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Thermal stability and long-chain fatty acid positional distribution on glycerol of argan oil

Farid Khallouki [a,*], Luisa Mannina [b,c], Stéphane Viel [d], Robert W. Owen [a]

[a] Division of Toxicology and Cancer Risk Factors, German Cancer Research Center (DKFZ), Im Neuenheimer Feld 280, D-69120 Heidelberg, Germany
[b] Università degli Studi del Molise, Dip. STAAM, I-86100 Campobasso, Italy
[c] CNR, Istituto di Metodologie Chimiche, I-00016 Monterotondo Scalo, Italy
[d] Aix-Marseille Université, ISM2-UMR-6263, Centre de Saint Jérôme, Avenue Escadrille Normandie Niémen, Case 512, F-13397 Marseille cedex 20, France

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Abstract

The primary aim of this study was to determine the oxidative stability of argan oils by using peroxides and conjugated diene hydroperoxides measurements as analytical indicators. Both food and cosmetic argan oils were investigated. Their oxidative stability was also determined by monitoring the relative changes of their fatty acid profiles by ^{1}H NMR. In addition, valuable information regarding minor components as well as the acyl positional distribution, were obtained for both grades by high field ^{1}H and ^{13}C NMR, respectively. Given that the cosmetic and food grades have a similar profile and content of phenolic antioxidants, vitamers, and squalene, it appears that the ratio of fatty acid aliphatic to bisallylic CH_2 groups, much higher in argan oils than in other vegetable oils, is responsible for their higher thermal stability.
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Keywords: Argan oil; Thermal stability; Regiospecificity; High field; ^{1}H and ^{13}C NMR

1. Introduction

Lipid oxidation is not only responsible for unpleasant flavours in foods but can also produce harmful reactive oxygen species (ROS) that may lead to carcinogenesis, mutagenesis and ageing in humans (Ferrari & Torres, 2003, chapter 7). Increasing evidence shows that antioxidant compounds may prevent cardiovascular diseases and cancers generated by ROS (Bartsch, Nair, & Owen, 2002; Gutteridge & Halliwell, 1994). Vegetable oils are important sources of antioxidants and contain essential long-chain fatty acids necessary for the proper development of human tissue (FAO, 1978).

Recent studies (Charrouf & Guillaume, 1999; Drissi et al., 2004; Khallouki, Spiegelhalder, Bartsch, & Owen, 2005) suggest that the dietary argan oil, an endemic Moroccan seed oil ecologically and socioeconomically important in the South–West of Morocco, plays a relevant role in disease prevention.

Traditionally, argan oil is mostly used for nutritional and cosmetic purposes (Charrouf & Guillaume, 1999). The unsaponifiable fraction of argan oil contains a large range of bioactive substances including tocopherols, terpenes, alcohols, sterols, as well as traces of phenolic compounds. (Farines, Charrouf, & Soulier, 1981; Khallouki et al., 2003). Moreover, with respect to other seasoning oils, argan oils contain a higher amount of squalene, which can be as high as 3.2 g kg^{-1} (Khallouki et al., 2003).

Typically, rancidity generated in oils during oxidation processes is commonly evaluated by measuring the amount of peroxides (AOAC, 1990) and diene hydroperoxides (Chan & Levett, 1977) formed over time. Vegetable oils have also been characterized by ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy (Gunstone, 1990; Mannina, Luchinat, Carmela Emanuele, & Segre, 1999; Mannina et al., 2000); in particular, this technique has been applied to estimate the

* Corresponding author. Tel.: +49 622 142 3317; fax: +49 622 142 3359.
E-mail address: Khallouki.Farid@claudiusregaud.fr (F. Khallouki).

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thermal stability of canola and soybean oils (Wanasundara, Shahidi, & Jablonski, 1995).

In this paper, we have investigated two argan oil grades (food and cosmetic). Firstly, by using both peroxide measurements and ^{1}H NMR, we have studied the impact of changing the storage condition of argan oils. Secondly, using high field ^{1}H and ^{13}C NMR, respectively, we have obtained valuable information on minor components and determined the fatty acid distribution of triglycerides on the glycerol moiety of the oils.

2. Materials and methods

2.1. Samples

Food and cosmetic grades of argan oil were kindly donated by the argan Oil Women's Cooperative (Targanine), Tamanar (Essaouira region), Morocco. Cosmetic and food argan oils were extracted from kernels by mechanically cold press. For the food grade the extraction was performed on roasted kernels.

