Food Chemistry 127 (2011) 216–221

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

A spectroscopic and chemometric study of virgin olive oils subjected to thermal stress

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ARTICLE INFO

Article history:
Received 2 August 2010
Received in revised form 13 October 2010
Accepted 2 December 2010
Available online 10 December 2010

Keywords:
Virgin olive oil
Thermal treatment
Spectroscopic analysis
Chemometry

ABSTRACT

The paper describes a study of thermal stress of three different samples of virgin olive oil in terms of oxidative stability. Fatty acid composition, evaluation of oxidative stability under forced conditions (OSI), determination of UV-spectrophotometric oxidation indexes (k_{232} and k_{270}) and spectral properties were explored along the thermal treatment. The samples were subjected to heating treatment at 180 °C and evaluated after 0, 30, 60, 90, 120, 150 and 180 min. Middle infrared (MIR) and visible–near infrared (Vis–NIR) spectra were elaborated by partial least squares modelling to individualise regions and bands where critical variations were present. Two bands were found as principal influential ones (1245–1180 cm^{-1} and 1150–1030 cm^{-1}) on MIR while one primary region was identified on Vis–NIR (2200–1325 cm^{-1}).

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1. Introduction

Extra virgin olive oil (EVOO) is widely known because of its high health benefits and sensory quality in comparison to other oils and fats (Bendini et al., 2007), especially due to the presence of a high ratio between monounsaturated and polyunsaturated fatty acids and its antioxidant fraction (principally lipophilic and hydrophilic phenolic compounds) (Aparicio, Roda, Albi, & Gutiérrez, 1999).

Virgin olive oil is a principal ingredient in the Mediterranean diet and it is consumed in different ways: raw in salads, on traditional food (i.e. as breakfast in "tostada" in the South of Spain or as meal in pasta or "bruschetta" in the South of Italy), toasts and other foodstuffs (Cerretani, Biasini, Bonoli-Carbognin, & Bendini, 2007), but often it is also consumed after domestic heating, such as fried, boiled or after conventional and microwave heating (Brenes, García, Dobarganes, Velasco, & Romero, 2002). These thermal treatments are commonly utilised for home-cooking, food catering and industrial processes (Brenes et al., 2002; Carrasco-Pancorbo et al., 2007; Cheikhousman et al., 2005). Several studies published in literature up to now have compared the effects of conventional and microwave heating on the physical and chemical parameters of extra virgin olive oil (Albi, Lanzón, Guinda, Pérez-Camino, & León, 1997; Brenes et al., 2002; Caponio & Gomes, 2001; Vieira & Regitano-D'Arce, 1999; Valli et al., 2010).

It has been observed that heating can affect the phenolic fraction and the oxidation stability and degradability of oil. In fact, Cerretani, Bendini, Rodriguez-Estrada, Vittadini, and Chiavaro (2009) have studied the effect of microwave heating treatments on phenols compared to the effects produce by oxidation or heating by conventional oven; particularly lignans have shown the highest stability to the thermal treatments due to their strong antioxidant properties (Carrasco-Pancorbo et al., 2007). The parameters that have been proven to influence the extent of oxidation and the degradation of oils in a highest extension during heating are oil composition, time and temperature of heating, food (in the case that some food is in contact with the oil), ratio between surface and volume of the oil (Andrikopoulos, Kalogeropoulos, Falirea, & Barbagianni, 2002; Christie, Brechany, Sebedio, & Le Quere, 1993). However, strong interactions exist among these variables and because of that, they are difficult to control and define (Jorge, Márquez-Ruiz, Martín-Polvillo, Ruiz-Méndez, & Dobarganes, 1996).

