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Analysis of the Antioxidant Activity, Lipid Profile, and Minerals of the Skin and Seed of Hazelnuts (*Corylus avellana* L.), Pistachios (*Pistacia vera*) and Almonds (*Prunus dulcis*)—A Comparative Analysis

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Abstract: Nuts are dry, single-seeded fruits with a combination of beneficial compounds that aid in disease prevention and treatment. The aims of this research are to evaluate the total antioxidant activity (AI) by ferric reducing antioxidant power (FRAP) assay, fatty acids by acid-catalyzed esterification method, and minerals by inductively coupled plasma optical emission (ICP-OE) spectrometer in hazelnuts, pistachios, and almond seeds and skins. Considering total AI, the results demonstrated that the highest activity was found in hazelnut and pistachio skin. The results considering minerals demonstrated that manganese, zinc, and iron levels are high in almond and hazelnut skins, copper is dominant in pistachio skin and hazelnut seed, and selenium is high in pistachio and almond skins and seed. Finally, the results showed palmitic acid is present in almond skin and pistachio seed, palmitoleic acid is high in almond and pistachio skins, and stearic acid is present in almond and hazelnut skins. Oleic acid was found in hazelnut seeds and their skin, linoleic acid in almond skin and pistachio seeds, and α -linolenic acid in almond and pistachio skins. In conclusion, hazelnut, pistachio, and almond skins are a great source of antioxidants, minerals, and healthy fatty acids, making them useful for nutraceutical development.

Keywords: almond; antioxidant activity; hazelnut; fatty acid content; pistachio; minerals; nuts

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1. Introduction

Nuts are nutrient-dense, dry fruits that consist of a leaf, a green leafy cover, a seed, hard shell, and a skin. Nuts are, widely consumed as components of healthy diets all over the world [1]. They contain the best nutritional density and possess high quantities of protein and fat, especially unsaturated fatty acids (UFAs) [2]. Nuts also contain dietary

fibers, minerals, vitamins, and various bioactive compounds. Tree nuts are a great source of antioxidants, containing polyphenols and other compounds that can delay or inhibit lipid oxidation and neutralize free radicals [3]. Various epidemiological and experimental data showed that nut consumption is associated with favorable changes in cardiovascular disease (CVD) markers and lower prevalence of CVDs [4]. A randomized cross-over study suggested that incorporating hazelnuts into the diet of hypercholesteremic individuals can reduce CVD risk [5]. This suggestion has been made as a result of measured improvements in lipoprotein profiles and α -tocopherol concentrations in hypercholesteremic participants. Another study concluded that a healthy diet should be enriched with nuts and foods rich in UFAs to reduce blood cholesterol and cardiovascular risk [6].

According to a review covering 20 studies from different regions, including Europe, America, the Western Pacific, and Southeast Asia, it is recommended to consume a handful of nuts regularly to get all the daily required nutrients from nuts. [7]. A recent study demonstrated that exposure to nuts can be hazardous because they contain some toxic elements such as arsenic (As), lead (Pd), and mercury (Hg), but in very low amounts that do not cause any harm to human health. Generally, consuming products with toxic elements above the admissible amount can be threatening to health [8]. Growing interest is nowadays focused on hazelnuts, almonds, and pistachios.

Hazelnut, Corylus avellana L., is classified under the Betulaceae family. The hazelnut tree can adapt well to various climatic conditions, although it prefers cooler areas with moderate altitudes [9]. Typically, hazelnuts are composed of 62% fat (mostly consisting of oleic acid), 16% protein, and 11% carbohydrates, and these values differ depending on cultivation variables like soil, climate, and cultural interventions [10,11]. The protein content in hazelnuts can reach up to 15 g/100 g of the edible part [12]. The major amino acids found in hazelnuts are arginine, glutamic acid, aspartic acid, and alanine. In addition, hazelnuts contain 8.7% fiber and α -tocopherol (vitamin E), that reaches up to 40.6 mg/100 g [12–14]. Hazelnuts have a high antioxidant index, containing 291–875 mg/100 g of polyphenols [15,16]. Usual consumption of hazelnuts seems to aid in the prevention of various diseases like atherosclerosis, coronary heart disease (CHD), and strokes, as well as reducing Alzheimer's disease symptoms [10]. Also, hazelnut consumption lowers overall blood cholesterol in mildly hypercholesterolemic individuals [5], with a significant reduction of low-density lipoprotein (LDL) cholesterol [17]. Hazelnut skin represents approximately 2.5% of the total hazelnut seed weight, and it is considered a by-product of the roasting process [18]. The skin contains 14.5% fat, 8% protein, 7.5% moisture, and 1.7% ash. The main content of hazelnut skin is dietary fiber (67.7%), of which 57.7% is insoluble fiber [19,20]. Moreover, the skin contains about 27% polyphenols that favorably influence antioxidant activity (AI) [21].