Oil samples (25 mL) were placed in sealed clear Pyrex containers (20 mm diameter and 50 mm height) wrapped with aluminium foil and kept in the dark in an oven at 60 °C for a period of 30 days. To estimate the oil thermal stability, samples were periodically removed after a period of 0, 5, 10, 20, 25, and 30 days. After removal and prior to the chemical analysis, all samples were flushed with nitrogen.

2.2. Peroxides and dienes hydroperoxides analysis

The peroxide values were determined iodometrically (AOAC, 1990). Specifically, 5.0 g of oil were introduced into a 250 mL Erlenmeyer glass with 50 mL of an acetic acid–chloroform solution (3/2, v/v). The flask was vortexed until dissolution and then 0.5 mL of a saturated KI solution was added. This solution was allowed to stand for one minute, and then 30 mL of distilled water were added. Titration was performed by adding exactly 0.010 N of $Na_2S_20_3$ until the yellow colour disappeared: a starch indicator (0.5 mL) solution was used. Peroxide (P) values are expressed in milliequivalents of active oxygen per kilogram of oil (meq O_2 kg^{-1}).

The conjugated diene hydroperoxide values were determined spectrophotometrically with a Kontron UNVIKON 930 spectrophotometer by using an absorptivity of 26,000 ($\lambda_{max} = 234$ nm), as previously reported by others (Chan & Levett, 1977). Specifically, every 5 days, the oil samples were diluted in isooctane and the absorbance of the resulting solutions were measured. Conjugated diene (CD) values are expressed in millimoles per kilogram of oil (mmol kg^{-1}).

2.3. NMR spectroscopy

Low field ^{1}H NMR spectra were recorded on a BRUKER AC250 NMR spectrometer operating at a ^{1}H Larmor frequency of 250 MHz. Argan oil samples (35 mg) were dissolved in $CDCl_3$ (0.7 mL). The ^{1}H spectra were monitored every five days during the thermal treatment.

In addition, high field ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 600 NMR spectrometer operating at a Larmor frequency of 600 and 150 MHz for ^{1}H and ^{13}C, respectively. To record the ^{1}H spectrum, 0.02 mL of the argan oil samples were dissolved in a mixture composed of DMSO-d_6 (0.02 mL) and $CDCl_3$ (0.7 mL). For the ^{13}C spectrum, 0.1 mL of the samples were dissolved in 0.7 mL of $CDCl_3$.

In all cases the ^{1}H and ^{13}C chemical shifts were referenced to tetramethylsilane, used as an internal standard.

The experimental procedure required for calculating the aliphatic/diallylmethylene ratio (R_{ad}) and the aliphatic/oleic ratio (R_{ao}) as well as the full experimental methodology required for estimating the percentage of fatty acids on the glycerol positions, have been described elsewhere (Wanasundara et al., 1995; Mannina et al., 1999). Specifically, in the case of the acyl positional distribution, it is sufficient to measure the intensity of each of the six ^{13}C NMR signals between 172 ppm and 173 ppm in the spectrum (Fig. 4). The results are reported as molar percentages calculated by measuring the intensity of each carbonyl resonance with respect to the sum of the intensities of all carbonyl resonances taken as 100%.

2.4. Statistical analysis

Peroxide (P) and conjugated diene (CD) measurements as well as ^{1}H and ^{13}C NMR experiments were run in duplicate. Differences were evaluated using Student's test at the 5% significance level.

3. Results and discussion

3.1. Thermal stability

To evaluate their thermal stability, both argan oil grades were kept in the dark at 60 °C for 30 days, and the peroxide (P) and conjugated diene (CD) values were monitored for both argan oil grades. Note that, although the P value may not entirely reflect the actual extent of oil deterioration, it is typically used for monitoring the storage condition of oils (AOAC, 1990). Accordingly, the evolutions as a function of time of the P and CD values are reported in Figs. 1, 2, respectively. In both cases, the extremely low P and CD values observed at the very beginning of the thermal treatment, probably due to the oil storage at the Cooperative, suggest the good quality of the oils.

Clearly, hydroperoxides are formed in both grades, and the P value observed for the cosmetic grade is higher after 30 days.

On one hand, it is important to observe that in argan oils the P value does not show any initial stability, often present in other vegetable oils, thus not giving any indication on an induction period. This result suggests that the

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