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Unlocking cold-pressed nut potential: focus on tocopherol content of oils and defatted cakes

Marco Panzanini[1], Martina Genesi[1], Giuseppe Zeppa[2], Roberta Dordoni[1]*

[1]Dipartimento di Scienze e Tecnologie Alimentari per una filiera agro-alimentare Sostenibile (DiSTAS), Università Cattolica del Sacro Cuore, via Emilia Parmense, 84, 29122 Piacenza, Italy; [2]Dipartimento di Scienze Agrarie, Forestali e Alimentari (DISAFA), Università degli studi di Torino, largo Paolo Braccini, 2, 10095 Grugliasco, Torino, Italy

***Corresponding Author:** Roberta Dordoni, Dipartimento di Scienze e Tecnologie Alimentari per una filiera agro-alimentare Sostenibile (DiSTAS), Università Cattolica del Sacro Cuore, via Emilia Parmense, 84, 29122 Piacenza, Italy. Email: roberta.dordoni@unicatt.it

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ORIGINAL ARTICLE

Abstract

The research aimed to survey the composition of oil and partially defatted cakes obtained by cold-pressing various tree nuts to enable their use as ingredients for modulating the nutritional properties of final food products. Different types of pistachios (*Pistacia vera)*, hazelnuts *(Corylus avellana)*, and apricot kernels *(Prunus armeniaca)* were evaluated in terms of colour, water activity, moisture, ash, fat, protein, fibre, total phenolic, and tocopherol contents. They were extracted by hydraulic presses, giving oils rich in vitamin E and defatted cakes with high nutritional potential: the cakes preserved significant antioxidant compounds, as well as fat, protein, and fibre levels based on the oil extraction yield. Products derived from cold-pressed nuts revealed promising compositions that could be exploited to develop healthy foods with improved sensorial and techno-functional properties, increasing the sustainability of the process and zeroing waste.

Keywords: apricot kernel, cold-pressed oil, defatted cake, hazelnut, pistachio, tree nuts

Introduction

Thanks to their organoleptic and structural characteristics, tree nuts are suitable for being consumed in their original form or as an ingredient in various food preparations. In addition, they represent an important source of nutrients, unsaturated and polyunsaturated fatty acids, vitamins, and fibre (Brufau *et al*., 2006). Pistachios and hazelnuts are the world's most consumed and produced tree nuts (Alalwan *et al*., 2022). Although not as popular as them, apricot kernel is the by-product of one of the most produced fruits in temperate areas (Gómez *et al*., 1998). The main issue about apricot kernel seed and oil use is the presence of amygdalin (Akinci Yildirim and Atilla Askin, 2010). This can be easily solved by using a sweet variety that contains a small quantity of it, compared to the bitter one (Gorrepati *et al*., 2015). Dried nuts are generally constituted of 50 to 70% fat with unsaturated fatty acid (UFA), mono-unsaturated fatty acid (MUFA) and poly-unsaturated fatty acid (PUFA), proportionally more present than saturated fatty acid (SFA) (Astrup *et al*., 2011; Tvrzicka *et al*., 2011).

Fats should constitute 30% of the nutritional energy requirements in a healthy and balanced diet (Kaya *et al*., 2008). Since the maximum recommended amount of SFA in a diet is 10%, PUFA and MUFA must be most of the intake; in this way, the probability of chronic heart disease can be reduced as much as LDL cholesterol concentration in blood (Król and Gantner, 2020). The apricot kernel contains 7% of SFA and 93% of UFA (Mandalari *et al*., 2021), in hazelnut, the amount of SFA is always

