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ORIGINAL PAPER

Effects of peeling and/or toasting on the presence of tocopherols and phenolic compounds in four Italian hazelnut cultivars

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Abstract

Hazelnuts are a well-known source of different healthy molecules. However, only few studies have investigated deeply their amounts considering simultaneously the contribution of the cultivar, the pellicle and the effect of roasting. For such purpose, peeled/unpeeled and raw/toasted samples of "Nocchione", "Tonda di Giffoni", "Tonda Gentile delle Langhe" and "Tonda Gentile Romana" hazelnuts were investigated as regards to their fatty acid composition, tocopherols and total phenolic compounds. Our results indicate that all four cultivars contain a high fraction of mono- and poly-unsaturated fatty acids, about 110–210 mg/kg of tocopherols and, when unpeeled, 1250–2100 mg/kg of phenolic compounds. In particular, unpeeled and toasted "Tonda Gentile delle Langhe" hazelnuts contain more than 2 g/kg dry weight of hydrophilic phenolics and more than 200 mg/kg dry weight of tocopherols. The study confirms that the highest concentration of bioactive compounds is contained in hazelnut's pellicle. Accordingly, a principal component analysis (PCA) demonstrates that removal of the pellicle is associated with reduced amounts of phenolic compounds and α- and γ-tocopherols. The PCA also indicates that β-tocopherol, together with total fat, are the variables that most characterize the cultivar. Toasting, on the other hand, induces the oxidation of monounsaturated fatty acids, but does not influence the presence of tocopherols and has a positive impact on the presence of phenolic compounds whose concentration significantly increased regardless of kernel's pellicle.

Keywords Hazelnut · Toasting · Kernel pellicle · Tocopherols · Phenolic compounds

Introduction

Nuts are an important source of a great number of healthy bioactive molecules [1], that are recognized as acting in reducing inflammation [2] and the risk for cardiovascular diseases [3, 4], cancer [5] and type-2 diabetes [6].

Hazelnuts (*Corylus avellana* L.) are the second most popular nuts worldwide (just after almonds) and are widely consumed both raw and toasted or industrially transformed in spreads, additives or oils.

The world global production of hazelnuts is around 1 million tons per year, mainly produced in Turkey, whereas Italy is the second largest producer [7]. Several hazelnut cultivars exist in the world, only few are cultivated and commercialized, mainly because of their well-established over the years commercial features.

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Even so, some studies have been published on the chemical composition of different hazelnut cultivars [8–11], and, for some cultivars, on the influence of environmental conditions [12] and agronomic applications [13]. Moreover, it is well known that the chemical composition of nuts is strongly modified after harvesting by the technological procedures employed before commercialization. This is true especially for toasting that, besides leading to physical changes (dehydration, colour modification), determines significant chemical modifications to bioactive substances [14], affecting also organoleptic characteristics, due to the release of several volatiles compounds (ketones, aldehydes, pyrazines, alcohols, hydrocarbons, furans, pyrroles, terpenes) [15].

To our knowledge, hazelnuts still lack an exhaustive analysis of the roles of roasting and peeling and, on the other hand, of their genetic background on the occurrence of a number of bioactive molecules. To overcome this requirement, we focussed on four Italian hazelnut cultivars ("Tonda di Giffoni", "Tonda Gentile delle Langhe", "Tonda Gentile Romana" and the previously uncharacterized "Nocchione"), taking into account the contribution of the pellicle and the

effect of the toasting process on the presence of tocopherols, fatty acids and phenols.

Materials and methods

Sampling

Samples of "Tonda Gentile delle Langhe" were collected in the Piemonte region, in the north of Italy; "Tonda Gentile Romana" and "Nocchione" in the Lazio one (in the centre of Italy), whereas "Tonda di Giffoni" has been collected in Campania, in the centre–south of Italy.

For each cultivar ("Nocchione", "Tonda di Giffoni", "Tonda Gentile delle Langhe", "Tonda Gentile Romana"), two samples (2 kg each) were collected from two trees in five different farms.