Almond (*Prunus dulcis*) is known as a stone fruit belonging to the *Rosaceae* family. Their trees require sustainable irrigation practices for cultivation and development, specifically in arid and dry regions [22]. Almonds, like all nuts, contain high amounts of fat. The European Food Safety Authority (EFSA) panel has indicated that almonds contain around 40–50% fat, with 22% of it being polyunsaturated fatty acids (PUFAs) (mostly linoleic acid) and 70% of monounsaturated fatty acids [23-25]. Furthermore, almonds are observed as a great source of vitamin E, dietary fiber, riboflavin (vitamin B2), and essential minerals including copper, magnesium, phosphorus, and manganese [23]. In addition, almonds contain sugars, mainly fructose and sucrose [26]. Almond also contains high quantities of phenolic compounds that can be highly variable due to the different methods of detection, extraction, quantification, and analysis of these compounds [22]. Various studies have reported the beneficial effects of almond nuts and their extracts for treating diseases. Regular consumption of almonds could reduce CVD risk factors [27] and inflammatory markers such as E-selectin and C-reactive protein [28]. Almond skin is a protective coat for the seed against oxidation and microbial contamination. Furthermore, the skin comprises several quantities of triterpenoids, especially betulinic acid, ursolic acid, and oleanolic

acid, that have anticancer, anti-inflammatory, and antiviral activities against the human immunodeficiency virus (HIV) [22].

Pistachio nuts (*Pistacia vera*) belong to the *Anacardiaceae* family. They are the only commercially cultivated species, while others are mainly used as rootstocks [29]. Pistachios have a high fat content (45.3 g/100 g), are a good source of protein (20.2%) and total dietary fiber (10.6%), with 27.5% of carbohydrates [30]. Pistachio skin is a soft seed coat that is observed as a great source of anti-inflammatory and phenolic compounds, including gallotannins, myricetin, and flavonoids [31,32]. According to Sari et al., consuming 30–80 g/day of pistachios was able to lower total cholesterol by 10.1% and LDL cholesterol by 8.6% [33]. London et al. also reported that healthy and young men had enhancements in their endothelial function, blood glucose levels, and some indices of oxidative and inflammation status when pistachios were added to their usual diet [34]. Furthermore, increasing the consumption of nut seeds may lead to improved sustainability and economic outcomes for total global nut consumption because they are plant-based protein sources rich in antioxidants, minerals, and healthy fatty acids, and they are encouraged by national dietary recommendations.

The aim of the current study is to evaluate and compare samples of hazelnut, almond, and pistachio seeds and skins through the analysis of total antioxidant activity, fatty acid profile, and concentration of selected minerals.

2. Materials and Methods

2.1. Materials

Chemicals used in this study include potassium hydrogen carbonate (purchased from NEN TECH LTL, USA), sodium chloride, hexane, hydrochloric acid, hydrogen peroxide, 2, 4, 6-tripyridyl-s-triazine (purchased from Sigma-Aldrich, Chemie, Schnelldorf, Germany), hexane isopropanol, sodium acetate trihydrate, 2,4,6-Tri(2pyridyl)-s-triazine, ferric chloride (purchased from Fluka Chemicals, Switzerland), methanolic sulfuric acid, acetic acid (AnalaR, United States), and nitric acid (purchased from Kommerling Chemische Fabrik GmbH & Co, Cologne, Germany).

2.2. Sample Preparation

Pistachios (cultivar *P. vera* produced in California), almonds (cultivar *P. dulcis* from Texas), and hazelnuts (cultivar *C. avellana* L. from Oregon) produced in the USA were used for the study. A 500 g of raw pistachios, almonds, and hazelnuts were added to boiling water to separate the seed from its skin. After drying at room temperature or in the oven at 60 $^{\circ}$ C, both seeds and skins were ground into powder and placed in separate air-tight bottles (three replicates of the samples were used).