More recently, Valli et al. (2010) have studied the phenolic fraction of two EVOO and their admixtures after thermal treatments using microwave and conventional oven by HPLC-DAD/MSD and NMR spectroscopy. In this work authors have observed an increase of the dialdehydic forms of secoiridoids (dialdehydic form of elenolic acid lacking a carboxymethyl group, EDA; *p*-hydroxyphenylethanol linked to the dialdehydic form of elenolic acid,

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doi:10.1016/j.foodchem.2010.12.018

p-HPEA-EDA) after microwave and conventional heat treatments. It is likely that reasonable chemical conversions from elenolic acid (EA), *p*-hydroxyphenylethanol linked to elenolic acid (*p*-HPEA-EA), and 3,4-dihydroxyphenylethanol linked to elenolic acid (3,4-DHPEA-EA) to their respective dialdehydic forms (EDA; *p*-HPEA-EDA; 3,4-dihydroxyphenylethanol linked to the dialdehydic form of elenolic acid, 3,4-DHPEA-EDA) were induced by heating.

Other analytical techniques as FT-IR have been recently applied to the analysis of phenolic fraction of EVOO (Cerretani et al., 2010). Spectroscopic FT-IR coupled with chemometrics methods have been successfully used to detect olive oil adulteration (Lerma-García, Ramis-Ramos, Herrero-Martínez, & Simó-Alfonso, 2009; Maggio, Cerretani, Chiavaro, Kaufman, & Bendini, 2010; Ozen & Mauer, 2002) and freshness (Sinelli, Cosio, Gigliotti, & Casiraghi, 2007). The chemometric algorithm partial least square (PLS) has been repeatedly and extensively used to obtain different quality parameters of edible oils (Al-Alawi, Van de Voort, & Sedman, 2004; Iñón, Garrigues, Garrigues, Molina, & De la Guardia, 2003; Li, Van de Voort, Ismail, & Cox, 2000b; Li et al., 2000a).

In this work three different EVOOs have been subjected to heating treatment by conventional oven with the following aims:

(1) to study the changes in the oxidative stability (k_{232}, k_{270} and OSI time) and in the spectroscopic properties (Vis–NIR and FT-MIR) occurring in this process;

(2) to find, by spectroscopic analysis, the compounds or the families of compounds that are most important in this oxidation pathway;

(3) to explore the opportunity of adopting some rapid spectroscopic methods (Vis–NIR and FT-MIR) for the control of cooked olive oils.

2. Materials and methods

2.1. Apparatus

Fatty acid (FA) analyses were performed using an Autosystem XL Perkin Elmer (Shelton, CT, USA) gas chromatograph equipped with a flame ionisation detector (FID). The determination of k_{232} and k_{270} was carried out using an UV–vis 1800 instrument (Shimadzu Co., Kyoto, Japan), which had a six slot shuttle and a system for temperature control of working conditions. The oxidative stability of samples was evaluated using an eight-channel oxidative stability instrument (Omnion, Decatur, IL, USA). The FT-MIR spectra were acquired on a Tensor 27™ FTIR spectrometer system (Bruker Optics, Milan, Italy), fitted with a Rocksolid™ interferometer and a DigiTect™ detector system coupled to an attenuated total reflectance (ATR) accessory. NIR analysis was carried out by NIR Lab Near Infra Red by transmittance instrument (SACMI Imola S.C., Imola, Bologna, Italy).

2.2. Materials, reagents and standards

Potassium hydroxide, methanol, *n*-hexane, isooctane and acetone were purchased from Merck (Darmstadt, Germany). The standard mixture of FA methyl esters (GLC 463) was supplied by Nu-Chek (Elysian, MN, USA).

2.3. Samples and thermal treatment

Three different samples of extra virgin olive oil (named A, B and C) from different Italian regions (Abruzzo, Marche and Puglia) harvested in the fall of 2009, were analysed in this experimental study. The oils were different in terms of cultivar and ripening degree.

For analytical purposes, six aliquots (50 g) of each sample were inserted in 250 mL opened glass beakers (7.2 cm i.d.) and subjected to conventional heating at 180 °C in a oven (model M20-VN, Instruments s.r.l, Bernareggio, Milan, Italy). The beakers were removed from the oven at fixed intervals of 30 min, obtaining samples with different heating treatments (30, 60, 90, 120, 150, 180 min) to be analysed. All heated samples were cooled at room temperature (23 ± 1 °C) for 30 min and stored in bottles without headspace at 12 °C before chemical analysis.

