. The AV is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds [29].

Peroxide value (PV) measures the peroxides and hydroperoxides that are in the initial stages of lipid oxidation. Milliequivalents of active oxygen per kg of oil sample are measured by titration with sodium thiosulfate solution (0.01N) according to the SR EN ISO 3960:2010.

Extraction of the phenolic fraction

The extraction was carried out with the method reported by Mraicha et al. (2010). In short, 4 g of the oil sample was added to 2 ml of n-hexane and 4 ml of a methanol/water (60:40, v/v) solution in a 20 ml centrifuge tube. After vigorous mixing, the sample was centrifuged for 10 min at 1500 rpm. The hydroalcoholic phase was collected, and the hexanic phase was re-extracted twice with 4 ml of methanol/water (60:40, v/v) solution each time. Finally, the hydroalcoholic fractions were combined, washed with 4 ml of n-hexane to remove the residual oil, and then concentrated.

Free radical scavenging activity

The free radical scavenging activity of the extracts was measured by the 1,1-diphenyl-2-picrylhydrazyl (DPPH) method proposed by Bouaziz et al., 2008. In succinct terms, aliquots (50 µl) of various concentrations from the tested compound were added to 5 mL of a 0.004% methanol solution of DPPH. When DPPH reacts with an antioxidant compound, which can donate hydrogen, it is reduced. The changes in colour (from deep violet to light yellow) were read at 518 nm after 30 min of reaction at room temperature using a UV VIS - NIR Spectrometer (Shimadzu, 3600, Japan). Methanol was used to zero the spectrophotometer. The inhibition of free radicals DPPH in percent (*I*%) was calculated in the following way: $I\% = [(A_{blank} - A_{sample})/A_{blank}] \times 100$, where A_{blank} is the absorbance of the control reaction (containing all reagents except the test compound) and A_{sample} is the absorbance of the test compound.

2.3. Statistical analysis

The experimental results were expressed as means ± standard deviation (SD) of the

duplicate measurements. Differences among the means were evaluated by the analysis of variance (ANOVA) using SPSS v.16.0 software. Mean values with a statistical difference of $p \leq 0.05$ were considered as significant.

3. Results and discussion

Physicochemical characteristics

Refractive index

Fig. 1 shows the obtained results of the refractive index (RI). Significant differences at $p < 0.05$ were obtained between GSO and SFO, and their blends with 1%, 2 % GSO. It can be seen that SFO presents the highest RI while GSO has the lowest RI.

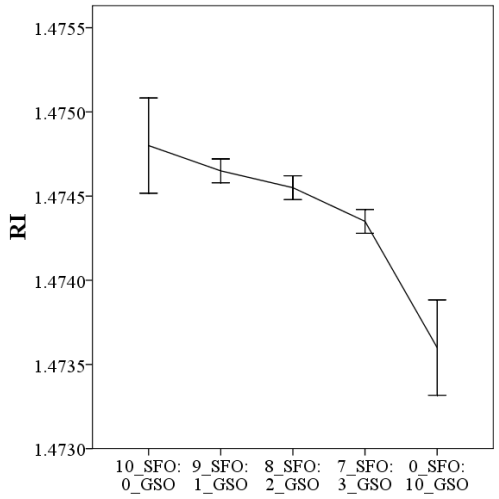

Fig. 1. Variation of Refractive index (RI) in oil samples formulation: SFO – sunflower oil; GSO – grape seed oil. Line show means.

The low RI value for GSO can be due to its higher content in linoleic acid, comparatively with the SFO. It can also be related to the nature of the fatty acids present, since RI decreases with the molecular weight of the fatty acids and with unsaturation [31]. The decrease of RI with the increase level of GSO from blends may be due to the increase in the number of double bonds, the RI of oils being related with the degree of unsaturation in a linear way [32].

Iodine value

The results for iodine value (IV) of the oil samples are shown in Fig. 2.

Grape seed oil has positive effect on the IV of the oil blends and led to a significant decrease ($p < 0.05$) of the IV with the increase of the GSO level from 10 to 30%.