lower than 10% (Lobo *et al*., 2010), while in pistachio, there are 14 % SFA and 86% of UFA (D'Evoli *et al*., 2015). The fatty acid profile is not the only factor influencing the nutritional quality of the dried nuts: they can also contain micronutrients, such as tocopherols, with antioxidant activity (Cherif *et al*., 2021). Considering their importance, EFSA suggests their daily assumption for a healthy lifestyle evaluated as α-tocopherol equivalent (α-TE) (EFSA, 2015a and b). In α-TE calculation is considered the nutritional value of the four homologues (α, β, γ, and δ) for being able to sort them according to their importance and effect (D'Evoli *et al*., 2015). Vitamin E is the most present homologue in the apricot kernel and pistachio is γ – tocopherol, while hazelnut contains predominantly α – tocopherol (Maestri *et al*., 2020; Özcan *et al*., 2013). Nutritional values of the fat fraction, thanks to fatty acids composition and the micronutrients, explain the importance of oil extraction. It is also fundamental to preserve them to obtain a high-value product. According to Özcan *et al*. (2013) and Ahmed *et al*. (2019) there are three main methods for oil extraction: by pressure, by solvent or with a combination of both (Ajibola *et al*., 2002). The most used industrial technique is by solvent, but as demonstrated that this is not the best for preserving the quality of fatty acid composition and tocopherols (Oyinlola *et al*., 2004). The nutritional value loss is a result of the high temperature applied during the process (Ghiasi *et al*., 2022). In recent years, the top-quality oil industry has been developing an interest in the cold-extraction technique thanks to its simplicity, quickness, and safety (Catalán *et al.*, 2017). Cold-pressed extraction is when the temperature never exceeds 30°C (Fantino *et al*., 2020). The two main pressure systems for cold extraction are the screw press and the hydraulic press. Even though being considered cold extraction, the screw press can generate heat and the temperature can go way over 30°C (Sena-Moreno *et al*., 2015) because of friction and pressure required for yield optimisation (Álvarez-Ortí *et al*., 2012). With a hydraulic press, no heat is generated and, as a consequence, the product never goes over room temperature, having a positive impact on the oil, which will achieve a minor level of K270 and peroxides compared to a screw press (Sena-Moreno *et al*., 2015; Roncero Heras *et al*., 2022). However, the temperature reached by the screw press can also have a positive impact on the final product's sensory profile if the raw material is not roasted (Celenk *et al.*, 2020). On the other hand, roasting nuts before extraction with hydraulic pressure improved organoleptic and physicochemical characteristics (Zhang *et al*., 2022). The main issue regarding mechanical cold-press extraction is the yield, which can be around 80% with maximum optimisation (Helstad *et al*., 2022). Thanks to the higher yield and the capacity to work continuously during time screw-press has replaced hydraulic presses in industries and laboratories (Senkoylu and Dale, 1999; Aldobouni *et al*., 2015; Ozyurt *et al*., 2021). The extraction process generates a product that consists of a significant amount of solid, called defatted cake (DFC), which has been used as feed (Deshmukh *et al*., 2022) or biofuel (Calvo *et al*., 2011) in the past years. Unfortunately, the progressive abandonment of the hydraulic press took place without considering its potential. With no heat and only by pressure, it can generate a high-quality product (Sena-Moreno *et al*., 2015; Roncero Heras *et al*., 2022) and a by-product with a potentially higher value than the oil. In the present study, three different types of tree nuts, for a total of five samples including hazelnuts, pistachios, and apricot kernels, were studied with the respective cold-extracted oil and de-oiled cake aiming to evaluate the main changes in the nutritional composition occurring after the oil extraction, by focusing on content and quality of tocopherols. The characterisation will allow different combinations of oils and DFC to achieve the desired nutritional composition in a food product. DFCs are an ideal solution to increase the protein content of nut-based spread creams or, in general, of products for elderly and sports people (without adding different protein sources); they can also exert an important role in the modulation of food structural/lubricant performances.

Materials and Methods

Five different nut kernels (BASE) with the corresponding oils and defatted cake (DFC) were kindly provided by Pariani S.r.l. (Givoletto, Torino, Italy). In detail, samples from two types of hazelnuts (*Corylus avellana*) (a mix of Turkish *Tombur and Palaz cvs.,* and a Piedmont P.G.I. *cv. Tonda Gentile delle Langhe*), two types of pistachios (*Pistacia vera*) (a mix of pistachio types from Sicily *cv. Napoletana,* and a Bronte P.O.D. *cv. Napoletana*), and apricot kernels *(Prunus armeniaca)* (by different types from Turkey) were supplied. Extractions were performed following the industry's parameter: different kernels were roasted and cold-pressed under different pressures and times to separate oils and DFCs. BASEs and DFCs were milled (Retsch GM 200, Retsch, Düsseldorf, Germany) and then analysed for moisture, water activity (aw), ash, fat, protein, soluble and insoluble dietary fibre, total phenolics, tocopherols content, and colour. After the grinding, all samples were stored in vacuum-sealed bags at –21°C without exposure to light. Oils were analysed for tocopherol and colour and conserved at –21°C inside glass bottles with synthetic seals without light exposure.

Process conditions

The Pariani company receives the already shelled nuts and performs the roasting by itself with specific parameters for each type of nut, as described in Table 1.

Table 1. Roasting parameters applied by the company on different nut kernels. *Apricot kernels are only dried and not roasted.