Preparation of the samples

For each of the four cultivars, the two samples coming from the same farm were pooled, mixed thoroughly and split into four aliquots. Two of them were toasted for 20 min at 180 °C and, after cooling, one out of the two was manually deprived of kernel's pellicle. One of the remaining two aliquots was kept unchanged, the second was peeled.

Thus, for each cultivar 5 samples were analysed for each of the four treatments: raw with pellicle; raw without pellicle; toasted with pellicle and toasted without pellicle.

Each aliquot was immediately frozen and pulverized in liquid nitrogen using an IKA A 11 Basic mill (IKA, Staufen, Germany), and stored at − 80 °C until analyses were performed.

Chemical analyses

Moisture was determined in 4 g of hazelnut powder dried in oven at 105 ± 2 °C until constant weight (24 h).

The total fat content was determined as percentage of dry weight (DW) using a Soxhlet apparatus, according to the AOAC method 948.22 [16].

Tocopherols were analysed by HPLC-DAD (Agilent 1200 series, Agilent, Santa Clara, CA, USA). 1 gram of oil extracted from kernels was solubilised in calibrated flask with 10 ml methanol/chloroform (1:1). 20 µl aliquot was directly injected into the HPLC after filtration using 0.2-µm syringe filters (Phenex PTFE syringe filters; Phenomenex, Torrance, CA, USA). HPLC was equipped with a Cosmosil 5PYE (Nacalai, Kyoto, Japan) reversed phase column (4.6 ID x 250 mm); the mobile phase was methanol/water (95:5 v/v) running isocratically at 30 °C at a flow of 1 ml/min. DAD was set at 292 nm. Tocopherols were identified by their retention times and spectra as compared to those of standards obtained from Sigma-Aldrich and ran at the same conditions (St. Louis, MO, USA).

For the fatty acid composition determination, the methyl esters were prepared by vortexing vigorously (30 s) a solution of oil in heptane (0.1 g in 2 ml) with 0.2 ml of methanolic 2N potassium hydroxide and successively centrifuged at 3500 rpm (3 min). Two µl of the supernatant were injected into GC equipped with a FID detector (Perkin Elmer Autosystem, Waltham, MA, USA). A BPX70 capillary column, with 0.25 mm of ID, 0.25 µm of film thickness and 60 m of length (SGE Analytical Science, Victoria, Australia) was used. The carrier gas was helium, with a flow rate of 1 ml/min. Injector and detector temperatures were set at 250 °C. The temperature gradient of the oven was applied starting from 130 °C and reaching 230 °C in 40 min. Fatty acids were identified by their retention times as compared to those of standards obtained from Supelco (Bellefonte, PA, USA).

Total phenols were extracted from about 2 g of hazelnut powder that was weighted in a screw cone tube with 15 ml of a methanol/water mixture (80:20). The mixture was vigorously homogenized (orbital motion, 400 rpm, 25 mm orbital) for 5 min on a Certomat MO II shaker (Sartorius, Gottingen, Germany) and separated by centrifugation at 4000 rpm for 5 min. The procedure was repeated three times. The extracts were blended and defatted three times with 15 ml of hexane. The final extracts were then evaporated in a 50-ml flat-bottomed flask by a rotavapor, diluted with 10 ml methanol and filtered using 0.2-µm Phenex PTFE syringe filters (Phenomenex, Torrance, CA, USA). Total phenols were determined using Folin–Ciocalteu method [17] at 765 nm using gallic acid as reference standard.

Statistical analyses

Analytical variables were statistically tested for significant factors' effect by analysis of variance (ANOVA) (XLStat, v. 2012.1.01, Addinsoft). A Tukey's post hoc test was applied to compare means.

A principal component analysis (PCA) was applied on the data sets from different cultivar, peeled or unpeeled and raw or toasted hazelnuts using the mean value of the amounts of phenolic compounds, total fat, α-, β− and γ-tocopherol.