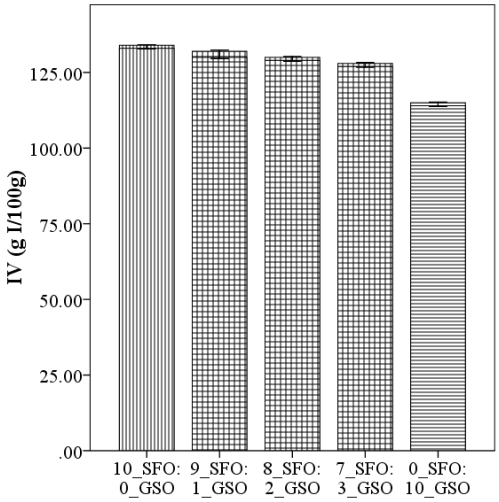

Fig. 2. Variation of Iodine value (IV) in oil samples formulation: SFO – sunflower oil; GSO – grape seed oil. Bars show mean.

The low IV for GSO may have contributed to its higher oxidative stability. Therefore, the oxidative stability of the oil blend increased with the increase of GSO level in the oil blend because the GSO is the most resistant oil to oxidation due to its highest natural antioxidants, namely tocotrienols, which are 40-60 times in a higher level than tocopherols [33].

Saponification values

The saponification value (SV) of the grape seed oil is lower comparatively with the SFO (Fig. 3), probably due to the fatty acids present in the GSO that have a larger number of carbon atoms. Therefore, this lower value of SV may be due to the higher molecular weight of the fatty acids from GSO, knowing that SV is inversely related to the average molecular weight of them. The SV of the binary blends were found to

be in decrease with the increase of GSO mixing proportion.

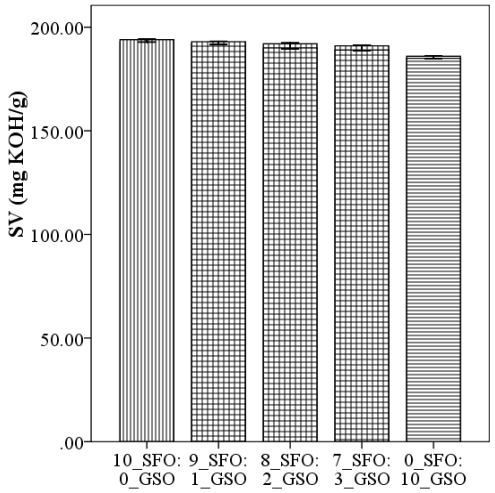

Fig. 3. Variation of Saponification value (SV) in oil samples formulation: SFO – sunflower oil; GSO – grape seed oil. Bars show mean.

Peroxide value

The peroxide value (PV) calculated for sunflower oil, grape seed oil and binary oil blends are shown in Fig. 4. The PV of GSO shows a relative good quality compared to the SFO. The high PV of SFO indicates an early lipid phase peroxidation.

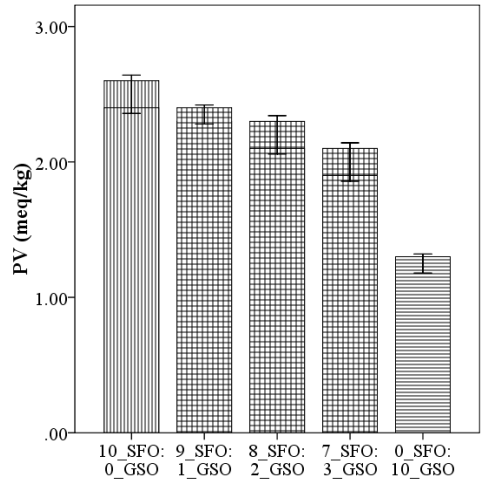

Fig. 4. Variation of Peroxide value (PV) in oil samples formulation: SFO – sunflower oil; GSO – grape seed oil. Bars show mean.

The addition of GSO to the SFO significantly decreases ($p < 0.05$) the PV value, this results in an enhancement of the oxidative stability of the formulated oil blends. Therefore, the PV value indicates an improvement of the product quality.