Samples	Temperature (°C)	Time (min)
Piedmont hazelnut P.G.I.	165	38
Turkey hazelnut	165	30
Apricot kernel*	–	–
Bronte pistachio P.O.D.	150	18
Sicilian pistachio	150	18

Table 2. Extraction parameters applied by the company on different nut kernels.

Samples	Pressure (bar)	Time (min)
Piedmont hazelnut P.G.I.	350	130
Turkey hazelnut	350	130
Turkey apricot kernel	400	140
Bronte pistachio P.O.D.	300	100
Sicilian pistachio	300	100

After the roasting treatment, the BASEs are cold extracted with a hydraulic press reaching 400 bar of pressure. The different extraction conditions are summarised in Table 2.

Characterisation analysis

Water activity (a_w)

A water activity meter to analyse solid samples (HygroPalm HP23-AW-A, Rotronic, Bassersdorf, Switzerland) was used to measure aw at room temperature (25°C). Before the analysis, the frozen sample has been removed from the freezer and left sealed, under vacuum, until reaching room temperature.

Moisture and ash

Moisture and ash contents were determined according to 925.40-1925 and 950.49-1950 official AOAC methods for nuts and nuts products, respectively.

Fat content

For fat determination, the 963.15 AOAC method was used as a reference with some modifications. Samples were subjected to a first 8h Soxhlet extraction with petroleum ether; the residual solid fractions underwent acid hydrolysis with HCl 4N and an additional 8h Soxhlet was further extracted. All chemicals used were purchased from Carlo Erba (Cornaredo, Milano, Italy). The oil extraction yields were calculated with a mass balance on the extraction process calculated on the fat percentage before and after the extraction.

Protein content

Protein contents were estimated following the 950.48 AOAC method. The mineralisation process was performed by SpeedDigester K-436 coupled with Scrubber K-415 (Buchi). Samples were distilled (Udk, Velp Scientifica SRL, Usmate Velate, Italy) and then titrated with sulphuric acid 0.1 N (AT1000Series, TitraLab).

Soluble and insoluble dietary fibre content

The analysis has been assessed on BASEs and DFCs previously defatted by 8h Soxhlet extraction with petroleum ether (Carlo Erba, Cornaredo, Milano, Italy). Samples were analysed with K-TDFR-200A Kit (Megazyme, Wicklow, Ireland) about the AOAC method 991.43.

Total phenolic content

The analysis was performed following the method Bassani *et al*. (2020) reported using a micro-volume version of Folin's assay. The absorbance was read at 750nm using a spectrophotometer, Jasco V730 (Jasco Europe S.r.l., Cremella, Lecco, Italy).

Tocopherols

Oil extraction

Five grams of solid sample were weighed into Falcon tubes, and 25 mL of n-hexane (Sigma Aldrich, Milan, Italy) were added; tubes were then covered with aluminium foil to avoid light exposure and left in an orbital incubator (SKI 4 ARGO LAB) at 25°C for 1 h at a shaking speed of 180 rpm. Falcons were centrifugated at 3000 rpm, at 15°C for 15 minutes (Thermo Scientific™ SL16R Centrifuge, Thermo Fisher Scientific Inc., Waltham, USA). Supernatants were filtered through pleated paper filters (Whatman No. 595) inside flasks, placed in the freezer to cool, and then covered with aluminium foil. Oil was collected after vacuum hexane evaporation. The so extracted oil was diluted with the mobile phase and injected. Cold-pressed oil samples were directly diluted into the mobile phase, filtered with paper filters (Whatman No. 595), and injected.

HPLC analysis

Analyses were carried out according to Calvo *et al*. (2011) procedure with an HPLC system composed of a Perkin Elmer (Norwalk, CT, USA) 200 Series pump equipped with a Perkin-Elmer 650-10S fluorescence detector, Jasco LC-Net II/ADC (Oklahoma City, OK, USA) communication module and ChromNAV Control Center as a software. As an injection column, LiChrosorb Si60-5 column 250 mm×4.6 mm, 5 µm (Supelco, Bellefonte, PA, USA) was used, the volume injected was 20 µL, and the mobile phase was hexane:isopropanol:ethanol (98.5:1:0.5) with a flow of 0.6 mL/min. The fluorescence detector was set at 290 nm excitation and 330 nm emission wavelengths.

Each run had a duration of 25 min. The homologue α; γ; β; and δ were identified and quantified in comparison with commercial standards (Sigma Aldrich, Milan, Italy). The results were expressed as mg/100g of oil and mg/100g of product.