2.4. Fatty acid composition

The FA composition of oil samples was determined as fatty acid methyl esters (FAMEs) after alkaline treatment, obtained by mixing 0.05 g of oil dissolved in 2 mL of *n*-hexane with 1 mL of 2 N potassium hydroxide in methanol, and subsequent gas chromatographic analysis, according to Bendini, Cerretani, Vecchi, Carrasco-Pancorbo, and Lercker (2006), with slight modifications. Analytes were separated on a RTX-2330 capillary column (30 m × 0.25 mm i.d., 0.2 μm film thickness) from Restek (Bellefonte, PA, USA). Column temperature was held at 140 °C for 5 min and then it was increased at 2.5 °C min^{-1} until 240 °C. The FID and the injector temperatures were both set at 250 °C. Peak identification was accomplished by comparing the peak retention times with those of the GLC 463 FAME standard mixture, injected under the same gas chromatographic conditions. The GC response factor of each FA was also calculated by using the GLC 463 FAME standard mixture.

2.5. Determination of k_{232} and k_{270}

The UV-spectrophotometric indexes (k_{232} and k_{270}) were determined according to the European Communities official methods and the following amendments (European Union Commission, 1991). To calculate the k_{270} and k_{232} values, the oil samples were diluted in isooctane (1:100 v/v for k_{270} and 1:1000 v/v for k_{232}), placed into a 1 cm quartz cuvette, and analysed at the wavelengths of 270 and 232 nm, against a blank of isooctane. Three replicates were prepared and analysed per sample.

2.6. Evaluation of oxidative stability under forced conditions

An eight-channel oxidative stability instrument (OSI) (Omnion) was used. To obtain the OSI induction time, a stream of purified air

Table 1
FA composition, OSI values, k_{232} and k_{270} values of samples before the thermal treatment.[a]

	A	B	C
C16:0	15.43 ± 0.01	10.52 ± 0.02	12.79 ± 0.12
C16:1 A	0.13 ± 0.00	0.11 ± 0.00	0.12 ± 0.01
C16:1 B	1.27 ± 0.00	0.58 ± 0.00	1.07 ± 0.01
C17:0	0.06 ± 0.00	0.16 ± 0.00	0.04 ± 0.01
C17:1	0.10 ± 0.00	0.23 ± 0.00	0.08 ± 0.00
C18:0	2.01 ± 0.01	2.73 ± 0.02	1.78 ± 0.01
C18:1 *n*−9	65.64 ± 0.01	76.01 ± 0.07	72.81 ± 0.13
C18:1 *n*−7	3.26 ± 0.01	1.68 ± 0.03	2.79 ± 0.02
C18:2	10.34 ± 0.01	6.40 ± 0.01	7.10 ± 0.03
C20:0	0.38 ± 0.00	0.40 ± 0.00	0.30 ± 0.00
C18:3 *n*−3	0.95 ± 0.00	0.77 ± 0.00	0.76 ± 0.01
C20:1	0.29 ± 0.01	0.27 ± 0.00	0.26 ± 0.01
C22:0	0.12 ± 0.00	0.13 ± 0.00	0.09 ± 0.00
OSI time (h)	11.35	32.15	20.20
k_{232}	2.59 ± 0.10	2.29 ± 0.35	3.23 ± 0.40
k_{270}	0.10 ± 0.01	0.15 ± 0.01	0.26 ± 0.00

[a] Data are expressed as mean of three determinations, with the standard deviations (except for OSI time). Fatty acid composition, determined by gas chromatography analysis and expressed as percentages; OSI time, oxidative stability index expressed as hours and hundredths of hours; k_{232} and k_{270} values determined by spectroscopic analysis.

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