Acid value

Acid value (AV) is a parameter used for the assessment of the oil quality, representing free fatty acid content due to its enzymatic activity. An increase in acid value can be due to the hydrolysis of glycerides, due to humidity and temperature. Higher AV for SFO gives an idea about increased susceptibility to rancidity due to the free fatty acid present in the oil. On the other hand, GSO contains high levels of phenolic compounds that have antioxidant and anti-hydrolitic effects. Therefore, a significant decrease ($p < 0.05$) in the AV of the SFO when it is blended with GSO (Fig. 5) was obtained. GSO blended with SFO improved the quality of the oil blend as compared with pure SFO, this fact suggesting low levels of hydrolytic and lipolytic activities in the oil blends.

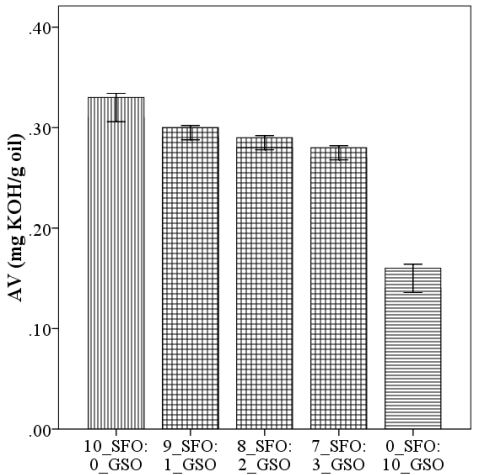

Fig. 5. Variation of Acid value (AV) in oil samples formulation: SFO – sunflower oil; GSO – grape seed oil. Bars show mean.

Radical scavenging activity

To evaluate the antioxidant activity of the phenolic fraction, the well known DPPH antiradical test was performed. The inhibition of free radicals DPPH in percent (*I*%) is higher for the grape seed oil (32.39%) in comparison with the sunflower oil (24.6%) (Fig. 6). These results indicate that the grape seed oil showed the highest antioxidant activity in comparison with the sunflower sample. Also, from this study it was observed that the inhibition of free radicals DPPH in percent (*I*%) increases with the increasing amount of added grape seed oil in sunflower oil (28.24%; 28.59%; 29.78%). Therefore, the antioxidant activity increased in the sunflower oil, with the increasing level of grape seed oil in the oil blends.

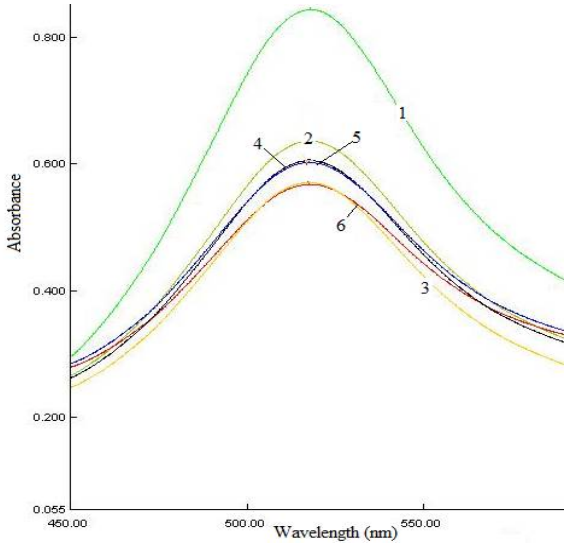

Fig. 6. Spectrum in the VIS range of the DPPH radical in presence of oils: 1 – blank; 2 - SFO:GSO (10:0); 3 - SFO:GSO (0:10); 4 - SFO:GSO (9:1); 5 - SFO:GSO (8:2); 6 - SFO:GSO (7:3).

4. Conclusion

Various physical and chemical parameters have been studied and may be used for the quality control of edible oil samples. The physical and chemical parameters decrease in oil blends with the increase proportion of grape seed oil mixed in sunflower oil, while radical scavenging activity increased. Quality parameters of oil blends were better than for the sunflower oil, probably due to the changes in the fatty acids profile of oil blends, and to the minor bioactive lipids that the grape seed oil presents. The grape seed oil was found to be edible oil with high qualitative properties that can be used in order to improve the quality of sunflower oil.

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