2.3. Evaluation of Antioxidant Activity (AI)

Benzie and Strain (1996) were the first to use the FRAP assay [35]. According to Al-Laith et al., the Ferric Reducing/Antioxidants Power Assay (FRAP) was used to measure the AI [36]. A volume of 9 mL of acetic acid was added to 1 g of each sample. After being frequently shaken for 1 h, the extracts were centrifuged for 5 min at 4000 rpm. The FRAP solution was prepared by mixing 20 mL of acetate buffer, 2 mL of FeCl₂, and 2 mL of TPTZ (2, 4, 6-tripyridyl-s-triazine). After centrifugation, 3 mL of FRAP solution was added to 0.1 mL of supernatant. At room temperature, the absorbance (A) of each sample was measured at 593 nm immediately after adding the reagent (time = 0 min) and after 6 min in order to assess the changes in absorbance level. To generate the standard curve, ascorbic acid was used in a range of 50–1000 μ M of concentration. The FRAP value has been calculated using the following formula:

FRAP value (μm) = (A593 sample/A593 ascorbic acid) \times concentration of ascorbic acid

2.4. Mineral Element Content

In microwave vessels, 0.5 g of each sample was mixed with 5 mL of 2% HNO₃ and 1 mL of 30% H₂O₂ and digested in the microwave digestion system model MARS 6 (One Tocuch Technology, iWAVE, Dubai, United Arab Emirate). After digestion was completed, samples were filtered using 5.5 cm filter paper (ensuring that all samples were clear) and then diluted to 25 mL with 2% HNO₃ in volumetric flasks. By using the analytical method developed by J.J. Thomson, and according to Naozuka et al., five standards were prepared from multielement stranded solutions containing manganese (257.610 nmg/L), copper (327.393 mg/L), zinc (206.200 mg/L), selenium (196.026 mg/L), and iron (Fe 238.204 mg/L) with different concentrations, diluted from 5 ppm to 1 ppm [37]. An inductively coupled plasma optical emission spectrometer (ICP-OES) (PetroEmphor Co., W.L.L.—avio 200, Doha, Qatar) was used to determine the amounts of mineral elements.

2.5. Extraction of Fatty Acids (FAs)

Following the method of Hara and Radin [38], Karatay et al., an amount of 5.0 g of each sample and homogenized it in 15 mL of a 3:2 (v/v) ratio of hexane-isopropanol [39]. The homogenized samples were centrifuged in an ultra-centrifuge at $11,000 \times g$ rpm and 4 °C for 30 s, then at $5000 \times g$ rpm for 10 min, and the supernatants were collected for the identification of FAs.

The acid-catalyzed esterification method was used to perform the gas chromatographic (GC) analysis of FAs in extracts where the methyl esters are converted to derivatives. For the preparation of methyl ester, the lipid extraction in the hexane/isopropanol phase was transferred to 30 mL test tubes, and then 5 mL of 2% methanolic sulfuric acid was added and vortexed. After that, the mixture was kept in the oven for 15 h at 50 °C for methylation. Subsequently, the tubes were cooled to room temperature, and 5 mL of 5% sodium chloride was added and thoroughly stirred. The methyl esters formed in the tubes were extracted with 5 mL of hexane; the hexane phase was removed, and 5 mL of 2% KHCO₃ was added and allowed to stand for 4 h to separate the phases. Under nitrogen gas flow, the solvent was evaporated from the mixture containing methyl esters at 45 °C. The residue was dissolved in 1 mL of hexane. Samples were transferred into vials and placed into the auto-sampler (with an injection volume of 10 μ L) to be analyzed using a GC with a flame ionization detector (FID) (Perkin Elmer, MA, USA). The separation was performed using a fused carbon-silica column (cross-bonded polyethylene glycol, CARBOWAXTM), with a 0.25 mm diameter, 30 m length, and 0.25 µm film thickness, and a temperature range between 40 and 260 °C. Nitrogen gas was used as a carrier gas (flow rate 0.76 mL/min), and other gases were used (air and hydrogen gases with a flow rate of 450 mL/min and 45 mL/min, respectively). However, the oven temperature was set at 200 °C and held constant for 80 min, the FID temperature was set at 300 °C, and the TCD temperature was set at 150 °C. The injector temperature was maintained at 250 °C with a split ratio of 1:20. The two standards (PUFA1 and PUFA2) that were used for the experiment, comprised of saturated fatty acids (14:00 myristic acid, 16:0 palmitic acid, C18:0 stearic acid), monosaturated fatty acids (C16:1 n7 palmitoleic acid, C18:1 n9 oleic acid, C20:1 n9), and polyunsaturated fatty acids (C18:2 n6 linoleic acid, C18:3 n6 γ-linolenic acid, C22:4 n6 arachidonic acid, C18:3 n3 alpha-linolenic acid, C18:4n3 stearidonic acid, C20:5 n3 eicosapentaenoic acid (EPA), C22:6 n3 docosahexaenoic acid (DHA), and C22:5 n3 docosapentaenoic acid).

