

Effect of pretreatment with microwaves on mechanical extraction yield and quality of vegetable oil from Chilean hazelnuts (*Gevuina avellana* Mol)

Edgar Uquiche^{a,b,*}, Marcia Jeréz^a, Jaime Ortíz^c

^a Department of Chemical Engineering, Universidad de La Frontera, P.O. Box 54-D, Temuco, Chile

^b Technology and Process Unit, Agri Aquaculture Nutritional Genomic Center, Universidad de La Frontera, P.O. Box 54-D, Temuco, Chile

^c Department of Food Science and Chemical Technology, Universidad de Chile, P.O. Box 233, Santiago, Chile

A B S T R A C T

The effect of microwave (MW) radiation on hazelnut seed (*Gevuina avellana* Mol) was studied as a substrate pretreatment prior to oil extraction by pressing. Samples were MW-treated at a frequency of 2450 MHz using a microwave oven. Six MW pretreatments were established, combining two potencies (400 W and 600 W) and three times of pretreatment (120, 180 and 240 s). Extraction oil yield increased with MW pretreatments of hazelnut seed with respect to untreated seeds, as a control. Conditions of 400 W and 240 s were selected (45.3% of extraction oil yield). Observations under light microscopy showed that the microstructure of treated samples to 400 W and 240 s, was modified comparing with that of untreated samples, thereby improving the extraction efficiency. The quality characteristics (e.g. acid value, peroxide value), oil composition (e.g. fatty acids, α -tocotrienol content) and oil oxidative stability (e.g. induction time) were measured. These results were compared to those of an untreated oil sample. MW pretreatment had a positive effect on oxidative oil stability (induction time of 23.9 h) with respect to untreated oil (8.8 h).

Industrial relevance: Chilean hazelnut (*Gevuina avellana* Mol) is the southernmost Macadamieae species of the family Proteaceae that grows mainly in the southern part of Chile and Argentina. The oil is composed mainly of unsaturated fatty acids, which represent 93% of the total. Its main components are oleic and palmitoleic acids, which represent 70% fatty acids. Conventional vegetable oil extraction is carried out by pressing or solvent extraction. Solvent oil extraction is the most efficient method; however, its application presents some industrial disadvantages such as plant security problems, emissions of volatile organic compounds into atmosphere, high operation costs and poor quality products caused by high processing temperatures. Mechanical pressing oil extraction is technically less extensive and less labor-intensive than the extraction solvent method. The safety and simplicity of the whole process is advantageous over the more efficient solvent extraction equipment. Furthermore, materials pressed out generally have better preserved native properties, end products are free of chemicals and it is a safer process. However, extraction by just pressing the seeds is relatively inefficient. It is advisable to research new methodologies for pretreating substrates that also allow for better retention and availability of desirable plant metabolites. Within these pretreatments, the radiation microwave is included. There is not much information in the literature about the application of microwave radiation as a pretreatment for Chilean hazelnut and its effect on the microstructure of the substrate, extraction yield and quality of oil. The aim of the present study was to investigate the impact of pretreatment by microwave radiation prior to the oil extraction by pressing on the microstructure, recovery of oils and oil quality of Chilean hazelnut seeds (*G. avellana* Mol).

Keywords:

Chilean hazelnut
Mechanical pressing
Microwave pretreatment
Oil extraction
Oil quality

1. Introduction

Chilean hazelnut (*Gevuina avellana* Mol) is the southernmost Macadamieae species of the family Proteaceae that grows mainly in the southern part of Chile and Argentina (Bertoli, Fay, Stancanelli, Gumy, & Lambelet, 1998), and is characterized by its high-oil content, around 50% (Moure, Franco, Santa María, Soto, Sineiro, & Domínguez, 2001). The

oil is composed mainly of unsaturated fatty acids, which represent 93% of the total. Its main components are oleic and palmitoleic acids, which represent 70% fatty acids (Bertoli et al., 1998). The unsaturated fatty acid content of the hazelnut makes it a nutritious product, but also more susceptible to auto-oxidation (Frankel, 1991). The hazelnut seed can be processed for valuable edible and cosmetic oil due mainly to its UV filtering properties and to its excellent penetrating ability, attributed to the high palmitoleic acid content (37% of the fatty acid content) (Moure et al., 2001).

Oil-bearing materials for extraction can be divided into low-oil materials (18–22%, dry basis) or high-oil materials (>22%). Lipids in

* Corresponding author. Department of Chemical Engineering, Universidad de La Frontera, P.O. Box 54-D, Temuco, Chile. Tel.: +56 45 325480; fax: +56 45 325053.

E-mail address: euquiche@ufro.cl (E. Uquiche).

oil-bearing materials are located in smaller units called spherosomes or oil bodies (Aguilera & Stanley, 1999). Chilean hazelnut can be classified as high-oil vegetable material.

Conventional vegetable oil extraction is carried out by pressing or solvent extraction. Solvent oil extraction is the most efficient method; however, its application presents some industrial disadvantages such as plant security problems, emissions of volatile organic compounds into atmosphere, high operation costs and poor quality products caused by high processing temperatures (Buenrostro & López-Munguía, 1986; del Valle & Aguilera, 1999). Mechanical pressing oil extraction is technically less extensive and less labor-intensive than the extraction solvent method (Oyinlola, Ojo, & Adekoya, 2004). The safety and simplicity of the whole process is advantageous over the more efficient solvent extraction equipment. Furthermore, materials pressed out generally have better preserved native properties, end products are free of chemicals and it is a safer process.

