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# Composition and properties of virgin pistachio oils and their by-products from different cultivars

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ABSTRACT

Pistachios (*Pistacia vera*) exhibit an interesting nutritional value, due to the high content of oleic acid and minor components with antioxidant and bioactive properties. This work aimed to characterize pistachio virgin oils and their partially defatted residual cakes, obtained from eight cultivars (Aegina, Avdat, Kastel, Kerman, Larnaka, Mateur, Napoletana, and Sirora). Interesting results on phenolics, tocopherols and antioxidant activity were observed, which were greatly affected by variety. Pistachio virgin oils are rich in healthy oleic acid (55–74%), phytosterols (3200–7600 mg/kg) and γ-tocopherol (550–720 mg/kg). A high content of phenolic compounds (8600–15000 mg/kg gallic acid equivalents) and the corresponding antioxidant activities (12–46 and 155–496 mmol/kg for DPPH and ORAC) of the residual cakes demonstrate their potential applications as functional ingredients and as rich sources of bioactive compounds. Moreover, virgin pistachio oils possess peculiar and pleasant sensory characteristics, contributing greater added value to the consumers compared to refined vegetable oils.



## 1. Introduction

Nuts (walnuts, pistachios and almonds) are considered a fundamental component of a healthy diet. They are rich in protein and fat, with a balanced content of mono- and polyunsaturated fatty acids, and contain other nutrients, as well as many bioactive compounds, such as antioxidants that can beneficially impact health outcomes (Kamal-Eldin & Moreau, 2010; Salas-Salvadó, Casas-Agustench, & Salas-Huetos, 2011). Evidence suggests that nuts can lower low-density lipoprotein-cholesterol levels and hence, reduce the risk of coronary heart disease (Kris-Etherton, Zhao, Binkoski, Coval, & Etherton, 2001). This has been confirmed by the PREDIMED study (Prevention with Mediterranean Diet) and other epidemiological or clinical trials, which have also indicated that a high intake of nuts can lower the incidence of hypertension, metabolic syndrome, diabetes, cancer, other inflammatory conditions and total mortality (Mohammadifard et al., 2015; Salas-Salvadó et al., 2008). In July 2003, the United States Food and Drug Administration (FDA) approved the first qualified health claim specific to seeds and the risk of heart disease, quoting that "scientific evidence suggests but does not prove that eating 1.5 oz (42.5 g) per day of most nuts, such as pistachios, as part of a diet low in saturated fat and cholesterol may reduce the risk of heart disease". Among nuts, pistachios (*Pistacia* spp.) exhibit interesting nutritional properties because they contain cardioprotective constituents, such as a high oleic acid content, phytosterols, phenolics and tocopherols, resulting in a high antioxidant and anti-inflammatory potential (Bulló, Juanola-Falgarona, Hernández-Alonso, & Salas-Salvadó, 2015; Yildiz, Gurcan, & Ozdemir, 1998).

*Pistacia* spp. is a plant of the Anacardiaceae family native to central and Western Asia and estimated to be ~80 million years old. *Pistacia vera* L. is cultivated as an agricultural crop in California, the near East and Mediterranean Europe (Couceiro et al., 2013). Iran has been a major pistachio producer for 3000–4000 years and is currently one of the main producers alongside USA and Turkey (415,000, 230,000 and 80,000 tons, respectively, in 2014; FAOSTAT data). Pistachio was first planted in Spain in 1996 and in 2016 the cultivation area was over 15,000 ha, with 12,000 ha (80%) corresponding to Castilla-La Mancha (MAGRAMA data, Spanish Ministry of Agriculture). The most important cultivars are Aegina, Avdat, Kastel, Kerman, Larnaka and Mateur (Couceiro et al., 2013), which were characterized in the current study. Pistachios are normally consumed as salted and roasted snacks or as an ingredient in bakery and confectionery products, desserts, and ice-creams.

With the increasing consumption and demand for novel edible oils, virgin oils obtained from nuts are receiving particular attention due to their potential nutritional properties, resulting in novel

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healthy oils. Moreover, their attractive and peculiar sensory characteristics give rise to gourmet oils, which provide added value to the consumer compared to traditional refined vegetable oils (Kamal-Eldin & Moreau, 2010); 'cold-pressed' oils (as defined by FAO-WHO Codex Stan 2010) are recognized as the highest quality oils. Virgin oils obtained from pumpkin, argan, avocado, sunflower, hazelnut, coconut and hemp seeds, for example, are commercially available as "specialty foods" and are principally used in gastronomy (Matthaus, 2008), confectionary (Martínez et al., 2016), but also in cosmetic formulations (Hannon, 1997). These virgin oils are often produced in small-scale artisanal mills and sold in gourmet and health markets. Pistachio oil is not described by the current Codex Alimentarius on Fats and Oils (FAO-WHO), but it is prized as a specialty oil, owing to its beneficial effects on human health. Commercial pistachio oil products have appeared in some Middle Eastern and European countries, mainly as a salad dressing or gourmet oil, although they are also used for cosmetic and therapeutic products.

Edible oils from nuts can be manufactured using various methods: mechanical systems (expeller or hydraulic press types), supercritical fluids and solvent extraction-based that requires refining processes greatly reducing its content in high value minor components, like antioxidants and aromatics. Pressure methods are the most common used to obtain virgin pistachio oil. It is relevant to remark that consumers are becoming more concerned about consuming more beneficial health products and less-processed foods. The pressing process generates a partially defatted by-product (residual cake), which retains polar bioactive compounds. Thus, there is considerable interest in the valorization of the cake as a functional ingredient in the production of various novel foods (Martínez et al., 2016).

