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# Impact of traditional and microwave roasting on chemical composition of hazelnut cultivar 'Tonda di Giffoni'

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**RESEARCH ARTICLE**

## Abstract

Roasting is a widespread practice for the preservation of hazelnuts. Because traditional treatments conducted by electrical ovens are associated with high energy costs and production of undesired chemical compounds, roasting based on microwaves has been tested by scientists in recent years as an attractive alternative to traditional process. In this study the impact of traditional and microwave roasting on the chemical composition of the Italian hazelnut cultivar 'Tonda di Giffoni' was investigated. Kernels roasted using microwave and microwave – infrared combined treatments showed dry weight, colour and fracturability values similar to those obtained by traditional treatment. Microwaves preserved hazelnut phenol compounds showing a loss of 7.5% with respect to unroasted hazelnut, whereas loss of total phenols higher than 44% were observed in traditional roasted hazelnuts. Microwave roasting produced the lowest amount of free Nε-(carboxymethyl)lysine (CML): 865.4 µg/kg, whereas up to 2,314.6 µg/kg was detected in traditional roasted hazelnuts. Microwaves roasting produced the lowest heat damage. Preservation of antioxidants compounds and production of lower CML matched the advantage of saving time and energy costs: 4 min of treatment and energy density of 6 kJ/kg for microwave roasting, while 40 min and 95 kJ/kg for traditional one.

**Keywords:** infrared, phenols, carboxymethyl lysine, lipid

## 1. Introduction

Italy is the second most important producing country of hazelnut (*Corylus avellana* L.) in the world, after Turkey (FAO, 2014). Hazelnuts are sold both in-shell, used for fresh consumption, and shelled as raw material in confectionary and bakery food products (90% of harvested yield). Consequently, the market standards are driven mainly by the high-quality nut requirements of the confectionary industry.

Recently, hazelnuts have been recognised as a heart-healthy foods by the FDA (2003), which has provided a major boost to their image. Hazelnuts fit well in the healthy Mediterranean diet, since they contain dietary fibre, essential minerals, vitamin E and B, as well as unsaturated fatty acids, plant sterols and tocopherols (Alasalvar *et al.*, 2003). Dietary benefits of hazelnuts are mainly related to fat components (around 60% of monosaturated fatty acids), which tend to raise high density lipoprotein cholesterol (Mercanligil *et al.*, 2007) and reduce low density lipoprotein cholesterol. The main traits considered for hazelnut quality include nut/kernel size, shape (misshapen or underdeveloped), shell thinness, low kernel defects, kernel taste (off-odour, off-flavour or mould), and a high content of fatty acids and protein.

The hazelnut cv. 'Tonda di Giffoni' is among the most highly appreciated Italian cultivars. Due to its round kernels and excellent processing quality, it was awarded a Protected Geographical Indication from the European Union as 'Nocciola di Giffoni'. Roasting is the most important practice for the preservation and improvement of sensorial qualities of hazelnuts (Basaran and Akhan, 2010). It involves important physico-chemical changes including dehydration and chemical reactions (Ciaramiello *et al.*, 2013).

Roasting is currently carried out by commercial electrical ovens equipped with rotating drum. Since these processes require high energy amounts, in the recent years there has been an increasing interest in microwave roasting, as attractive alternative to the traditional process. Microwave treatment results in higher energy efficiency and lower heating times with respect to traditional method (Zhu *et al.*, 2007), since the heating takes place only in the food material and not in the surrounding medium, reducing energy costs (Vadivambal *et al.*, 2008). Microwaves are already used by food industry for several processes, including heating, thawing and drying (Salazar-Gonzàlez *et al.*, 2012). With respect to conventional heating, microwaves retain food quality, preserving essential nutrients and vitamins (Ahmed and Ramaswamy, 2007; Suàrez *et al.*, 2000). They are largely used both for liquid and for solid foods. Many applications about microwave roasting of nuts were experimented in recent years. For instance, it has been demonstrated that pistachios and almonds can be successfully roasted using microwaves as a fast and economical method (Hojjati *et al.*, 2015, 2016). Moreover, Uysal *et al.* (2009) obtained a comparable hazelnut quality in terms of texture, humidity, colour and fatty acids composition by traditional and microwave-infrared combination roasting. Momchilowa and Nikolova-Damyanova (2007) reported that a 3 min kernel roasting by microwave produced ready-to-consume hazelnuts without significant changes in lipid composition.

The present study aimed to compare the physico-chemical characteristics of Italian hazelnut cultivar 'Tonda di Giffoni' roasted with traditional and microwave treatments. Moreover the study aimed to select the optimal microwave roasting settings able to preserve nutritional compounds, such as phenols, and to reduce the formation of toxic substances, providing at the same time appearance and texture typical of traditional roasted product.

