LWT - Food Science and Technology 51 (2013) 44–50

Contents lists available at SciVerse ScienceDirect

LWT - Food Science and Technology

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

Effect of natural and synthetic antioxidants on the oxidative stability of walnut oil under different storage conditions

Marcela L. Martínez [a], Ma. Cecilia Penci [b], Vanesa Ixtaina [c], Pablo D. Ribotta [d], Damián Maestri [a,*]

[a] Instituto Multidisciplinario de Biología Vegetal (IMBIV, CONICET-UNC), Instituto de Ciencia y Tecnología de los Alimentos (ICTA), Facultad de Ciencias Exactas, Físicas y Naturales (FCEFyN-UNC), Av. Vélez Sarsfield 1611, X5016GCA Córdoba, Argentina
[b] Facultad de Ciencias Exactas, Físicas y Naturales (FCEFyN-UNC), Av. Vélez Sarsfield 1611, X5016GCA Córdoba, Argentina
[c] Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), (CONICET La Plata), Facultad de Ciencias Exactas, UNLP. Calles 47 y 116, 1900, La Plata, Buenos Aires, Argentina
[d] Instituto de Ciencia y Tecnología de Alimentos Córdoba (ICTA), CONICET-UNC, Departamento de Química Industrial y Aplicada, Facultad de Ciencias Exactas, Físicas y Naturales (FCEFyN-UNC), Av. Vélez Sarsfield 1611, X5016GCA Córdoba, Argentina

ARTICLE INFO

Article history:
Received 5 July 2012
Received in revised form
25 October 2012
Accepted 26 October 2012

Keywords:
Walnut oil
Antioxidants
Storage conditions
Oxidative stability
Shelf life

ABSTRACT

The aim of the work was to evaluate the combined effects of the storage condition (six months under fluorescent light – 800 Lux – or darkness condition, both at room temperature) with the addition of natural (rosemary extract, RE) and synthetic (ascorbyl palmitate – AP -, and Tert-butylhidroquinone – TBHQ) antioxidants on quality indices related to walnut oil (WO) oxidative stability. Neither RE nor synthetic antioxidants contributed markedly on inhibiting photo-oxidative degradation, resulting in significantly increased amounts of primary and secondary oxidation products in oils exposed to light. Under darkness-storage condition, the addition of the mentioned antioxidants significantly reduced lipid oxidation and improved oil shelf life. Oils added with RE – alone or in combination with TBHQ or TBHQ plus AP – maintain an acceptable quality at least up to six months of storage. Results from this work stressed the influence of the illumination condition on WO oxidative stability, suggesting that this oil should be stored in containers with light-barrier properties, and may be added with the antioxidants examined in the current study.

1. Introduction

Walnut (*Juglans regia* L.) is a crop of high economic interest to the food industry. The edible part of the fruit (the seed or kernel) is globally popular and valued for its nutritional, health and sensory attributes. The high oil and essential fatty acid contents of the walnut kernel make it a good source for commercial production of edible oil. Oil contents as high as 740 g/kg kernel (Soxhlet extraction, *n*-hexane) have been reported for some commercial walnut varieties (Martínez, Mattea, & Maestri, 2006; Martínez & Maestri, 2008).

Walnut oil (WO) can be extracted easily by screw pressing (Martínez, Mattea, & Maestri, 2008). Employing a pilot plant screw-press, the highest oil recovery (660 g/kg kernel) was achieved at 7.5 g/100 g kernel moisture and 50 °C pressing temperature. Fresh WO is very low in free fatty acid concentration, peroxides and phosphatides (Martínez, Labuckas, Lamarque, & Maestri, 2010) because of which it may be consumed directly, without refining.