Colour analysis

Colour analyses were performed on milled solid products (BASE and DFC) and oil samples (Konica Minolta CR-310). The results were expressed according to CIEL*a*b* colour space. The colour was measured through the three-dimensional colour diagram (L*, a* and b*), where L* indicates lightness (L* = 0 (black), L* = 100 (white)), a* indicates greenness (−a*) or redness (+a*) chromaticity, and b* indicates blueness (−b*) or yellowness (+b*).

The mathematical description of colour difference was established to quantify the visible difference between the colours of two samples. Values of L* a* and b* were used to calculate the colour difference (ΔE) with the following equation:

$$\Delta E^* = \sqrt{(\delta L)^2 + (\delta a)^2 + (\delta b)^2}$$

ΔE can be evaluated in the following way:

- 0 < ΔE < 1 – the difference is imperceptible,
- 1 < ΔE < 2 – the difference is perceptible only for experienced evaluators,
- 2 < ΔE < 3.5 – the difference is noticeable also for inexperienced evaluators,
- 3.5 < ΔE < 5 – observable colour difference,
- 5 < ΔE – observers notice two different colours (Mokrzycki and Tatol, 2011).

Statistical analysis

Cold-press extractions were performed threefold, and each sample was analysed in triplicate. The experimental data's mean and standard deviations (SD) were calculated. The results obtained for samples were evaluated and ranked using a one-way analysis of variance (ANOVA) followed by Tukey's post-hoc test for means discrimination ($p \leq 0.05$). Statistical analyses were executed via the IBM SPSS Statistics 27 software (SPSS Inc., Chicago, IL, USA).

Results and Discussion

Pariani's extraction parameters have been optimised for obtaining the maximum organoleptic evaluation in both DFCs and oils, therefore different BASEs are submitted to different pressures and times to maintain an excellent organoleptic evaluation, not only in the oil but also in the DFC, making it an interesting ingredient for the food industry.

Moisture and water activity (a_w)

Moisture and aw were measured to assess the microbiological safety of raw materials and to analyse the variations that may occur during the extraction process (Table 3).

As shown in Table 3, roasted nuts had a lower and significantly different moisture value than apricot kernels, which were only dried. The roasting and drying processes decreased a_w, bringing all values to less than 0.55. The water activity had a trend that followed the humidity: the lowest value was related to Piedmont P.G.I., and the highest value was for the apricot kernel. With the previous consideration, this was a consequence of the different heat treatments applied to the raw materials. From a microbiological point of view, these values represent a safety limit for the growth of bacteria, moulds and yeasts that cannot be duplicated in that condition (Grant, 2004).

After the extraction, there was a general increase in moisture due to the oil removal and the consequent percentage redistribution of the other constituents. All

Table 3. Moisture and a_w values for nut kernels (BASE) and corresponding defatted cake (DFC) samples.

Samples	BASE		DFC	
	Moisture (g/100g)	a_w	Moisture (g/100g)	a_w
Piedmont hazelnut P.G.I.	0.91±0.00^a	0.40±0.02^a	2.17±0.15^a	0.30±0.01^a
Turkish hazelnut	2.47±0.04^c	0.50±0.01^b	5.36±0.05^d	0.47±0.00^b
Apricot kernel	3.93±0.07^e	0.55±0.00^c	7.80±0.11^e	0.55±0.00^c
Sicilian pistachio	2.18±0.03^b	0.42±0.01^a	4.86±0.10^c	0.50±0.00^c
Bronte pistachio P.O.D.	3.64±0.01^d	0.49±0.00^b	4.59±0.00^b	0.49±0.00^b

Note: Values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

Table 4. Proximate composition of the BASE samples. Results are reported as g/100g of product.

Samples	Ashes	Fats	Protein	Insoluble fibre	Soluble fibre
Piedmont P.G.I. hazelnut	2.01±0.04^{a}	76.17±0.82^{c}	13.43±0.40^{a}	10.93±0.32^{b}	2.56±0.02^{a}
Turkish hazelnut	2.21±0.05^{b}	67.50±0.23^{b}	17.88±0.77^{b}	11.81±0.78^{bc}	2.48±0.24^{a}
Apricot kernel	2.04±0.04^{a}	59.48±0.38^{a}	24.96±0.13^{c}	12.46±0.04^{c}	3.54±0.22^{b}
Sicilian pistachio	2.99±0.00^{d}	61.19±1.66^{a}	25.84±0.20^{c}	9.02±0.48^{a}	5.48±0.13^{c}
Bronte P.O.D. pistachio	2.89±0.00^{c}	57.69±2.94^{a}	25.95±0.59^{c}	9.83±0.32^{a}	3.19±0.11^{b}

Note: Values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

Table 5. Proximate composition of the DFC samples. Results are reported as g/100g of product.