## 2. Materials and methods

Hazelnut (*Corylus avellana* L.) 'Tonda di Giffoni' cultivar was chosen for its excellent quality. Unroasted hazelnuts (A) provided by industrial plant Caporaso Severino S.r.l. (Casamarciano, Naples, Italy) were shelled, sun-dried for 5 days at 20-25 °C and divided in several batches; each batch was subjected to a different experimental roasting treatment. Treatments were performed in triplicate and produced samples listed in Table 1.

The C-F samples were obtained by roasting kernels in a traditional electrical oven (Electrolux Rex, Porcia PN, Italy), simulating the traditional industrial roasting process at different time and temperature settings. Sample C was roasted following the industrial time/temperature settings (130 °C for 40 min) and used as roasting control. The G-O samples were obtained by roasting kernels in a microwave oven (GW71B; Samsung, Seoul, South Korea) (2.45 GHz of radiation) equipped with a near infrared lamp, at different power/time settings. In particular the G-I samples were microwave roasted keeping off the infrared lamp, whereas the L-O samples were obtained by adding to the microwave the effect of the infrared lamp at different time settings (Table 1). After each roasting treatment the kernel skin was completely removed and samples were analysed for physico-chemical and nutritional characteristics; the unroasted sample A was peeled and analysed without skin, too.

For all the samples, dry weight, colour, fracturability, lipid fraction, phenolic composition and free Nε-(carboxymethyl)

**Table 1. Parameters and energy consumption for roasting treatments.**

| Treatment | Sample code | Oven capacity (kg) | Energy (kJ) | Energy density (kJ/kg) |
|---|---|---|---|---|
| Non roasted | A | – | – | – |
| Traditional roasting: | | | | |
| 130 °C, 40 min (2,000 W) | C | 50.5 | 4,800 | 95.0 |
| 150 °C, 20 min (2,000 W) | D | 50.5 | 2,400 | 47.5 |
| 150 °C, 30 min (2,000 W) | E | 50.5 | 3,600 | 71.3 |
| 150 °C, 40 min (2,000 W) | F | 50.5 | 4,800 | 95.0 |
| Microwave roasting: | | | | |
| 600 W, 4 min | G | 23.4 | 144 | 6.2 |
| 450 W, 6 min | H | 23.4 | 162 | 6.9 |
| 450 W, 3 min | I | 23.4 | 81 | 3.5 |
| 600 W, 3 min | I | 23.4 | 108 | 4.6 |
| Microwave/infrared roasting: | | | | |
| 450 W/900 W, 3.5 min | L | 23.4 | 283.5 | 12.1 |
| 600 W/900 W, 2.0 min | M | 23.4 | 180 | 7.7 |
| 600 W/900 W, 2.5 min | N | 23.4 | 225 | 9.6 |
| 600 W/900 W, 3.0 min | O | 23.4 | 270 | 11.5 |

lysine (CML) content were determined. In addition the energy costs of each treatment were estimated in terms of energy density, according to the treatment time setting, the power and the oven capacity information, provided by oven producers.

### Dry weight, colour measurement and fracturability

The dry weight of all samples was determined using a moisture analyser (Ohaus, Parsippany, NJ, USA) equipped with an infrared radiator. Five grams of finely grinded hazelnuts were weighted and dried at 105 °C until constant weight.

The colour and fracturability of all samples were measured to evaluate kernels aspect and texture. The analysis were carried out on 15 hazelnuts for each treatment.

The colour measurements of L* (lightness or darkness), a* (redness/greenness) and b* (blueness/yellowness) coordinates were performed by using a Chroma Meter colorimeter (Konica Minolta, Milan, Italy). The hue angle ($h_{ab}$ = arctan2(b*, a*)) was also calculated to estimate total colour.

Fracturability, the force with which the sample cracks, was expressed as Newton (N) and was measured using a penetrometer (Humboldt, Co., Chicago, IL, USA) (Stevens *et al.*, 2004).

### Lipid analysis

Oil was extracted from 10 g of hazelnuts previously ground with petroleum ether using a Soxhlet apparatus (Velp Scientifica, Usmate MB, Italy) (Cristofori *et al.*, 2008). After extraction the solvent was evaporated and the residual oil was weighed.

The acidity, peroxides value (PV) and fatty acids composition (FA) were evaluated in oil extracts. The acidity was determined according to the European official methods of analysis (EEC, 1991) and was calculated as percentage (w/w) of oleic acid.

