Food Chemistry 111 (2008) 121–126

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

The antioxidant capacity and oxidative stability of virgin olive oil enriched with phospholipids

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ARTICLE INFO

Article history:
Received 11 December 2007
Received in revised form 25 January 2008
Accepted 13 March 2008

Keywords:
Phospholipids
Virgin olive oil
Radical-scavenging activity
Electron spin resonance spectroscopy
Oxidative stability

ABSTRACT

Virgin olive oil (VOO) enriched with phospholipids (soy lecithin) up to the levels present in seed oils (from 2.5 to 10.0 g/kg) was studied as a potential functional food. Lecithin addition slightly increased the concentration of tocopherols and considerably increased K270 values. In the fatty acid composition, an increase of linoleic and a slight decrease of oleic acid were observed, as the decrease of monounsaturated/polyunsaturated fatty acid ratio. The radical-scavenging activity was evaluated by two methods: electron spin resonance spectroscopy using galvinoxyl free radical and VIS spectroscopy measurement of the disappearance of 1,1-diphenyl-2-picryl-hydrazyl (DPPH) radical. Results indicate that lecithin addition retards the scavenging activity of VOO that is ascribed to the bipolar character of lecithin and its ability to entrap hydrophilic antioxidants. The effect of lecithin addition on the oxidative stability of VOO was evaluated by the Rancimat method, and a positive linear correlation ($r = 0.9849$) with induction time was found.

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1. Introduction

Phospholipids (PL) are minor constituents of seed oils, usually present in a concentration range of 10–20 g/kg (Bernardini, 1983). They are generally considered as synergists of phenolic antioxidants (Hidalgo, Nogales, & Zamora, 2005), but there is little information about those properties based on the determination of radical-scavenging activity. Ramadan, Kroh, and Mörsel (2003) have reported that PL could contribute to the radical-scavenging activity of different seed oils dissolved in toluene toward galvinoxyl free radical. The study of the lipid fraction of different vegetable oils by Espin, Soler-Rivas, and Wichers (2000) has concluded that PL have direct radical-scavenging activity toward the 2,2-diphenyl-1-picryl-hydrazyl (DPPH) free radical, although this is much lower than that of α-tocopherol.

In the context of functional food formulation, the addition of PL as synergists of phenolic antioxidants could be particularly interesting in the case of virgin olive oils (VOOs). They contain hydrophilic phenols, with known radical-scavenging activity (Carrasco-Pancorbo et al., 2005), in the range 40–800 mg/kg, as well as tocopherols in the range 100–400 mg/kg (Psomiadou, Tsimidou, & Boskou, 2000). On the other hand, the amounts of PL in VOOs are 300–400 times lower than those in seed oils (Koidis & Boskou, 2006).

The aim of this work was to investigate the possibility of PL enrichment of VOOs up to the concentration levels similar to those of seed oils. The influence of such high PL content on the antioxidant capacity of integral VOO was investigated using two direct determination methods. Electron spin resonance spectroscopy (ESR) applied on a sterically protected and resonance-stabilized galvinoxyl free radical was proposed by Quiles, Ramirez-Tortosa, Gomez, Huertas, and Mataix (2002) as a rapid and very sensitive method. The measurement of disappearance of DPPH free radical by VIS spectroscopy is the method widely used for the estimation of antioxidant activity of different foods, also applied to whole vegetable oils (Espin et al., 2000; Valavanidis et al., 2004). Besides, the influence of PL addition on the oxidative stability of VOO was evaluated by the accelerated oxidation test (Rancimat).

2. Materials and methods

2.1. Materials

A filtered extra VOO was purchased from the local Croatian olive oil producer. The commercial soy lecithin granules, containing

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doi:10.1016/j.foodchem.2008.03.045

<1% of water and 97% of phosphatides (approximately 70% of phosphatidylethanolamine, 20% of phosphatidylcholine and 7% of phosphatidylinositol) were supplied from Life Time Nutritional Specialities Inc. (Anaheim, USA). Ethyl acetate p.a., *n*-hexane p.a. and isooctane of UV-spectrophotometric quality were purchased from Panreac (Barcelona, Spain). Propan-2-ol for HPLC was obtained from Merck KGaA (Darmstadt, Germany). Methanol p.a. and toluene p.a. were supplied from Kemika (Zagreb, Croatia). DPPH and galvinoxyl free radicals, tocopherol standards and caffeic acid were from Sigma Chemical Co. (St. Louis, MO). Paraffin oil was bought from Ritosa d.o.o. (Porec, Croatia). Superclean TM LC-18 SPE Tubes (1 ml) were supplied from Supelco Inc. (Bellefonte, PA).

2.2. Sample preparation

Fifty grams of soy lecithin granules were mixed with 500 ml of oil heated to 40 °C, in order to prepare lecithin concentrate in extra VOO (primary solution). The blend was stirred for 30 min using a laboratory mixer with the propeller blade at 400–500 rpm, then, it was set aside for 10 min to allow precipitation of the undissolved part of lecithin. The same procedure of mixing and heating was applied on the pure extra VOO (without lecithin). The oil containing dissolved and dispersed lecithin was separated from the sediment and filtered over the quantitative filter paper with medium wide pores. The concentration of PL in the so obtained primary solution and in extra VOO was determined from the acetone insoluble matter, using the Lüde method described by Pardun (1964) and modified against the recommendation of List, Heakin, Evans, Black, and Mounts (1978). The real amount of the lecithin dissolved in primary solution was calculated as a difference between the PL concentration in the primary solution and extra VOO. The primary solution was used to prepare the samples in the concentration range of added lecithin, from 2.5 to 10.0 g/kg, by mixing the solution with appropriate portions of extra VOO.