2.6. Statistical Analysis

Statistical analysis was performed by Statistical Package for the Social Sciences (SPSS) version 26 (IBM Corporation, Armonk, NY, USA). All data were collected and processed using ANCOVA and descriptive statistics (mean \pm standard error).

3. Results

3.1. Evaluation of Antioxidant Activity

3.1.1. Evaluation of Absorbance

The data in Table 1 and Figure S1 show the total antioxidant value in seeds and skins. At time 0, the AI displays an increase in absorbance at 593 nm, recording the highest absorbance levels in almond nut (0.58 Au; SE = 0.248) and pistachio skin (0.67 Au). After 6 min, the highest absorbance is recorded for hazelnut skin (1.75 Au) and for pistachio skin (1.50 Au), while the highest measured absorbance is found in almond seed (0.63 Au).

Table 1. Variation in antioxidant absorbance at 593 nm of almond, hazelnut, and pistachio seeds and skins at 0 and 6 min, and the mean FRAP values.

Туре	Time (min)	Antioxidants Absorbance Mean (Au) (\pm SE) *	Mean FRAP Value (μ M/100 g) (\pm SE)
	0	0.58 (0.248)	
Almond seed	6	0.63 (0.248)	23.83 (12.54)
	Total	0.61 (0.030)	-
	0	0.20 (0.001)	
Almond skin	6	0.36 (0.002)	80.17 (12.54)
	Total	0.28 (0.300)	
	0	0.19 (0.005)	_
Hazelnut seed	6	0.28 (0.008)	49.17 (12.54)
	Total	0.23 (0.001)	
	0	0.52 (0.007)	
Hazelnut skin	6	1.75 (0.053)	610.50 (12.54)
	Total	1.13 (0.016)	
	0	0.36 (0.044)	
Pistachio seed	6	0.45 (0.046)	49.50 (12.54)
	Total	0.41 (0.030)	
	0	0.67 (0.030)	
Pistachio skin	6	1.50 (0.034)	415.50 (12.54)
·	Total	1.09 (0.001)	-
	0	0.42 (0.057)	
Total	6	0.83 (0.144)	-
	Total	0.62 (0.030)	-

^{*} SE: Standard error.

3.1.2. Evaluation of Antioxidant Activity by FRAP Value

Also, data in Table 1 show the mean FRAP values, showing high values for all skin samples, especially hazelnut skin (610.50 $\mu M/100$ g) and pistachio skin (415.50 $\mu M/100$ g). All groups have the same standard error (SE = 12.54). The mean difference of mean FRAP values is shown in Table 1, where the highest and most significant value detected is observed when hazelnut skin and almond seed (586.66 $\mu M/100$ g) are compared. A significant difference is observed between hazelnut skin, hazelnut seed, and pistachio nut, with a FRAP value of 561.33 $\mu M/100$ g and 561.00 $\mu M/100$ g, respectively. Hazelnut and almond skin have a high FRAP value of 530.33 $\mu M/100$ g.