The PV measures the formation of intermediate hydroperoxides in milliequivalents of active oxygen per kilogram and was determined on a mixture of oil and chloroform–acetic acid, left to react with a solution of potassium iodide in darkness; the free iodine was then titrated with a sodium thiosulphate solution, according to annex III in the Commission Regulation (EC) No 1989/2003 (EC, 2003). The FA composition was performed by a gas chromatographer PerkinElmer AutoSystem XL (PerkinElmer, Boston, MA, USA) equipped with a programmed temperature vaporiser, a flame ionisation detector and a capillary column of 100 m×0.25 mm ID and a film thickness of 0.20 μm using a stationary phase of 50% cyanopropyl methyl silicone (Supelco, Bellefonte, PA, USA) as previously described (Romano *et al.*, 2012).

### Extraction of phenolic compounds

The hazelnut samples were ground with a mechanical grinder. Hazelnut crumbs (5 g) were extracted for 45 min with 30 ml of methanol/water 80:20 (v/v) using vortex and sonication apparatus. The hazelnut extracts were centrifuged (Eppendorf centrifuge 5810 R; Eppendorf, Hamburg, Germany) at 8,000 rpm for 10 min and the supernatant was filtered through a 0.45 μm membrane filter (Macherey-Nagel, Duren, Germany).

Five ml of supernatant were mixed with 5 ml n-hexane for 3 min in a vortex apparatus. The mixture was transferred to a separatory funnel where the upper hexane layer was separated and wasted. The procedure was performed according to Jakopic *et al.* (2010) with some modifications and was repeated twice with 5 ml of n-hexane. The methanol/water extracts were stored for the following analysis.

### Analysis of total phenols

The total phenolic (TP) content, expressed as gallic acid equivalents (GAE) in milligrams per 100 grams of hazelnuts, was determined on methanol extracts diluted 1:5 (v:v) with distilled water according to Folin Ciocalteau method (Singleton and Rossi, 1965) using a spectrophotometer Shimadzu UV 1601 (Shimadzu, Milan, Italy). The total phenolic content was expressed as GAE in milligrams per 100 grams of hazelnut.

### Analysis of individual phenolic compounds

Individual phenolic compounds were determined as reported in Jakopic *et al.* (2010) with some modifications. The methanol extracts were concentrated in a rotary evaporator (Buchi, Flawil, Switzerland) and then the dry residues were dissolved in 1 ml of 1% acetic acid in water and filtered through a 0.45 μm membrane filter 20 ml were injected on a Agilent 1100 HPLC system (Agilent, Santa Clara, CA, USA) with a diode array detector. Thegallic and protocatechuic acid catechin, epicatechin and procyanidin B1 were detected at 280 nm, whereas quercetin-3-O-rhamnoside was detected at 365 nm. The compounds were separated on a Agilent Eclipse XDB C18 (150×4.60 mm, 5 μm) column and were quantified by calibration curves in the range 0-100 mg/kg. Standards of gallic acid (97.9% purity), protocatechuic acid (97% purity), catechin hydrate (98% purity), epicatechin (97% purity) and procyanidin B1 (90% purity) were provided by Sigma Aldrich (St. Louis, MO, USA) The limits of detection (LOD) and quantification (LOQ) were defined as the concentration of the analyte

that produced the signal to noise ratio of three and ten, respectively. LOD and LOQ expressed as mg/l were 0.05 and 0.15 for gallic acid, 0.11 and 0.38 for protocatechuic acid, 0.29 and 0.78 for catechin, 0.23 and 0.76 for epicatechin, 0.24 and 0.75 for procyanidin B1.

### CML analysis

Free CML analysis was performed by liquid chromatography high resolution mass spectrometry using a simplified approach focusing only on free analytes. CML separation was performed on an ultra-high performance liquid chromatography (U-HPLC) Accela system 1250 (Thermo Fisher Scientific, San Jose, CA, USA) consisting of a degasser, a quaternary pump, a thermostated autosampler, and a column oven. The system was equipped with a Synergi Hydro (150×2.0 mm, 4.0 µm; Phenomenex, Torrance, CA, USA). Mobile phase A was 0.1% formic acid, and mobile phase B was 0.1% formic acid in acetonitrile at a flow rate of 300 µl/min. The U-HPLC was coupled to an Exactive Orbitrap MS (Thermo Fisher Scientific) equipped with a heated electrospray interface operating in the positive mode and scanning the ions in the *m/z* range of 50-400. The exact mass of CML (*m/z*: 205.11883) was monitored with a mass tolerance of 3 mg/kg. The resolving power of the analyser was set to 50,000 full width at half-maximum (*m/z* 200), resulting in a scan time of 1 s and the maximum injection time was 100 ms. The interface parameters were setup according to Troise *et al.* (2015); the instrument was externally calibrated each day by infusion of a solution that consisted of caffeine, Met-Arg-Phe-Ala, Ultramark 1621, and acetic acid in a mixture of acetonitrile/methanol/water (2:1:1, v/v/v). CML calibration curve was built in the range of 5-5,000 ng/ml according to the limit of detection (LOD, lowest concentration for which the signal-to-noise ratio was >3) and the limit of quantification (LOQ, three times the LOD). Concentrations of <1 ng/ml resulted in no signal. The LOQ was 10 ng/ml for the standard solution, and the $r^2$ value was always >0.99 in the above-mentioned range. Reproducibility of the method was evaluated through the intraday and interday assay. The slope among the three subsequent calibration curves showed a % RSD of <7% and the retention time of the analyte was 3.1 min.