All statistical analyses were performed by XLStat, v. 2012.1.01, Addinsoft (France). Throughout all data analyses, effects were considered to be significant at a level $p < 0.05$.

Results and discussion

Fat content and fatty acid composition

Samples fat content ranged from 67.8% in "Tonda Gentile Romana" to 72.4% in "Tonda di Giffoni" (Table 1), with

Table 1 Fat content (%) and fatty acid composition (%) in the studied hazelnut cultivars (mean ± SD)

	Nocchione	Tonda di Giffoni	Tonda Gentile delle Langhe	Tonda Gentile Romana	Raw	Toasted	Kernel with pellicle	Kernel without pellicle
Total fat	69.0 ± 2.0^{BC}	72.4 ± 1.2^{A}	69.4 ± 1.3^{B}	67.8 ± 1.9^{C}	69.7 ± 2.4	69.7 ± 2.3	69.8 ± 2.4	69.5 ± 2.4
C16:0 (Palmitic)	7.52 ± 0.39^{A}	7.18 ± 0.31^{B}	7.72 ± 0.29^{A}	7.66 ± 0.33^{A}	7.55 ± 0.38	7.49 ± 0.4	7.49 ± 0.37	7.56 ± 0.41
C16:1 (Palmitoleic)	0.25 ± 0.03^{AB}	0.21 ± 0.04^{B}	0.28 ± 0.06^{A}	0.23 ± 0.06^{B}	0.25 ± 0.05	0.24 ± 0.06	0.24 ± 0.06	0.24 ± 0.06
C17:1 (Heptadecenoic)	0.03 ± 0.04	0.05 ± 0.04	0.05 ± 0.04	0.04 ± 0.04	0.05 ± 0.04	0.04 ± 0.04	0.04 ± 0.04	0.05 ± 0.04
C18:0 (Stearic)	3.01 ± 0.24^{A}	2.96 ± 0.17^{A}	2.55 ± 0.19 ^{B}	2.52 ± 0.45^{B}	2.8 ± 0.36	2.69 ± 0.36	2.68 ± 0.35	2.8 ± 0.37
C18:1 (Oleic)	81.1 ± 1.68^{B}	81.6 ± 1.14^{B}	83.1 ± 0.63^{A}	81.5 ± 2.07^{B}	82.23 ± 1.51^{D}	81.5 ± 1.68^{E}	81.4 ± 1.64^{G}	82.4 ± 1.47^{F}
C18:2 (Linoleic)	7.76 ± 1.85^{A}	7.54 ± 1.3^{A}	6.00 ± 0.61^{B}	7.76 ± 2.27^{A}	6.82 ± 1.55^{E}	7.50 ± 1.87^{D}	7.78 ± 1.72^{F}	6.67 ± 1.62^{G}
C18:3 (Linolenic)	0.06 ± 0.04	0.06 ± 0.03	0.07 ± 0.04	0.06 ± 0.05	0.06 ± 0.05	0.07 ± 0.03	0.08 ± 0.03^{F}	0.05 ± 0.04^{G}
C20:0 (Arachidic)	0.13 ± 0.01^{AB}	0.13 ± 0.01^{A}	0.11 ± 0.01^{C}	0.12 ± 0.02^{BC}	0.12 ± 0.01	0.12 ± 0.02	0.12 ± 0.01	0.12 ± 0.01
C20:1 (Gadoleic)	0.12 ± 0.01 ^{B}	0.13 ± 0.01^{A}	0.11 ± 0^{C}	0.12 ± 0.01^{B}	0.12 ± 0.01	0.12 ± 0.01	0.12 ± 0.01	0.12 ± 0.01
∑ SFA	10.66 ± 0.4	10.28 ± 0.3	10.38 ± 0.4	10.30 ± 0.7	10.47 ± 1.49	10.30 ± 0.48	10.29 ± 0.50	10.48 ± 0.47
∑ MUFA	81.50 ± 1.7^{B}	81.97 ± 1.2^{B}	83.54 ± 0.6^{A}	81.88 ± 2.1^{B}	82.64 ± 1.5^{D}	81.88 ± 1.71^{E}	81.76 ± 1.7^{G}	82.79 ± 1.5^{F}
∑ PUFA	7.82 ± 1.9^{A}	7.60 ± 1.3^{A}	6.08 ± 0.6^{B}	7.82 ± 2.3^{A}	6.88 ± 1.6^{E}	7.72 ± 1.9^{D}	7.86 ± 1.7^{F}	6.72 ± 1.6^{G}