3.2. Minerals

Data in Table 2 show the amounts (mg/L) of Mn, Cu, Zn, Se, and Fe in 1.0 g of skin and seed samples. The highest amounts of Mn are observed in almond skin and hazelnut seed, at 2.08 mg/L and 1.64 mg/L, respectively. The highest amounts of Cu are found in hazelnut seed (Cu = 0.90 mg/L) and pistachio skin (Cu = 1.76 mg/L). The highest amounts of Zn are found in almond skin (Zn = 2.96 mg/L) and hazelnut skin (Zn = 2.08 mg/L). The highest content of Se is measured in pistachio skin (Se = 1.02 mg/L) and hazelnut seed (Se = 0.52 mg/L). The highest amount of Fe was found in almond skin (Fe = 3.72 mg/L) and hazelnut skin (Fe = 3.06 mg/L).

Table 2. Mineral content (mg/L) in 1.0 g of seeds and skins of almonds, hazelnuts, and pistachios.

Mineral	Almond Seed Mean (±SE) (mg/L)	Almond Skin Mean (±SE) (mg/L)	Hazelnut Seed Mean (±SE) (mg/L)	Hazelnut Skin Mean (±SE) (mg/L)	Pistachio Seed Mean (±SE) (mg/L)	Pistachio Skin Mean (±SE) (mg/L)
Mn	0.44 (0.00)	2.08 (0.02)	1.64 (0.02)	1.48 (0.05)	0.02 (0.01)	0.34 (0.00)
Cu	0.18 (0.08)	0.16 (0.02)	0.90 (0.38)	0.30 (0.03)	0.02 (0.01)	1.76 (0.01)
Zn	1.72 (0.02)	2.96 (0.05)	1.98 (0.21)	2.08 (0.21)	1.80 (0.10)	1.86 (0.10)
Se	0.46 (0.01)	0.46 (0.02)	0.52 (0.01)	0.40 (0.01)	0.50 (0.00)	1.02 (0.24)
Fe	0.56 (0.02)	3.72 (0.08)	0.76 (0.13)	3.06 (0.16)	0.42 (0.05)	1.24 (0.03)

3.3. Measurement of Fatty Acids

The amounts in percentage (based on 100% of product) of different FAs in 100 g of samples, with significant differences between groups, are shown in Table 3. Palmitic acid is present in high quantities in pistachio seed (13.2%) and its skin (8.9%). In addition, they contain the highest amounts of FAs, with palmitoleic acid present in pistachio skin, followed by almond skin. While stearic acid is found at higher percentages in pistachio skin and hazelnut skin Furthermore, oleic acid is present at high concentrations in hazelnut skin and its seed, with percentages of 76% and 67%, respectively. Linoleic acid is present in high amounts in almond skin (34%) and in pistachio seed (34%). Furthermore, α -linolenic acid was found in high amounts in pistachio and almond skin.

Table 3. The mean percentages of fatty acid content in 100 g of almonds, hazelnuts, and pistachios.

Sample	Palmitic Acid, 16:0 Mean (±SE) (%)	Palmitoleic Acid, 16:1 Mean (±SE)	Stearic Acid, 18:0 Mean (±SE)	Oleic Acid, 18:1 Mean (±SE)	Linoleic Acid, 18:2 Mean (±SE)	α-Linolenic Acid, 18:3 Mean (±SE)
Almond seed	7.58 (0.57)	0.60 (0.06)	0.96(0.12)	62.04 (5.42)	26.52 (3.14)	1.12 (1.93)
Almond skin	8.36 (0.89)	1.11 (0.58)	1.37 (0.12)	43.08 (1.30)	36.98 (1.51)	5.65 (2.79)
Hazelnut seed	5.38 (0.63)	0.26 (0.01)	1.04 (0.20)	67.99 (3.26)	21.00 (0.89)	2.09 (1.54)
Hazelnut skin	6.02 (1.12)	0.00 (0.00)	1.41 (0.20)	76.53 (0.44)	14.89 (1.34)	0.00 (0.00)
Pistachio seed	13.12 (5.31)	0.80 (0.09)	0.88 (0.07)	48.20 (2.36)	34.12 (1.79)	4.28 (1.63)
Pistachio skin	8.94 (1.07)	1.45 (0.39)	1.44 (0.05)	44.42 (0.12)	34.04 (0.87)	5.87 (0.39)

SE: Standard error.

4. Discussion

The current study reports the analysis of hazelnut, pistachio, and almond seeds and skins by evaluating their AI, lipid profile, and mineral elements. And, to our best knowledge, there are a limited number of studies conducted to analyze the seeds and skins of tree nuts separately.