### Statistical analysis

All treatments and determinations were performed in triplicate, and the reported results are the average values of the three repetitions. One-way analysis of variance (ANOVA), Duncan's multiple-range test ($P \leq 0.05$) and principal component analysis (PCA) were conducted on the data using the software XLSTAT (Addinsoft, New York, NY, USA).

## 3. Results and discussion

### Dry weight, colour and fracturability

Changes in dry weight values of hazelnuts during roasting are shown in Table 2. Dry weight values increased from 95.29% for unroasted samples (A) to 99.46% after roasting. Dry weight of all roasted samples was significantly different compared to A, ranging between 97.82% (M) and 99.46% (H and L).

As expected, unroasted samples showed the highest value of fracturability (81.79 N) significantly different from all the treated samples. This parameter, indeed, can be related to percentage of moisture content (Kahyaoglu and Kaya, 2006).

**Table 2. Dry weight, colour and fracturability of hazelnut (mean value ± standard deviation).[1,2]**

| Samples | Dry weight(%) | L* | A* | B* | Hue angle | Fracturability (N) |
|---|---|---|---|---|---|---|
| A | 95.29±0.04 $^{d}$ | 71.73±2.18 $^{a,b}$ | 4.11±0.77 $^{e}$ | 32.07±3.16 $^{b,c,d}$ | 82.68 $^{a}$ | 81.79±7.21 $^{a}$ |
| C | 98.59±0.47 $^{b}$ | 71.98±3.12 $^{a,b}$ | 7.84±1.77 $^{c,d}$ | 28.48±2.46 $^{c,d,e}$ | 75.8±2.081 $^{b,c,d}$ | 49.69±3.70 $^{b}$ |
| D | 99.12±0.28 $^{a,b}$ | 68.30±6.16 $^{b,c,d,e}$ | 10.48±2.82 $^{a,b,c}$ | 34.43±1.92 $^{a,b,c}$ | 73.15±4.09 $^{b,c,d,e}$ | 49.16±4.25 $^{b}$ |
| E | 98.98±0.29 $^{a,b}$ | 68.10±4.65 $^{b,c,d,e}$ | 8.59±2.94 $^{b,c,d}$ | 31.82±3.74 $^{c,d,e}$ | 74.91±3.50 $^{b,c,d}$ | 37.53±2.38 $^{c,d}$ |
| F | 99.13±0.18 $^{a,b}$ | 67.15±4.85 $^{b,c,d,e}$ | 9.81±2.30 $^{b,c,d}$ | 32.53±1.69 $^{b,c,d}$ | 73.23±3.21 $^{b,c,d,e}$ | 36.12±2.72 $^{d}$ |
| G | 99.45±0.02 $^{a}$ | 63.30±7.06 $^{e,f}$ | 12.83±3.22 $^{a}$ | 35.40±3.14 $^{a,b}$ | 70.08±4.92 $^{e}$ | 50.12±3.02 $^{b}$ |
| H | 99.46±0.04 $^{a}$ | 69.89±3.87 $^{b,c,d}$ | 7.64±2.34 $^{c,d}$ | 31.43±2.87 $^{c,d,e}$ | 76.33±3.04 $^{b,c}$ | 53.85±3.96 $^{b}$ |
| I | 98.68±0.07 $^{b}$ | 64.25±5.96 $^{d,e,f}$ | 11.40±2.43 $^{a,b}$ | 36.59±1.40 $^{a}$ | 72.73±3.57 $^{c,d,e}$ | 52.36±1.15 $^{b}$ |
| L | 99.46±0.02 $^{a}$ | 63.79±6.28 $^{d,e,f}$ | 10.96±2.60 $^{a,b}$ | 33.76±3.57 $^{a,b,c,d}$ | 72.01±4.37 $^{d,e}$ | 47.17±1.19 $^{b,c}$ |
| M | 97.82±0.03 $^{c}$ | 76.66±2.49 $^{a}$ | 4.20±1.34 $^{e}$ | 30.55±3.21 $^{d,e}$ | 82.30±1.77 $^{a}$ | 49.91±3.10 $^{b}$ |
| N | 98.44±0.03 $^{b,c}$ | 70.70±6.89 $^{a,b,c}$ | 7.31±3.31 $^{d}$ | 31.30±3.91 $^{c,d,e}$ | 77.31±4.72 $^{a}$ | 36.41±2.40 $^{d}$ |
| O | 99.00±0.16 $^{a,b}$ | 59.59±7.30 $^{f}$ | 13.30±2.69 $^{a}$ | 36.96±2.60 $^{a}$ | 70.14±4.40 $^{e}$ | 36.49±2.12 $^{d}$ |