Different letters within a row indicates significant difference ($p < 0.05$) among

$^{A–C}$cultivars

$^{D, E}$Toasting

$^{F, G}$Presence of the pellicle of the kernel, by three-way ANOVA

amounts that are comparable to those reported for Turkish [18, 19] and Portuguese [9] cultivars.

The fatty acid composition of hazelnut oil is characterized by a high content of mono- and poly-unsaturated fatty acids (MUFA and PUFA) [10, 20]. Accordingly, the main fatty acid in all cultivars (Table 1) was oleic acid (above 80%), whereas saturated fatty acids (SFA) accounted only for values ranging 10.28 ± 0.3 to 10.66 ± 0.4%, predominantly palmitic and stearic acids.

Linoleic acid was the second most abundant fatty acid. Amounts were lower than those previously reported for Portuguese [20, 21] and Polish [10] cultivars, but comparable to those reported for Italian ones by Ghirardello et al. [22], confirming the inter-cultivar linoleic acid variability reported by Amaral et al. [9]; in addition, our data also showed a high linoleic acid intra-cultivar variability, as indicated by a very high coefficient of variation found between our four cultivars (10–29%), as compared to that of oleic acid (1–2%).

The ratio between poly- and monounsaturated fatty acids was quite similar among the cultivars grown in the centre–south of Italy ("Nocchione" 10.4; "Tonda Gentile Romana" 10.5; "Tonda di Giffoni" 10.8) but was significantly higher (13.7) in the "Tonda Gentile delle Langhe" cultivar, grown in the north.

Toasting affected the fatty acid composition of all samples, according to the fact that acids containing unsaturated bounds are oxidized at high temperatures [23]. In particular, oleic acid showed a slight but statistically significant drop from 82.23 ± 1.51 to 81.5 ± 1.68% in toasted samples. On the other hand, toasting did not induce a reduction of the theoretically more oxidizable linoleic acid that was instead slightly increased, possibly because the relative drop of the greater amount of oleic acid determines the rise of the relative levels of linoleic acid [21]. As expected, oxidation of the unsaturated fatty acids during toasting was associated with a significant decrease of the ratio between poly- and monounsaturated fatty acids on the saturated ones, which shifted from 12.0 in raw hazelnuts to 10.6 in toasted ones (Table 1).

Fatty acid composition was influenced also by the presence/absence of the kernel pellicle. In fact, elimination of the pellicle was associated with a significant increase of oleic acid (81.4–82.4%) in kernels and a simultaneous decrease of linoleic acid (7.8–6.7% on average), indicating that the lower amount of fats in the pellicle (14.5% as reported by Ozdemir et al. [14]) is composed by a

significantly lower amount of oleic acid and a consequent higher relative presence of linoleic acid. In all samples, the linoleic acid content varied inversely to that of the oleic acid, in accordance with previous data from Koyuncu et al. [24] and Amaral et al. [21].

Tocopherols

Concentration of α-, β- and γ-tocopherols is given in Tables 2, 3 and 4. These results were comparable to those found in other cultivars [8, 10].