Samples	Ashes	Fats	Protein	Insoluble fibre	Soluble fibre
Piedmont P.G.I. hazelnut DFC	4.82±0.10^{c}	31.77±0.48^{b}	37.30±1.39^{c}	17.22±0.75^{c}	7.26±0.22^{c}
Turkish hazelnut DFC	3.92±0.06^{b}	31.06±0.63^{b}	34.66±0.07^{b}	20.23±0.36^{d}	5.53±0.28^{b}
Apricot kernel DFC	3.74±0.02^{ab}	23.24±0.91^{a}	43.91±0.46^{d}	16.76±0.48^{c}	4.87±0.06^{d}
Sicilian pistachio DFC	3.43±0.18^{a}	43.21±0.46^{c}	32.55±0.48^{a}	13.52±0.60^{b}	4.43±0.25^{a}
Bronte P.O.D. pistachio DFC	3.46±0.14^{a}	45.71±0.07^{d}	32.04±0.01^{a}	10.79±0.44^{a}	5.00±0.23^{a}

Note: Values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

increments were related to the extraction yield (Table 6). The DFC apricot kernels showed the highest value, while Piedmont P.G.I. DFC resulted as the least humid. Before and after extraction, both the hazelnut samples showed a reduction in water activity (Piedmont P.G.I. switched from 0.4 to 0.3), both the pistachio types showed an increase, while the apricot kernel remained unchanged. They all generally remained below the critical safety threshold of 0.55 (Grant, 2004).

Table 6. Oil extraction yield obtained from the different nut kernels (BASEs).

Samples	Extraction yield (%)
Piedmont P.G.I. hazelnut	85.6
Turkish hazelnut	78.1
Apricot kernel	79.3
Sicilian pistachio	50.2
Bronte P.O.D. pistachio	38.4

Nutritional evaluation

To better evaluate the nutritional modifications that occurred during the extraction process, a comparison between the five BASEs and the respective DFCs was necessary. Values reported in Table 4 are related to BASEs characterization.

The sample of Piedmont P.G.I. hazelnuts had a slightly higher fat content than that reported by CREA (2019) (64.1 on 100g of product). The apricot kernel also showed a higher fat content than those described by Femenia *et al*., (1995) (43.4–53.3%). As for Sicilian and Bronte pistachios, the values were quite in line with those described by Celenk *et al*. (2020) (45–59% on 100g), while the sum of insoluble and soluble fibre values was higher than the total dietary fibre content found by Mandalari *et al*., (10.6%) (2021). By correlating data related to the DFC composition (Table 5) with oil extraction yields (Table 6), it can be confirmed that a lower extraction pressure applied on the BASE during processing (Table 2) induced a lower decrease in the oil content and, therefore, a lower yield. This was the case, specifically of both pistachio samples. Instead, the other three samples underwent a significant reduction in fat content leading to a redistribution of the other components within the DFCs.

Li *et al*. (2015) identified 150 °C for 20 min as an optimal time-temperature combination to apply to peanuts before extracting. The authors noted an increase in free oil in peanuts, reaching its maximum value under the previously mentioned conditions. The roasting treatment involves a reduction of the emulsification layer optimising the yield. However, exceeding the temperature can lead to insoluble protein aggregates, which trap the oil and reduce the yield. The same was observed by Ahmed *et al*. (2019) on hazelnuts: increasing the roasting time also improved the yield but also gave a substantial increase in K232 and K270 for treatments over 20 min. Therefore, optimising the roasting step can be considered quality-leading for the entire oil extraction process. This was the only heat treatment to which nut kernels were subjected before being pressed and during which the major transformations of the raw product took place.

Apricot kernel DFC showed the highest protein concentration after oil removal (Table 5). However, the most evident change was in Piedmont P.G.I. DFC, whose protein content switched from the lowest value among samples before extraction, 13.43±0.40% w/w, to 37.30±1.39% w/w in the DFC, thanks to the higher extraction yield. Pistachios offer the opposite example: while overall they were the most protein-rich BASEs, after extraction with the lowest pressure, they had the lowest concentration. These considerations also apply to the other components (i.e., fibre) and can be useful for evaluating the use of DFCs in formulating new products to improve their nutritional properties.