[1] For identification of the samples see Table 1.

[2] Different letters in the same column correspond to significant differences among samples ($P \leq 0.05$).

C, M, N samples showed the highest values of lightness, even if no statistical significant differences were observed compared to the unroasted sample (A). Roasting treatments showed generally an increased a*-value, due to the formation process of brown pigments. Particularly, the D, G, I, L and O samples showed the highest redness value.

C had the lowest b*-value (yellowness value) even if not statistically significant differences were detected for samples treated with microwaves in combination with infrared lamp (L, M and N).

The Hue angle value, deriving from a combination of a*-value and b*-value, is an important parameter to evaluate total colour. Microwave roasted hazelnuts (G, I) showed the lowest hue angle values not statistically different from hazelnuts roasted using traditional oven (D and F), and microwave oven with use of infrared lamp (L, O), while unroasted hazelnuts (A) reached the highest value.

In order to select the treatments that produced comparable results to those obtained for control sample (C), dry weight, Hue angle and fracturability values of all samples were submitted to PCA (Figure 1). The treatments that produced colour, dry weight and fracturability values similar to the control sample (C) were highlighted in the circle: 20 min in electrical oven at 150 °C (D), 4 min at 600 W (G), 6 min at 450 W (H), 3 min at 450 W and 3 min at 600 W (I) in the microwave and 3.5 min in microwave with combined infrared lamp radiation (L). PCA identified two significant principal components that accounted for 94.85% of the variance.

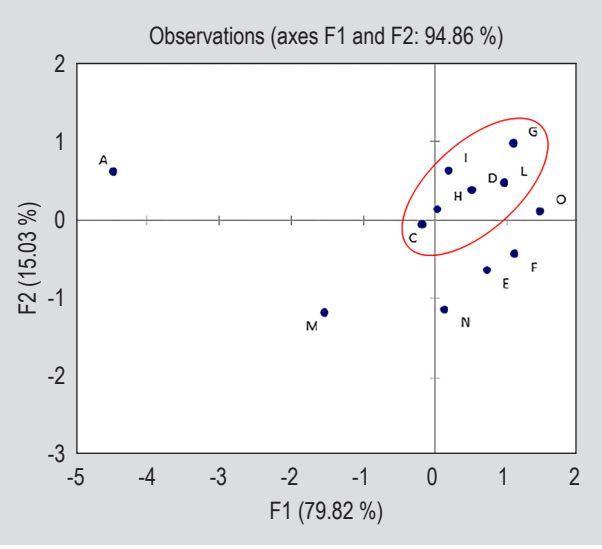


**Figure 1. Principal component analysis of dry weight, Hue angle and fracturability values.**

## Energy costs evaluation

Considering oven power, roasting time and oven capacity (Table 1), microwave roasting treatment G required the lowest energy density of 6.2 kJ/kg. This value is approximately 15-fold less than value of traditional roasting treatment C. These data show that the traditional method is at an obvious disadvantage regarding energy consumption and the treatment G should be preferred.

## Lipid content

As expected, both the acidity and PV values (Figure 2) of the extracted oils were higher in the roasted hazelnuts with respect to unroasted hazelnuts (A). All roasted samples were significantly different from the unroasted ones: acidity was no significantly different between the traditional and microwave roasting treatments, but PV is significantly higher in traditional roasted samples submitted to a higher thermic treatment (C, E and F).

The fatty acid compositions of the analysed samples are shown in Table 3. Fourteen fatty acids were identified: in the table only fatty acids detected in amounts higher than 0.1% are reported. As expected, oleic acid was the most abundant fatty acid, ranging from 81.29 to 82.59% in sample A and C, respectively. Linoleic and palmitic acids showed values ranging respectively from 7.95 to 8.88% and from 5.21 to 5.74%. These results are consistent with the literature (Alasalvar *et al.*, 2003; Amaral *et al.*, 2006). No statistically significant differences ($P>0.05$) were detected in the amount of fatty acids of the samples roasted in different conditions.