Walnut oil is composed mainly of triglycerides, in which monounsaturated (oleic acid mainly) and polyunsaturated fatty acids (PUFAs, linoleic and α-linolenic acids) are present in high amounts (Amaral, Casal, Pereira, Seabra, & Oliveira, 2003; Crews et al., 2005; Martínez et al., 2006). According to Simopoulos (2002) WO has a perfect balance of *n*-6:*n*-3 PUFAs, a ratio of 4:1, which was showed to decrease the incidence of cardiovascular risk (Bucher, Hengstler, Schindler, & Meier, 2002). Although it seems clear that such fatty acid composition is favorable from a nutritional point of view, higher contents of linoleic and linolenic acids result in poorer oxidative stability and shorter shelf life of the oil. When PUFAs are exposed to environmental factors such as air, light and temperature, oxidation reactions produce undesirable flavors, rancid odors, discoloration and other forms of spoilage. The primary autoxidation products are hydroperoxides, that have no

Abbreviations: AP, ascorbyl palmitate; CD, conjugated dienes; CT, conjugated trienes; DPPH, 2,2-diphenyl-1-picrylhydrazyl; FAMEs, fatty acid methyl esters; OSI, oxidative stability index; p-AV, *p*-anisidine value; PF, protection factor; PUFAs, polyunsaturated fatty acids; PV, peroxide value; RE, rosemary extract; RSC, radical scavenging capacity; TBHQ, tert-butylhidroquinone; WO, walnut oil.

* Corresponding author. Tel.: +54 0351 4334141; fax: +54 0351 4334439.
E-mail address: dmaestri@efn.uncor.edu (D. Maestri).

0023-6438/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.lwt.2012.10.021

taste and flavor, but their degradation products (aldehydes, ketones) are very potent taste and flavor modifiers (Frankel, 2005).

Beyond their chemical composition, the susceptibility of vegetable oils to oxidation also depends on the processing, packing and storage conditions. In a recent work (Martínez, Barrionuevo, Nepote, Grosso, & Maestri, 2011) we determined that WO is highly susceptible to photo-oxidative degradation. When it was stored in transparent glass bottles, exposed to fluorescent light (1100 Lux) and room temperature conditions, without addition of any antioxidant, it could maintain an acceptable quality until two months of storage. This time represents a very short shelf life. Protection against light and addition of appropriate natural or synthetic antioxidants are necessary to preserve WO from oxidation.

Antioxidants can increase shelf life of food products by retarding lipid oxidation. Although synthetic antioxidants are extensively used as food additives, their safety has been questioned (Shahidi & Zhong, 2005) stimulating the search and evaluation of natural compounds with antioxidant properties. As a result, there is a great interest for obtaining and utilizing the antioxidants from natural sources because they are presumed to be safe (Shahidi & Zhong, 2005). Many naturally-occurring compounds from herbs and spices have been extensively studied for their antioxidant activity (Frankel, 2005; Maestri, Nepote, Lamarque, & Zygadlo, 2006; Yanishlieva & Marinova, 2001; Zhang et al., 2010). Among these, rosemary extracts (RE) have been widely used in food systems, and some of them are today available in the market.

Ascorbic acid (AA) is an organic acid occurring widely in the vegetable world. It has a number of antioxidants actions including reaction with free-radical species, as singlet oxygen quencher (Frankel, 2005). Unfortunately, it has very low solubility in pure oils. Ascorbyl palmitate (AP) is a synthetically-derived oil-soluble ester of AA. Although the mechanism of action is not well known, Lee, Jung, and Kim (1997) have reported that AP can act as an effective oxygen scavenger in photosensitized oxidation reactions of vegetable oils.

A number of works have reported on the effect of storage and packing materials on shelf life of shelled walnuts (Bakkalbaşi, Yilmaz, Javidipour, & Artik, 2012; Mexis, Badeka, Riganakos, Karakostas, & Kontominas, 2009): However, up to the moment, there are no reports regarding the effect of added antioxidants and storage conditions on WO oxidative stability. Packing materials with barrier properties against light have been successfully used to protect oils from photo-oxidation (Frankel, 2005; Torres & Maestri, 2006). Ideal containers for oils should be opaque to light and impermeable to air and moisture. Plastic containers are generally used mainly because they allow saving on cost. However, the storage stability of oils containing added antioxidants seems to be lower in plastic containers than in glass bottles (Frankel, 2005).