Table 2 α-Tocopherol (mg/kg DW; mean ± SD) in the studied hazelnut cultivars according to toasting and presence of the pellicle on the kernel

Cultivar	Raw kernel with pellicle	Raw kernel without pellicle	Toasted kernel with pellicle	Toasted kernel without pellicle	Mean[c]
Nocchione[a]	136 ± 10^{BCD}	103 ± 14^{D}	177 ± 18^{AB}	123 ± 27^{BCD}	135 ± 32^{I}
Tonda di Giffoni[a]	169 ± 29^{AB}	110 ± 42^{CD}	170 ± 27^{AB}	161 ± 21^{ABC}	153 ± 38^{I}
Tonda Gentile delle Langhe[a]	211 ± 18^{A}	168 ± 13^{AB}	205 ± 15^{A}	173 ± 6^{AB}	189 ± 23^{H}
Tonda Gentile Romana[a]	163 ± 22^{ABC}	109 ± 12^{CD}	147 ± 18^{BCD}	132 ± 42^{BCD}	138 ± 31^{I}
Mean[b]	171 ± 33^{E}	124 ± 35^{G}	175 ± 28^{E}	149 ± 32^{F}	

By three-way ANOVA

Interaction roasting vs pellicle $p < 0.05$

[a]Different letters (A–D) within cultivars raw/toasted with/without pellicle indicate significant difference ($p < 0.05$) among cells

[b]Different letters within the row (E–G) indicate significant difference ($p < 0.05$) among cells

[c]Different letters within the column (H–I) indicate significant difference ($p < 0.05$) among cells

Table 3 β-Tocopherol (mg/kg DW; mean ± SD) in the studied hazelnut cultivars according to toasting and presence of the pellicle on the kernel

Cultivar	Raw kernel with pellicle	Raw kernel without pellicle	Toasted kernel with pellicle	Toasted kernel without pellicle	Mean[c]
Nocchione[a]	0.8 ± 0.5	1.7 ± 0.7	1.3 ± 1.7	$0.8 \pm 0.0.9$	1.2 ± 1.1^{B}
Tonda di Giffoni[a]	1.4 ± 1.1	2.2 ± 0.6	2.3 ± 1.4	1.9 ± 0.6	2.0 ± 1.0^{A}
Tonda Gentile delle Langhe[a]	1.9 ± 0.8	2.3 ± 0.6	1.6 ± 0.6	1.7 ± 0.8	1.9 ± 0.7^{AB}
Tonda Gentile Romana[a]	1.1 ± 0.6	2.1 ± 0.7	1.3 ± 0.5	1.5 ± 0.8	1.5 ± 0.7^{AB}
Mean[b]	1.3 ± 0.8^{B}	2.1 ± 0.6^{A}	1.7 ± 1.1^{AB}	1.5 ± 0.8^{AB}	

By three-way ANOVA

Interaction roasting vs pellicle $p < 0.05$

[a]NS within cultivars raw/toasted with/without pellicle indicate significant difference ($p < 0.05$) among cells

[b]Different letters within the row (A, B) indicate significant difference ($p < 0.05$) among cells

[c]Different letters within the column (C, D) indicate significant difference ($p < 0.05$) among cells

Table 4 γ-Tocopherol (mg/kg DW; mean ± SD) in the studied hazelnut cultivars according to toasting and presence of the pellicle on the kernel

Cultivar	Raw kernel with pellicle	Raw kernel without pellicle	Toasted kernel with pellicle	Toasted kernel without pellicle	Mean[c]
Nocchione[a]	0.4 ± 0.4^{C}	n.d.^{C}	2.8 ± 0.7^{BC}	0.7 ± 0.7^{C}	1.0 ± 1.2^{GH}
Tonda di Giffoni[a]	n.d.^{C}	n.d.^{C}	0.4 ± 0.5^{C}	n.d.^{C}	0.1 ± 0.3^{H}
Tonda Gentile delle Langhe[a]	5.4 ± 2.6^{AB}	0.6 ± 0.6^{C}	6.3 ± 4.0^{A}	2.2 ± 1.2^{C}	3.7 ± 3.3^{F}
Tonda Gentile Romana[a]	2.2 ± 0.8^{C}	n.d.^{C}	2.9 ± 1.2^{BC}	0.6 ± 0.8^{C}	1.5 ± 1.5^{G}
Mean[b]	2.1 ± 2.5^{D}	0.2 ± 0.5^{E}	3.1 ± 3.0^{D}	0.9 ± 1.1^{E}	