## Phenolic composition

Hazelnuts are generally rich in phenolic compounds that have many beneficial effects on human health (Shahidi *et al.*, 2007; Yurttas *et al.*, 2000), but traditional roasting can reduce the abundance of these important molecules (Cristofori *et al.*, 2008; Pelvan and Alasalvar, 2012). Figure 3 shows the TP content of the samples. Results of unroasted hazelnuts (126.27 mg GAE/100 g) seem to be consistent with results reported by Kornsteiner *et al.* (2006). Among all roasting treatments, samples from G to L showed the lowest reduction in the TP compared to unroasted hazelnuts with an average loss of nearly 7 and 26% for microwave and combined treatments, respectively. All traditional roasted hazelnuts (samples C, D, E and F), instead, showed a higher reduction of TP (>44%). Table 4 shows the individual phenolic composition of the hazelnut samples. Among the identified phenolic compounds (gallic acid, protocatechuic acid, catechin, epicatechin and procyanidin B1) catechin and epicatechin were the most abundant in hazelnuts. Roasting significantly affected all detected phenolic compounds except for protocatechuic acid. The gallic acid and procyanidin B1 content significantly increased

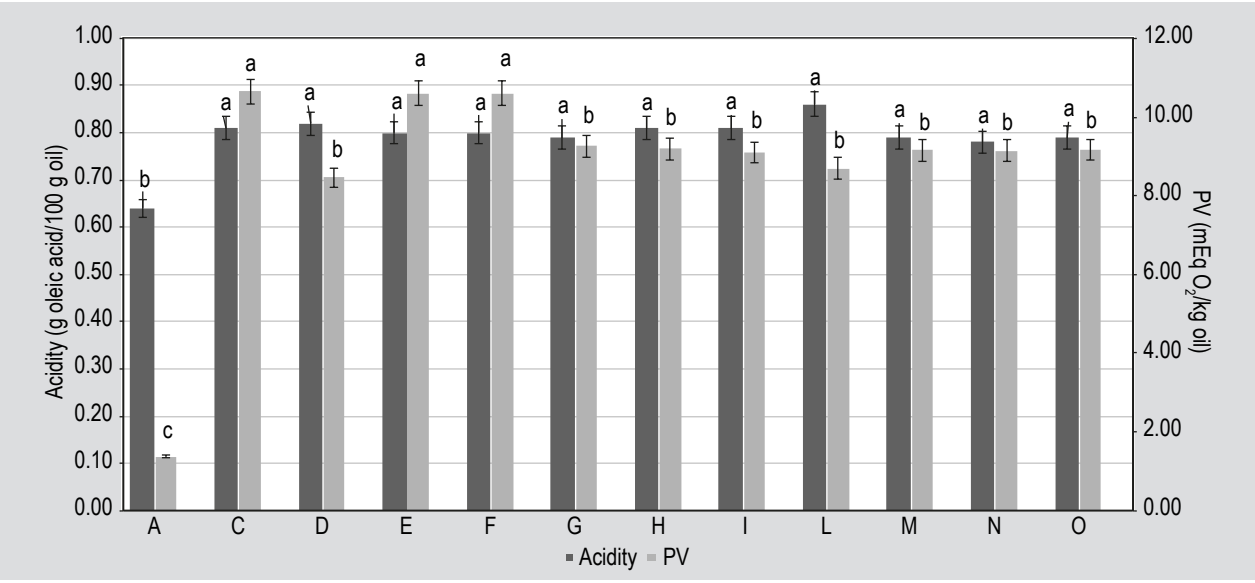


**Figure 2. Acidity and peroxide value (PV) of oil extracted from different samples treated as reported in Table 1 (a-c: different letters for each parameter correspond to statistically significant differences; $P \leq 0.05$).**