Total phenolic content

It was possible to observe that pistachios were the samples containing the highest amount of total phenolics (Table 7) and the highest quantity found in the oil. Among hazelnuts, the phenolic content of Turkish ones stands out because of the presence of the skins in the BASE sample. In both hazelnut types, there was minimal transfer of phenolics from the BASE to the oil, which, for the Piedmont PGI hazelnut sample, was because the quantity was already reduced at the outset.

It can be observed that in DFCs, the total phenolic content increased due to oil extraction, as detected by Ojeda-Amador *et al.* (2019) and Melo *et al.* (2021), who also noted that a minority of phenolic compounds were transferred to the oil during extraction. The information on nutritional values per 100 g of product relating to DFCs highlighted a lower tocopherol content (see Table 8) but an increase in total phenolic content (Table 7) with a consequent positive effect on the residual antioxidant activity.

Table 7. Total phenolic content (mg GAE/100g of product) in BASE, oil, and DFC samples.

Sample	Total phenolic content (mgGAE/100g of product)	
Piedmont P.G.I. hazelnut	Base	11.11±0.52^{b}
	OIL	7.00±0.20^{a}
	DFC	14.61±0.41^{c}
Turkish Hazelnut	BASE	64.41±1.45^{b}
	OIL	9.59±0.73^{a}
	DFC	141.70±4.45^{c}
Apricot kernel	BASE	58.62±1.59^{b}
	OIL	15.32±0.01^{a}
	DFC	98.77±0.58^{c}
Sicilian Pistachio	BASE	167.56±3.39^{b}
	OIL	35.13±0.08^{a}
	DFC	199.89±10.13^{c}
Bronte pistachio	BASE	150.07±0.73^{b}
	OIL	34.02±0.07^{a}
	DFC	173.64±8.77^{c}

Note: For the same nut sample, values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

Tocopherol quali-quantification

Alpha-tocopherol was the major homologue in Piedmont's P.G.I. and Turkish hazelnuts. At the same γ-tocopherol was predominant in the apricot kernel, and in the Sicilian and Bronte's pistachios (Table 8), as reported by previously cited studies (Turan *et al.*, 2007; Evoli *et al.*, 2015).

In the lipid fraction of DFCs and oils (Table 8), the most present homologues were the same which also appeared to be predominant within the BASEs. The results showed an increase in the concentration of some tocopherols from BASE to DFC samples: in terms of α-tocopherol, for example, Piedmont's and Turkish hazelnut DFCs reached values of 32.74±1.03 and 25.34±3.07 mg/100g oil, respectively. Gamma-tocopherol had a similar trend: apricot kernel and Bronte Pistachio DFCs contained 30.94±2.18 and 29.56±1.85 mg/100g oil, both higher values concerning their BASE samples.

There are few studies correlating tocopherols in oils and their respective cakes. Ojeda-Amador *et al.* (2018b) studied the changes in the cold oil extraction from pistachios. They found variations in the concentration of tocopherols expressed as tocopherol in 100 g of oil. The 400-bar pressure applied for extraction falls into the medium-high pressure category (between 100 and 1000 bar). In this condition, the plant tissues are destroyed, the cell wall is disrupted, and so is the membrane facilitates oil release (Mwaurah *et al.*, 2020). The changes in tocopherol concentration and the apparent increase in the sum of DFC and oil contents, relative to BASE, could be explained as increased extractability due to pressure treatment. Similar results in tocopherol concentration have been reported by Ojeda-Amador *et al.* (2018a), describing an increase in the concentration of the α-homologue in partially defatted flour. A fascinating perspective is offered Melo *et al.* (2021) observed an unexpected distribution of tocopherols, particularly the α- and γ-homologs, among oil, DFC, and BASE. They found lower values of α-tocopherol in the oil than in the residue cakes and an increase in the quantity of γ-tocopherol present in the cold-pressed oil than the original BASE. Seeking an explanation, they noted that Bermúdez *et al.* (2018) highlighted a different distribution of tocopherols based on specific

Table 8. Tocopherols content (mg/100g of oil and mg/100g of product) in BASE, oil, and DFC samples: α, β, γ, δ homologues and total phenolic content of BASEs and DFCs.