Torres and Maestri (2006) showed that glass bottles wrapped with aluminum foil were the most appropriate containers to protect olive oils against both photo-oxidative degradation and hydrolytic rancidity. On the other hand, aluminum-coated packages were successfully used to preserve partially defatted walnut flour, mainly because of their light-barrier properties (Labuckas, Maestri, & Lamarque, 2011).

Walnut oil is produced at a small scale in many countries such as France, Spain, Chile and Argentina. Increasing demand for WO consumption encourages finding appropriate methods to enhance its shelf life keeping oil oxidation at the lowest possible level. This work was aimed to evaluate the combined effects of the storage condition (six months under fluorescent light – 800 Lux – or darkness condition, both at room temperature) with the addition of natural (RE) and synthetic (AP and TBHQ) antioxidants on quality indices related to WO oxidative stability.

2. Materials and methods

2.1. Materials

Walnut fruits (*J. regia* L. var. Franquette) were obtained from commercial plantations at Belén location, Catamarca Province, Argentina. At full maturity, fruits were hand-picked directly from the trees. Immediately after harvest, fruits were hulled manually and nuts were dried in an oven at 30 ± 2 °C, in the dark, for one day. Then, nuts were shelled manually, and kernels containing about 740 g oil/kg (dry basis) and 40 g water/kg were immediately processed for oil extraction. Kernels were ground using a home-made stainless steel roller crusher and particles between 2.4 and 4.8 mm (mesh 8-4, Tyler standard screen scale) were selected using an automated screen. This material was sprinkled with distilled water according to Singh and Bargale (2000). Sprinkling was achieved by using a predetermined quantity of water so that the final moisture content of the sample to be pressed was about 75 g/kg. This moisture level was found to give the highest oil recovery when kernels where screw-pressed (Martínez et al., 2008). The water sprinkled sample was then packed in an air-tight, cylindrical stainless steel container, and stored about 48 h for equilibration. The container was shaken at regular time intervals to distribute moisture uniformly throughout the sample. Walnut oil extraction was carried out essentially following the procedure of Martínez et al. (2008). Oil expression was carried out at 50 °C using a Komet screw press (Model CA 59 G, IBG Monforts, Mönchengladbach, Germany), with a 5 mm restriction die and a screw speed of 20 rpm. The screw press was first run for 15 min without seed material but with heating *via* an electrical resistance-heating ring attached around the press barrel, to raise the screw-press barrel temperature to the desired temperature. Running temperature was checked with a digital thermometer inserted into the restriction die. The oil obtained was filtered through a series of cartridge filters from 100 to 2 μm pore size. This procedure allowed eliminating very fine solid particles, so that a filtered oil sample subjected to centrifugation (11,000 × g for 30 min) did not show precipitated solids.

2.2. Experimental design for storage stability test

The antioxidants (RE, AP, TBHQ) or their mixtures were added to oil samples (filtered WO) according to quantities stated in Table 1. Briefly, the additives were dissolved in 50 mL-oil aliquots by using a shaker (approximately 5 min) until a homogeneous oil appearance was achieved. The mixtures (oil plus additive) were transferred separately into transparent glass bottles (250 mL) each containing 200 mL fresh WO. The bottled oils (final volume 250 mL) were mixed thoroughly and then placed inside a thermostated chamber at 25 ± 1 °C. Two sets of bottled oils were prepared: one set was stored under illumination (800 Lux); the other one was kept in the darkness by wrapping each bottle with an aluminum foil. Each treatment (consisting of a combination from oil plus additive/illumination condition) was prepared in duplicate. For the control treatments, oil samples without added antioxidants were used. Oils were stored for six months. Every fifteen days each individual oil sample was withdrawn from the chamber for scheduled analyses.

2.3. Chemical analyses

Acid, peroxide (PV), K_{232} (conjugated dienes, CD), K_{270} (conjugated trienes, CT) and *p*-anisidine (p-AV) values were evaluated using standard AOCS (2009) methods.