**Table 3. Fatty acids composition (% ± standard deviation) of hazelnut oil.[1,2]**

| Samples | C16:0 | C16:1 | C18:0 | C18:1n9c | C18:2n6c | C20:0 | C18:3n3 |
|---|---|---|---|---|---|---|---|
| A | 5.74±0.25 | 0.20±0.04 | 3.84±0.29 | 81.29±0.99 | 8.29±0.28 | 0.11±0.02 | 0.13±0.03 |
| C | 5.70±0.18 | 0.12±0.02 | 3.46±0.25 | 82.59±0.61 | 7.95±0.17 | 0.10±0.02 | 0.14±0.02 |
| D | 5.62±0.27 | 0.20±0.06 | 3.83±0.18 | 82.28±0.52 | 8.30±0.29 | 0.10±0.02 | 0.14±0.03 |
| E | 5.21±0.23 | 0.13±0.02 | 3.85±0.17 | 82.19±0.31 | 8.07±0.28 | 0.11±0.02 | 0.18±0.02 |
| F | 5.74±0.14 | 0.13±0.03 | 3.75±0.08 | 81.64±0.49 | 8.14±0.07 | 0.09±0.01 | 0.12±0.01 |
| G | 5.41±0.27 | 0.13±0.01 | 3.62±0.34 | 82.10±0.60 | 8.06±0.17 | 0.12±0.01 | 0.15±0.02 |
| H | 5.63±0.16 | 0.13±0.02 | 3.90±0.05 | 82.21±0.09 | 8.10±0.12 | 0.11±0.02 | 0.15±0.00 |
| I | 5.59±0.09 | 0.14±0.01 | 3.69±0.10 | 81.51±0.49 | 8.25±0.12 | 0.10±0.01 | 0.13±0.02 |
| L | 5.54±0.06 | 0.13±0.02 | 3.41±0.21 | 81.59±0.41 | 8.88±0.18 | 0.11±0.01 | 0.13±0.03 |
| M | 5.49±0.26 | 0.14±0.01 | 3.63±0.26 | 82.09±0.47 | 8.09±0.06 | 0.11±0.01 | 0.14±0.02 |
| N | 5.58±0.25 | 0.14±0.00 | 3.63±0.18 | 81.99±0.43 | 8.07±0.11 | 0.11±0.01 | 0.14±0.02 |
| O | 5.22±0.23 | 0.15±0.01 | 3.58±0.07 | 81.96±0.44 | 8.43±0.28 | 0.11±0.01 | 0.15±0.00 |

[1] For identification of the samples see Table 1.
[2] No significant differences ($P \leq 0.05$) were found.

in roasted samples, possibly due to the degradation of polymerised polyphenols, specifically hydrolysable tannins (Monagas *et al.*, 2009; Shahidi *et al.*, 2007). On the other hand, the content of catechin and epicatechin significantly decreased with thermal processing and sample control C showed the highest loss of these compounds, indicating that roasting can reduce the levels of naturally protective substances in hazelnuts, due to chemical degradation of many phenolic compounds.

## CML content

The results of free CML concentration are shown in Figure 4. CML was present at trace levels in the unroasted hazelnuts (A). The concentration of the Maillard-derived compound in samples C, which was prepared using traditional treatments, was 2,314.6 μg/kg. The micro-waved roasted hazelnuts (sample G) showed the lowest CML content (865.4 μg/kg). These results highlighted the low thermal impact of microwave processing on CML formation. This paper represents the first example of the evaluation of the thermal damage through the monitoring the free CML. Free

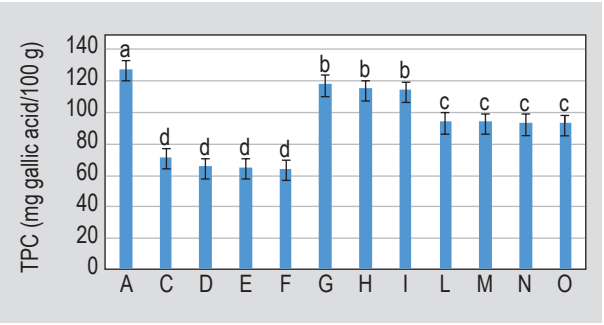


**Figure 3. Total phenol content (TPC) in the hazelnut samples treated as reported in Table 1 (a-d: different letters correspond to statistically significant differences; *P*≤0.05).**

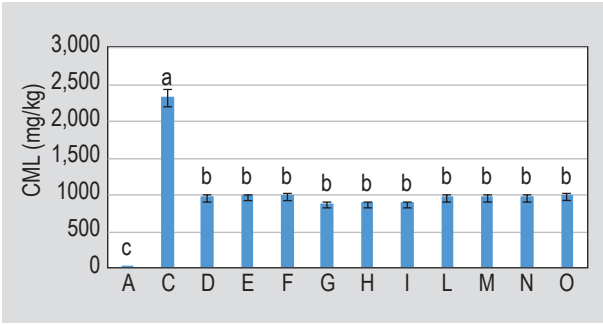


**Figure 4. Nε-(carboxymethyl)lysine (CML) content (µg/kg) in the hazelnut samples treated as reported in Table 1 (a-c: different letters correspond to statistically significant differences; *P*≤0.05).**