The current study aimed to determine the composition of virgin pistachio oils and their residual cakes, obtained from eight different pistachio cultivars, as well as characterize the corresponding antioxidant and sensory properties, to highlight their added-value and potential applications. Indeed, an increasing demand for advancing in the knowledge on virgin edible nut oils and nuts functional extracts, for their potential nutritional and healthy properties as well as their attractive and peculiar sensory characteristics, is shown by both consumers and producers.

## 2. Materials and methods

### 2.1. Pistachio samples

Eight pistachios varieties (Aegina, Avdat, Kastel, Kerman, Larnaka, Mateur, Napoletana and Sirora; 10–15 kg each) were provided by the regional research centre 'Centro de Mejora Agraria El Chaparrillo' (Ciudad Real, Spain) during the 2013/14 and 2014/15 harvest seasons.

### 2.2. Virgin pistachio oils

The oil was extracted using a screw press (Komet Screw Vegetable Oil Expeller CA59G-CA563, IBG Monforts Oekotec GmbH & Co. KG, Mönchengladbach, Germany) equipped with a 6 mm diameter nozzle and operating at a screw speed of 30 rpm. The screw press was first run empty for 10–15 min to raise the screw-press barrel temperature to the minimum required for extracting the oil (about 50 °C) using the electrical resistance ring attached around the press barrel. The resulting crude oil (approximately 1.0–1.2 L of each variety) was centrifuged at 5000 rpm to remove the residual plant material. Oil samples were stored in amber bottles, without headspace, to protect them from light and the residual cakes were placed in labeled pouches and vacuum-packed to prevent any oxidative degradation. All samples were stored in the dark at 4 °C until analyzed. Three commercial pistachio virgin oils were also studied.

### 2.3. Moisture and fat content

The water content of the pistachio kernel and the residual cake was determined by desiccation in a vacuum oven at 100 °C to a constant weight. The fat content was determined by Soxhlet extraction, according to the UNE Spanish Standard method 55032.

### 2.4. Fatty acid composition

The methyl esters were prepared by vigorous shaking of a solution of oil in hexane (0.5 g in 3 ml) with 0.5 ml of 2 N methanolic potassium hydroxide and then analyzed by GC using an Agilent Technologies (HP 6890; Santa Clara, CA) chromatograph equipped with a FID detector. A fused silica capillary column (60 m length × 0.25 mm i.d.) coated with SP™-2380 phase (0.2 μm thickness; Supelco, Madrid, Spain) was used. Helium was used as the carrier gas at a flow rate of 1 ml/min. The injector and detector temperature were set at 220 and 250 °C, respectively. The oven temperature was maintained at 185 °C and the injection volume was 1 μl. Individual fatty acid results were expressed as a percentage of the total, according to the European Regulation (EC) 2568/91 and subsequent amendments, corresponding to the American Oil Chemists' Society (AOCS) method Ch 6–91.

### 2.5. Tocopherols

Tocopherols were determined after double extraction**,** according to the AOCS Method Ce 8–89. Briefly, 0.4 g of ground pistachio kernel or residual cake in *n*-hexane (6 + 4 mL) was vortexed for 2 min, followed by 5 min of ultrasound and then centrifugation at 2000*g* for 10 min. Then, the combined extracts were filtered prior to analysis. For pistachio oils, a solution of 0.1 g in 10 mL *n*-hexane was prepared and analyzed on an Agilent Technologies HPLC (1100 series) using a silica gel LiChrosorb Si-60 column (particle size 5 μm, 250 mm × 4.6 mm i.d.; Sugerlabor, Madrid, Spain), with *n*-hexane/2-propanol (98.5:1.5) at a flow rate of 1 ml/min, as the eluent. A fluorescence detector (Waters 470, Milford, MA) was used with excitation and emission wavelengths set at 290 and 330 nm, respectively.

### 2.6. Phenolic compounds

The total polar phenolic (TPP) content was analyzed following the method described by Vázquez, Janer, and Janer (1973) and Gutfinger (1981). Briefly, a double extraction of the solid residue obtained from the *n*-hexane extraction described above was performed in MeOH:$H_2O$:HCOOH (80:20:0.1; 10 + 10 mL), with 2 min vortex, followed by 5 min ultrasound and centrifugation at 2000*g* for 10 min. The combined extracts were filtered prior to analysis.

Virgin oil (5 g) was dissolved in *n*-hexane (10 mL) and 10 ml of MeOH:$H_2O$:HCCOH (80:20:0.1). The mixture was vortexed for 2 min, followed by 5 min of ultrasound and then centrifuged at 2000*g* for 10 min. Finally, the polar fraction was isolated and filtered. Suitable aliquots (100–500 μl) of the polar extracts were transferred into a 10-ml volumetric flask. Water (up to 8 ml) and the Folin–Ciocalteu reagent (0.5 ml) were added. After 3 min, 1.5 ml of saturated (20%, w/v) sodium carbonate solution was added to the reaction mixture. After 30 min, the absorbance of the solution was measured at 725 nm against a blank solution with a UV–visible spectrophotometer (Agilent Technologies 8453). A