By three-way ANOVA

Interaction cultivar vs pellicle $p < 0.001$

[a]Different letters (A–C) within cultivars raw/toasted with/without pellicle indicate significant difference ($p < 0.05$) among cells

[b]Different letters within the row (D, E) indicate significant difference ($p < 0.05$) among cells

[c]Different letters within the column (F–H) indicate significant difference ($p < 0.05$) among cells

α-Tocopherol accounted for about 96% of total tocopherols, and amounts were significantly higher in "Tonda Gentile delle Langhe" hazelnuts (mean of raw and toasted with and without pellicle samples 189 ± 23 mg/kg DW) as compared to "Tonda di Giffoni", "Tonda Gentile Romana" and "Nocchione" ones (153 ± 38, 138 ± 31 and 135 ± 32 mg/kg DW respectively).

Although it represents only a small fraction of the entire kernel, the pellicle is the part that contains the highest concentration of tocopherol, as its removal was associated with a great and significant loss of both α- and γ-tocopherol (α-tocopherol from 171 ± 33 to 124 ± 35 and from 175 ± 28 to 149 ± 32 mg/kg DW in the raw and toasted hazelnuts, respectively, Table 2; γ-tocopherol from 2.1 ± 2.5 to 0.2 ± 0.5 and 3.1 ± 3.0 to 0.9 ± 1.1 mg/kg DW in the raw and toasted hazelnuts, respectively, Table 4), whereas β-tocopherol was almost equally distributed between pellicle and kernel (Table 3).

As regards the effect of the toasting process on α-tocopherol, conflicting results have been reported in the literature: Stuetz et al. reported a 20% α-tocopherol decrease after 15 min toasting at 160/170 °C [25], Amaral et al. described a 10% decrease after 15 min at 180 °C [21], whereas no significant effects, even after longer times (up to 30 min at 160 °C or 60 min at 130 °C), were found by Mazzocchi et al. [15]. According to the latter, we did not observe significant reductions of α-tocopherol amounts in unpeeled hazelnuts, whereas we found a slight but significant increase of α-tocopherol after toasting in peeled hazelnuts (Table 2), which is consistent with the statement that α-tocopherol can be stable during heath treatment [26]. No major changes were observed by toasting on both β- (Table 3) and γ-tocopherol (Table 4) concentration in hazelnuts.

Phenolic compounds

High variability in total phenolic compounds of unpeeled raw hazelnuts was found among cultivars, ranging from 1252 ± 150 mg/kg DW in the "Nocchione" cultivar to 1756 ± 346 mg/kg DW in the "Tonda Gentile delle Langhe" one (Table 5). As previously described [27–29], phenolic compounds are mainly localized in the pellicle of the hazelnut. Accordingly, pellicle removal determined a 59–79% loss of total phenolic compounds in toasted and raw hazelnuts, respectively (from 1516 ± 438 to 315 ± 44 mg/kg DW in raw hazelnut; from 1702 ± 372 to 691 ± 77 mg/kg DW in toasted hazelnut; Table 5). Like for α-tocopherol, controversial data exist on toasting effects on total phenols: Pelvan et al. [30] showed that the process determines a decrease of total phenolic compounds, while Marzocchi et al. [15] described a significant increase of total phenolics during the heat treatment. Our data agree with results of the latter. In fact, toasted samples showed on the average an increase of total phenolic compounds of, respectively, 186 and 376 mg/kg DW in unpeeled and peeled hazelnuts (Table 5, mean values on all the cultivars). This increase can be explained if we hypothesize that the chemical degradation of unstable phenolic compounds during heat treatment [31] may be counterbalanced by the degradation of polymerized polyphenols (mainly hydrolysable tannins) and by the hydrolysis of various glycosylated flavonoids, whose evidence has been described by Monagas et al. [32]. Moreover, molecules found in toasted nuts could be a consequence of the Maillard reaction, occurring between reducing sugars and amino acids. Such products might, on the one hand artificially overestimate phenolics absorbance readings obtained using of the Folin–Ciocalteu reagent [33], and, from the other, yield sub-products that effectively enhance the antioxidant capacity of hazelnut [34].