The results of this study for total AI evaluation found that hazelnut and pistachio skins have high AI, 610.50 $\mu M/100$ g and 415.50 $\mu M/100$ g, respectively (Figure S1). These results are consistent with the findings summarized in a review using four assays to test the AI, including the FRAP assay, with high AI found in both hazelnut (42.3 μ mol Fe²+/g) and pistachio (192.7 μ mol Fe²+/g) seeds. The high AI values found in their studies are due to the fact that the seeds and skins of nuts are not separated before the analysis. However,

it was unexpected in our study to find that the skins have a higher AI, an indication that the skins may be richer in phenolic compounds in comparison to the seeds.

Regarding the mineral elements, variations were detected in the skin and seed content of Mn, Cu, Zn, Se, and Fe (Figure S2). Our finding showed that pistachio skin samples have the highest amounts of Cu (1.76 mg/L) and Se (1.02 mg/L), while almond skin contains the highest amounts of Mn (2.08 mg/L), Zn (2.96 mg/L), and Fe (3.72 mg/L). These findings are in agreement with another study measuring mineral element contents, where the almond sample had high amounts of Mn (15.62 mg/kg) and Zn (45.38 mg/kg) [40,41]. On the other hand, the pistachio sample had the highest content of Fe (69.57 mg/kg) [42]. The reason behind these differences may be attributed to the different cultivars used, their amounts, and analyzing the whole nut. The mineral content of Mn and Cu in pistachio seed was very low (0.02 mg/L for both) in the present study, which was unexpected.

This study has also investigated the FA profile (Figure S3). It was observed that palmitic acid was high in pistachio seed (13.12%) and pistachio skin (8.94%), while palmitoleic acid and stearic acid were the highest in pistachio skin, at 1.45 and 1.44%, respectively. Hazelnut skin contains the highest amount of oleic acid (76.53%), almond skin with the highest amount of linoleic acid (36.98%), and pistachio skin with the highest amount of α -linolenic acid (5.87%). These findings are similar to those of a study performed in 2012 analyzing the FA content of nuts [43]. The importance of evaluating FA profiles relies on FAs being essential to human health. For example, research indicates that palmitic acid is important for human development and is more commonly found in natural human milk than its substitute [44]. A study conducted among Japanese elders reported positive effects of consuming foods containing oleic acid on cognitive functions, although further analysis is implied [45]. Meanwhile, the lack of α -linolenic or palmitoleic acid amounts in hazelnut skin was unexpected in the current study.

The present study has several strengths, including analyzing the tree nut skins and seeds separately and conducting three methods of analysis while also comparing each nut seed and skin. On the contrary, a few limitations are found, such as the low number of replicates used in our study (three replicates for each sample) and the fact that only a few minerals' elements were detected.

For future studies, researchers may focus on the skin and do further analysis of its phenolic compounds. The main importance of this research is to show the benefits of nut skin and its contents, which may potentially be useful for nutraceutical treatments instead of considering skin as waste material.

5. Conclusions

In conclusion, nuts are nutrient-rich foods that are widely consumed as a part of daily diets. Focusing on hazelnuts, pistachios, and almonds, their seeds and skins are a great source of antioxidants, minerals, and fats (MUFA and PUFA), making them beneficial to overall health. The key findings of this study demonstrated that nut skins have high AIs due to their great quantity of phenolic compounds. Mineral elements were mainly found at high concentrations in almond skin, including Mn, Fe, and Zn and in pistachio skin, including Se and Cu. Regarding fat content, it was found at higher levels in hazelnut skin, specifically oleic acid. These results confirm the importance of consuming hazelnuts, pistachios, and almonds with their skins to optimize the positive effect of these foods on health, in particular on cancer, diabetes, CVDs, and mental disorders. Research projects are needed for the development of nutraceuticals with identification in quantity, dosage, and time of treatment.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/appliedchem3010008/s1, Figure S1: Comparing mean differences of antioxidants values between seeds and skins samples. Figure S2: Different amounts of minerals in mg/L in almond, hazelnut, and pistachio. Figure S3: The fatty acid content in almond, hazelnut, and pistachio seeds and skins.

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