		Homologue							
		Alfa		Gamma		Beta		Delta	
		mg/100g of oil	mg/100g of product	mg/100g of oil	mg/100g of product	mg/100g of oil	mg/100g of product	mg/100g of oil	mg/100g of product
Piedmont P.G.I. hazelnut	BASE	21.75±2.64^{a}	16.13±1.61^{b}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	OIL	31.75±0.27^{b}	31.75±0.27^{c}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	DFC	32.74±1.03^{b}	10.40±0.23^{a}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Turkish Hazelnut	BASE	21.00±0.05^{a}	13.80±0.67^{b}	5.30±0.01^{c}	3.48±0.17^{c}	n.d.	n.d.	n.d.	n.d.
	OIL	19.95±0.97^{a}	19.95±0.97^{c}	3.03±0.07^{a}	3.03±0.07^{b}	n.d.	n.d.	n.d.	n.d.
	DFC	25.34±3.07^{b}	7.87±0.68^{a}	5.19±0.09^{b}	1.61±0.02^{a}	n.d.	n.d.	n.d.	n.d.
Apricot kernel	BASE	0.35±0.02^{b}	0.21±0.01^{b}	29.38±2.16^{b}	17.57±1.15^{b}	n.d.	n.d.	3.05±0.18^{c}	1.81±0.08^{c}
	OIL	0.27±0.00^{a}	0.27±0.00^{c}	19.80±1.05^{a}	19.80±1.05^{c}	n.d.	n.d.	1.45±0.03^{a}	1.45±0.03^{b}
	DFC	0.42±0.02^{c}	0.10±0.00^{a}	30.94±2.18^{b}	7.00±0.24^{a}	n.d.	n.d.	2.81±0.01^{b}	0.65±0.00^{a}
Sicilian Pistachio	BASE	1.00±0.01^{b}	0.61±0.01^{b}	25.51±0.82^{c}	15.61±0.36^{b}	6.66±0.07^{b}	4.08±0.03^{b}	1.54±0.02^{b}	0.94±0.01^{b}
	OIL	1.20±0.02^{c}	1.20±0.02^{c}	22.80±0.02^{b}	22.80±0.02^{c}	n.d.	n.d.	1.86±0.04^{c}	1.86±0.04^{c}
	DFC	0.88±0.04	0.38±0.01^{a}	19.85±0.20^{a}	8.58±0.06^{a}	4.35±0.27^{a}	1.88±0.08^{a}	1.42±0.06^{a}	0.61±0.02^{a}
Bronte pistachio	BASE	1.07±0.08^{b}	0.62±0.03^{a}	28.38±0.36^{b}	16.38±0.15^{b}	4.35±0.15^{a}	2.51±0.06^{b}	1.46±0.01^{a}	0.84±0.00^{a}
	OIL	0.86±0.00^{a}	0.86±0.00^{b}	25.66±0.51^{a}	25.66±0.51^{c}	5.39±0.04^{b}	5.39±0.04^{c}	1.49±0.03^{a}	1.49±0.03^{b}
	DFC	1.24±0.10^{c}	0.56±0.05^{a}	29.56±1.85^{c}	13.51±0.84^{a}	4.45±0.03^{c}	2.04±0.02^{a}	1.77±0.01^{b}	0.81±0.01^{a}

Note: For the same nut sample, values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

tocopherol-binding proteins found in tomato cells' chloroplasts. Moreover, the different distribution and quantification may be due to the extraction solvent, which uses hexane for HPLC analysis while the oils are extracted with a hydraulic press, potentially resulting in a different distribution of homologs. Further studies are needed to evaluate better the possible variations that occur by solvent extracting the oil fraction from the BASE and DFC samples for tocopherol HPLC analysis (Rodríguez *et al*., 2023). However, tocopherols (in particular the α-homolog) are generally thermostable (Amaral *et al*., 2006): as a matter, the concentration of α-tocopherol remained high even in the Piedmont hazelnut sample subjected to long roasting treatment at high temperatures. It should be considered that the roasting process is fundamental in creating the aromas of the final product. With a screw press, it is possible to extract the oil and at the same time heat the sample, creating a toasted flavour; conversely, with a hydraulic press, there is no heat involved in the extraction process so that the final product will taste just like raw. Roasting nuts before extraction represents an effective method to increase the flavour of derived products (oil and DFC) (Rabadán *et al*., 2017). If the final aim is to enhance the quality of the final products not only for the aroma but also for the nutritional point of view, nuts containing the most α-tocopherols are preferable. This fact is associated with the role of tocopherols as antioxidant agents, being their antioxidant capacity in vivo α > β > γ > δ (Rodríguez *et al*., 2023).