**Table 4. Concentration (mg/100 g ± standard deviation) of phenolic compounds in hazelnut kernels.[1,2]**

| Sample | Phenolic compounds | | | | |
|---|---|---|---|---|---|
| | Gallic acid | Protocatechuic acid | Catechin | Epicatechin | Procyanidin B1 |
| A | 0.91±0.12 $^{b}$ | 1.06±0.12 $^{a}$ | 6.63±0.29 $^{a}$ | 3.75±0.09 $^{a}$ | 0.13±0.01 $^{c}$ |
| C | 1.24±0.13 $^{a,b}$ | 1.13±0.04 $^{a}$ | 2.58±0.10 $^{e}$ | 1.38±0.05 $^{b}$ | 0.14±0.02 $^{c}$ |
| D | 2.22±0.22 $^{a}$ | 1.66±0.16 $^{a}$ | 5.28±0.57 $^{a,b,c}$ | 3.73±0.25 $^{a}$ | 0.38±0.02 $^{b}$ |
| E | 2.10±0.30 $^{a}$ | 1.70±0.28 $^{a}$ | 4.32±0.50 $^{b,c,d}$ | 3.32±0.20 $^{a}$ | 0.31±0.09 $^{b}$ |
| F | 2.00±0.12 $^{a,b}$ | 1.63±0.60 $^{a}$ | 4.10±0.40 $^{c,d}$ | 3.10±0.40 $^{a}$ | 0.34±0.01 $^{b}$ |
| G | 1.37±0.06 $^{a,b}$ | 1.48±0.14 $^{a}$ | 3.26±0.44 $^{d,e}$ | 2.15±0.26 $^{b}$ | 0.33±0.03 $^{b}$ |
| H | 1.31±0.26 $^{a,b}$ | 1.42±0.32 $^{a}$ | 3.21±0.51 $^{d,e}$ | 2.10±0.30 $^{b}$ | 0.32±0.03 $^{b}$ |
| I | 1.35±0.40 $^{a,b}$ | 1.40±0.20 $^{a}$ | 3.11±0.52 $^{d,e}$ | 1.90±0.20 $^{b}$ | 0.30±0.01 $^{b}$ |
| L | 2.33±0.51 $^{a}$ | 1.69±0.51 $^{a}$ | 6.61±0.11 $^{a}$ | 3.77±0.31 $^{a}$ | 0.67±0.07 $^{a}$ |
| M | 2.40±0.51 $^{a}$ | 1.70±0.30 $^{a}$ | 5.58±0.20 $^{a,b}$ | 3.55±0.15 $^{a}$ | 0.60±0.04 $^{a}$ |
| N | 2.30±0.51 $^{a}$ | 1.62±0.44 $^{a}$ | 5.47±0.52 $^{a,b,c}$ | 3.40±0.20 $^{a}$ | 0.63±0.04 $^{a}$ |
| O | 2.29±0.40 $^{a}$ | 1.65±0.28 $^{a}$ | 5.30±0.56 $^{a,b,c}$ | 3.21±0.31 $^{a}$ | 0.65±0.08 $^{a}$ |

[1] For identification of samples see Table 1.
[2] Different letters correspond to significant statistical differences (*P*≤0.05).

CML was investigated in order to evaluate the effects of the roasting process on free amino acids and in particular on the modification on the α- and ε-amino groups of free lysine by following a modified procedure previously described for free amino acids and Amadori products (Troise *et al.*, 2015). CML arises from the degradation and fragmentation of *N*-(1-deoxy-D-fructos-1-yl)-lysine or via a β-dicarbonyl cleavage of 2,4-dioxo intermediate (Kasper and Schieberle, 2005) CML in its protein-bound form is considered as one of the most reliable markers of the Maillard reaction (Nguyen *et al.*, 2014) while the detection in free form was firstly described by Hegele *et al.* (2008) in dairy products. The analysis of free markers can provide an useful snapshot of the chemical modifications occurring during the thermal processing of foods by avoiding the acidic or enzymatic hydrolysis. This procedure is gaining growing interests and it has been already used for the impact of MR on the manufacturing process of beer, organic-produced milk and tomatoes. (Hellwig *et al.*, 2016; Schwarzenbolz *et al.*, 2016; Troise *et al.*, 2015).

## 4. Conclusions

The results of this study showed that both microwave and microwave-infrared roasting produced hazelnuts with a higher concentration of phenolic compounds and a lower content of CML compared to traditionally roasted hazelnuts. Roasting using microwave at 600 W for 4 min is the recommended method mainly due to the lowest energy cost that is approximately 15 times lower than traditional roasting, and to the saving time. This treatment produced hazelnuts with colour, texture and humidity values similar

to the industrial roasting process and with the highest total phenolic content and the lowest CML content compared to other micro wave treatments.

Considering the promising results of physical and chemical composition analyses and energy costs, micro wave roasting technology should be strongly considered as a method for hazelnut processing.

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