Table 5 Total phenolic compounds (mg/kg DW; mean ± SD) in the studied hazelnut cultivars according to toasting and presence of the pellicle on the kernel

Cultivar[a]	Raw kernel with pellicle	Raw kernel without pellicle	Toasted kernel with pellicle	Toasted kernel without pellicle	Mean[c]
Nocchione	1252 ± 150^{BCD}	295 ± 38^{E}	1587 ± 431^{AB}	741 ± 86^{DE}	969 ± 549^{J}
Tonda di Giffoni	1421 ± 611^{BC}	374 ± 40^{E}	1441 ± 234^{B}	753 ± 31^{CDE}	998 ± 553^{IJ}
Tonda Gentile delle Langhe	1756 ± 346^{AB}	304 ± 32^{E}	2095 ± 310^{A}	678 ± 51^{DE}	1209 ± 788^{I}
Tonda Gentile Romana	1562 ± 496^{AB}	295 ± 8^{E}	1608 ± 158^{AB}	615 ± 51^{DE}	1020 ± 638^{IJ}
Mean[b]	1516 ± 438^{F}	315 ± 44^{H}	1702 ± 372^{F}	691 ± 77^{G}	

Interaction cultivar vs pellicle $p < 0.01$

[a]Different letters (A–E) within cultivars raw/toasted with/without pellicle indicate significant difference ($p < 0.05$) among cells

[b]Different letters within the row (F–H) indicate significant difference ($p < 0.05$) among cells

[c]Different letters within the column (I, J) indicate significant difference ($p < 0.05$) among cells

Principal component analysis

To obtain a comprehensive view of the effect of the technological approach (presence/absence of the kernel's pellicle; toasted/row hazelnuts) on the presence of bioactive molecules (total phenolic compounds, α-, β- and γ-tocopherols and total fats) in hazelnuts, a PCA was applied (Fig. 1).

The first two components (accounting for 79.9% of total variance) indicate a clear different pattern that depends on kernel's pellicle and hazelnut's cultivar (Fig. 1a). The score plot (Fig. 1a) indicates that toasting has no particular effects on sample distribution among the first two principal components, as raw ("R" in the labels) and toasted ("T") hazelnuts are almost randomly distributed in the four quadrants of the plot. On the contrary, the first component (explaining 50.5% of total variance) clearly describes the role of the pellicle, as indicated by the distribution of peeled and unpeeled samples, respectively, in the negative and positive quadrants (Fig. 1a). As this component is mainly explained by the presence of phenolic compounds, α- and γ-tocopherol (see loading plot, Fig. 1b), the PCA confirms that the removal of kernel's pellicle is responsible of the observed significant loss of these compounds.

The second principal component (explaining 29.4% of the variance) is mainly explained by the content of total fat and β-tocopherol (Fig. 1b). The score plot (Fig. 1a) clearly indicates that this component describes the role of the cultivar. In fact, as shown by the score plot (Fig. 1a), the two cultivars cultivated in the central Italy Lazio region ("Nocchione" and "Tonda Gentile Romana", underlined in Fig. 1a) are localized in the negative quadrant of the second principal component, whereas "Tonda di Giffoni" (dashed underlined in Fig. 1a) and "Tonda Gentile delle Langhe" (not underlined in the figure) are, respectively, localized in the upper and lower part of the positive quadrant of the second component. Such data are in agreement with that reported by Taş indicating a wide variability in the occurrence of bioactive compounds in different hazelnut varieties [35].