Each sample was also stated and evaluated as α-tocopherol-equivalent (Table 9) according to EFSA definition (EFSA, 2015b). This conversion allows for a better assessment of the total antioxidant capacity and is not just the sum of the total value of the homologues. The samples rich in α-tocopherol had an advantage compared to the poor ones; this was evident by comparing the two hazelnuts with the other nuts. As noted for individual homologues, a higher concentration of α-TE can be found in DFCs than in BASEs and oils as a general trend. The data, such as α-TE, showed a general increase in concentration in the DFCs that can be almost double that originally present, as in the case of Bronte where BASE had α-TE value of 6.13 while the DFC had 11.82; the only exception was, for the Sicilian pistachio where there was a slight reduction in the DFC and a more significant one in the oil. The extracted oil generally showed a lower α-TE value than the related BASE and DFC, except for Bronte, which had a similar value and the Piedmont hazelnut, which showed a higher value than the BASE.

Colour

The colour differences between BASE and correspondent DFC samples were evaluated by calculating the ΔE value. As they all were greater than 3 (Table 10), it can be stated that the differences in the colours between each BASE and the respective DFC sample were perceptible to the

Table 9. α-tocopherol-equivalents (α-TE/100g of oil, and α-TE/100g of product) referred to the different samples.

Sample	α-TE				
	Base		Oil	DFC	
	on 100g of oil	on 100g of product	on 100g of oil	on 100g of oil	on 100g of product
Piedmont P.G.I. hazelnut	21.75	16.57	31.75	32.74	10.40
Turkish hazelnut	21.53	14.53	20.25	25.86	8.03
Apricot kernel	3.38	2.01	2.30	3.60	0.84
Sicilian pistachio	6.93	4.24	3.54	5.08	2.20
Bronte P.O.D. pistachio	6.13	3.54	6.16	11.82	5.40

Table 10. CIELAB values for oils, and colour differences (ΔE) between DFC and BASE of the related tree nuts.

	Oil			DFC vs. BASE
	L	a	b	ΔE
Piedmont P.G.I. hazelnut	98.41±0.14^{d}	–2.68±0.14^{a}	36.39±0.09^{b}	31.48±0.53
Turkish hazelnut	96.57±0.05^{c}	–1.48±0.05^{b}	45.02±0.10^{c}	11.92±0.30
Apricot kernel	98.31±0.28^{d}	–1.48±0.00^{b}	30.64±0.05^{a}	9.92±0.07
Sicilian pistachio	53.67±0.04^{b}	3.03±0.06^{c}	85.38±0.01^{e}	8.83±0.15
Bronte P.O.D. pistachio	47.94±0.06^{a}	2.87±0.04^{c}	80.90±0.01^{d}	6.47±0.03

Note: Values reported within the same column with different lowercase letters are significantly different ($p \leq 0.05$).

human eye (Mokrzycki and Tatol, 2011). It is possible to make a point on the brightness value (L*): the tendency of L* was to increase on the transition from BASE to DFC with a negative correlation between DFC values and the fat content. Furthermore, the final value of L* was the main factor influencing the ΔE values. A comparison between the oils obtained by pressing the same types of nuts was performed, showing a perceptible difference between the two pistachios and the two hazelnuts with an ΔE value bigger than 7. The colour of the DFC was affected by the removal of the oil, resulting in a whitening effect. It is important also to consider the visual changes in the final product. Using DFCs as ingredients will have a visual impact important for the consumer's perception. If DFCs are intended for direct consumption, colour, especially for pistachios, is a determining factor. Instead, if intended as an ingredient, consumers expect the product to display the typical green colour that characterizes them.

Figure 1. Cold-pressed oil samples.

Conclusions

Cold oil extraction carried out using hydraulic presses has been able to preserve the nutritional value of nuts, giving rise to precious derived products: oils rich in tocopherols and defatted cakes (DFCs) with interesting nutritional properties. The DFCs maintained a valuable amount of fat and an increased concentration of protein, and fibre proportional to the extraction yield. They appeared depleted in lipophilic antioxidants (tocopherols) but at the same time showed an increase in the polar antioxidant components (hydrophilic phenols) due to the concentration effect resulting from oil removal. The

applied oil extraction technique has proven to preserve the above-mentioned examined compounds during the process: the DFCs of Piedmont and Turkey hazelnuts showed the highest values of α-tocopherol equivalents (α-TE) denoting the best biological activity as an antioxidant, while DFCs of Sicilian and Bronte pistachios were the samples containing the highest amount of total phenolics. The results pave the way for further analysis of the technological application for DFCs in the food industry. In particular, by separating the phases as a part of a fractionation and recombination process it will be possible to ensure greater control over the process and the derived products. DFCs will undergo an evaluation of their functional properties to formulate new products.

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