2.3. Determination of standard quality and composition parameters

The free fatty acids, expressed as oleic acid, the peroxide value in mmol of oxygen per kg of oil, the coefficients of specific extinction at 232 and 270 nm (K232 and K270), and the fatty acid composition were determined according to EC Regulation 2568 (1991).

2.4. Determination of tocopherols

Tocopherols were analyzed by HPLC (Varian ProStar HPLC equipped with a Varian ProStar 363 fluorescence detector) according to the standard method (ISO, 1997). 0.1 g of oil sample was weighed into a 10 ml volumetric flask and diluted to the mark with *n*-hexane. The individual tocopherols were separated on a Restek Pinnacle II silica column, 15 cm × 4.6 mm i.d. (particle size 5 μm) which was held at 30 °C. Detection was performed at an excitation wavelength of 290 nm and an emission wavelength of 330 nm. A solution of 0.7% propan-2-ol in *n*-hexane was used as eluent at a rate of 0.60 ml/min. Tocopherol standards (α-, γ- and δ-tocopherol) were used for the setup of calibration curves that covered concentrations from 5 to 750 mg/kg of tocopherols in oil.

2.5. Determination of total phenol content

Hydrophilic phenols were extracted from the oil samples using the method for bitter index determination described by Gutiérrez Rosales, Perdiguero, Gutiérrez, and Olias (1992). A C18 SPE tube of 1 ml was activated with 6 ml of methanol and then washed with 6 ml of hexane; 1.00 ± 0.01 g of oil dissolved in 4 ml of hexane was passed through the column. After the elution, 10 ml of hexane were passed to eliminate the fat, and the retained compounds were eluted with 25 ml of methanol/water mixture (1:1, v/v). Folin–Ciocalteau reagent was added to a suitable aliquot of the eluate. The absorbance of the solution at 725 nm was measured after 2 h.

2.6. ESR measurements of radical-scavenging activity

ESR measurements were performed at room temperature (22 °C) using a Varian E-109 spectrometer equipped with a Bruker ER 041 XG microwave bridge. The spectroscopic parameters were: frequency 9.27 GHz, field sweep 10 mT, microwave power 4.9 mW and modulation amplitude 0.11 mT. Samples were prepared according to the method described by Papadimitriou et al. (2006). The freshly prepared 0.15 mM galvinoxyl free radical solution in isooctane was added to the VOO samples in order to obtain a 4% (w/v) oil solution. The oil solution was quickly mixed in the flask and immediately put into the standard ESR tube. ESR spectra were recorded during 30 min, starting from the first minute after the oil and free radical solution contact. Recording intervals were 1 min during the first 10 min of the reaction and 2 min during the rest of the measuring process. The signal intensities of galvinoxyl free radical were calculated by the double integration of ESR spectra, using the EW (EPRWare) Scientific Software Service program and expressed in arbitrary units. The signal intensity of the pure 0.15 mM galvinoxyl solution, measured immediately before starting the sample measurement, was taken as the reference signal intensity, i.e. signal intensity of the sample (A_0) for the reaction time zero ($t = 0$ min). The loss of the signal intensity (I) after the reaction time t was calculated as: $(I) = [(A_0 - A)/A_0] \times 100\%$, where A is the signal intensity of galvinoxyl radical in oil solution measured at time t. Each sample was analyzed in triplicate and the results are presented as mean values ± standard deviation.

2.7. Measurements of radical-scavenging activity using VIS spectroscopy

The reaction mixture of oil and DPPH· solution was prepared according to the procedure described by Kalantzakis, Blekas, Pegkildou, and Boskou (2006). One millilitre of oil solution (10% w/v) was added to 4 ml of a freshly prepared DPPH· solution (0.1 mM) in 20 ml test tube, which was immediately tapped and vigorously mixed during 10 s in a vortex apparatus. The ethyl acetate was used as a solvent. Absorbance of the mixture was measured during 30 min at 515 nm, using a HACH spectrophotometer DR/400, (Colorado, USA). Recording intervals were 1 min, starting from the first minute after the oil and free radical solution contact. The absorbance for $t = 0$ (A_0) was calculated as: $A_0 = A_B + A_S$, where A_B is the absorbance of blank solution (DPPH· in ethyl acetate, 0.1 mM) and A_S is absorbance of oil solution in ethyl acetate (10% w/v). The loss of DPPH· absorbance (I) was calculated as described for the loss of signal intensity in ESR measurements. Each sample was analyzed in triplicate and the results are presented as mean values ± standard deviation.

2.8. Determination of oxidative stability by Rancimat method

Oil samples having a mass of 3.0 g were heated in the Rancimat equipment at 120 °C (Metrohm Ltd., Herisau, Swiss) with a continuous air flow of 10 l/h passing through the samples. The conductivity cells were filled with 60 ml of deionised water (2 μS/cm). The time needed for the appearance of a sudden water conductivity rise, caused by the adsorption of volatiles deriving from oil oxidation, was registered as the induction time in hours.

2.9. Statistical analysis

One-way analysis of variance at 5% significance level was used to determine any significant difference in the radical-scavenging

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