Conclusions

Hazelnuts are characterized by high nutritional value, due to a favourable fatty acid composition and the presence of high amounts of tocopherols and phenolic compounds. Here we demonstrate that skin is the kernel's portion that contains the higher concentration of phenolic compounds and α- and ϒ-tocopherols. In fact, our analyses indicate that unpeeled and toasted "Tonda Gentile delle Langhe" hazelnuts contain more than 2 g/kg DW of hydrophilic phenolics and more than 200 mg/kg DW of tocopherols. Moreover, the PCA analysis indicates that the cultivar background has a major role on β-tocopherol and total fat levels.

With respect to mono- and poly-unsaturated fatty acids, representing about 90% of total fatty acids, our data confirm that toasting induces oxidation of the formers and a slight reduction of oleic acid. On the other hand, toasting does not influence the presence of tocopherols, but has a strong positive impact on soluble phenolic compounds.

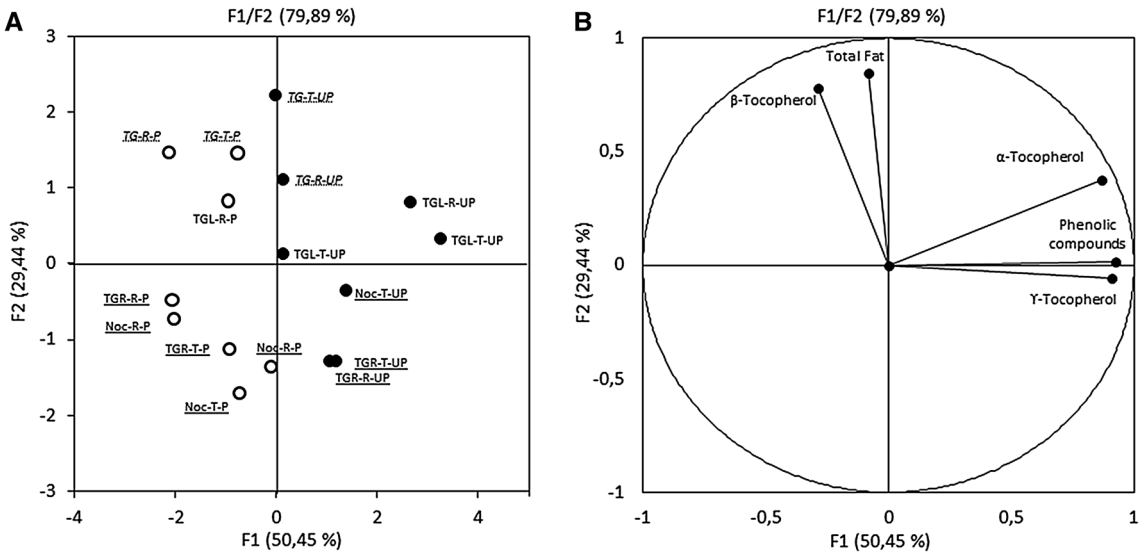

Fig. 1 Principal components analysis. **a** Scores plot. Label codes: cultivar: *Noc* Nocchione, *TG* Tonda di Giffoni, *TGL* Gentile delle Langhe, *TGR* Gentile Romana; Toasting: *T* Toasted, *R* Raw; Kernel: *UP* Unpeeled, *P* Peeled; Color codes: Black dots: Unpeeled, white dots: Peeled; underlined label: cultivar from Lazio (central Italy), italic dashed underlined label: cultivar from Campania (south Italy); non-underlined label: cultivar from Piemonte (north Italy). **b** Loading plot

Finally, as substantiated by a PCA analysis, our results indicate that in "Nocchione", "Tonda di Giffoni", "Tonda Gentile delle Langhe" and "Tonda Gentile Romana" hazelnuts' higher concentration of bioactive molecules is achieved by keeping kernel pellicles.

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Compliance with ethical standards

Conflict of interest The authors report no conflicts of interest.

Compliance with ethics requirements No humans nor animals were involved in the study.

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