Mechanical pressing is used on high-oil vegetable materials to extract most oil prior to solvent extraction of the rest (Khan & Hanna, 1983). However, extraction by just pressing the seeds is relatively inefficient. During the expression of oilseeds it should be effectively pressed, so that the capillaries through which the oil is expelled are not sealed by the increased pressure. A major route appears to be the plasmodesmata (cell wall pores) (Aguilera & Stanley, 1999).

Efforts have been made to improve the oil extraction efficiency of mechanical presses. Conventional pretreatment may include dehulling, size reduction, breaking, grinding, thermal treatment (cooking) and enzymatic hydrolysis (Galloway, 1976; Singh & Bargale, 2000) with the purpose of debilitating the cell coats and preparing the material for optimum oil extraction. It is advisable to research new methodologies for pretreating substrates that also allow for better retention and availability of desirable plant metabolites.

Within these pretreatments, the radiation microwave is included. The use of radiation microwave offers reduced processing times and energy savings because the energy is delivered directly to materials through molecular interaction with the electromagnetic field, so that the heat is generated throughout the volume of the material and it is possible to achieve rapid and uniform heating of relatively thicker materials (Decareau, 1985; Ayappa, Davis, Davis, & Gordon, 1991; Thostenson & Chou, 1999; Venkatesh & Raghavan, 2004). A bigger extraction yield can be obtained as a result of an cell membrane rupture obtained using microwave radiation, and permanent pores can be generated, enabling the oil to move through the permeable cell walls.

The dielectric properties of substrates affect the heating rate when the substrates are subjected to high-frequency or microwave electric fields (Takagi, Ienaga, Tsuchiya, & Yoshida, 1999). The dielectric properties of materials are dependent on their chemical composition and especially on the permanent dipole moments associated mainly with water molecules and any other molecules such as salts. The dielectric properties depend too on the frequency of the alternating electric field applied, the temperature of the substrate, as well as on the density, composition, and structure of the substrate (Datta, 1990; Venkatesh & Raghavan, 2004).

There is not much information in the literature about the application of microwave radiation as a pretreatment for Chilean hazelnut and its effect on the microstructure of the substrate, extraction yield and quality of oil. The aim of the present study was to investigate the impact of pretreatment by microwave radiation prior to the oil extraction by pressing on the microstructure, recovery of oils and oil quality of Chilean hazelnut seeds (*G. avellana* Mol).

2. Materials and methods

2.1. Substrate characterization

The hazelnuts (*G. avellana* Mol) were acquired from Las Ñochas Cooperative (Temuco, Chile). The hazelnut seed were hand-selected to

eliminate those with cracked or otherwise damaged seed coats. Prior to analysis and MW pretreatment, the hazelnuts were manually cracked and shelled and then packed in polyethylene packages and stored at 4 °C until their subsequent use.

Moisture content was determined gravimetrically by drying in the oven Memmert (model UM-400, WTB Binder, Tuttingen, Germany) at 105 °C for 15 h to reach a final constant weight. Untreated and spent samples were finely ground with a mortar and pestle prior to analyzing moisture and oil content. Oil content from untreated and spent samples were determined gravimetrically by extraction from 20 g of fine ground samples with technical grade hexane (TCL, Santiago, Chile) to exhaustion in a Soxhlet apparatus for 4 h at 70 °C. Hexane was mostly recovered in a Janke & Kunkel (model RVO5-ST, IKA Laboratories, Staufen, Germany) rotary evaporator that was operated with a Welch (model 2522C-02, Thomas Compressors & Vacuum Pumps, Skokie, IL, USA) vacuum pump and residual solvent traces were removed in the oven (2 h at 80 °C).

Light microscopy was carried out using the procedure reported by Uquiche, del Valle, and Ortíz (2004), for the evaluation of the microstructural destruction of hazelnut seeds due to the radiation microwave effect. Samples were embedded with paraffin prior to cutting thin slices (30- μ m thick) using a manual microtome (Jung, Heidelberg, Germany). Paraffin was removed by treating samples with xylol and the staining was done with safranin and fast green, followed by washing out excess stain with eugenol. A Nikkon (model Optiphot 142915, Kawasaki, Japan) light microscope equipped with a Nikkon (model FX 35A, Kawasaki, Japan) photographic camera was utilized to view and record representative images.

2.2. Microwave pretreatment

For each microwave (MW) pretreatment, 15 g of shelled whole hazelnut were arranged in a single layer in Pyrex petri dishes (9-cm diameter). 90 g of samples distributed in six petri dishes were placed on the external border of the turntable plate of the microwave variable power oven Practique (model MW 2300 NC, Somela S.A., Chile). Samples were MW-treated at a frequency of 2450 MHz. Based on preliminary tests, we established six treatments with microwave, combining two variables: two levels of potency (400 W and 600 W) and three times of radiation (180 s, 210 s, 240 s). Each one of the six treatments was carried out in triplicate. Later the samples MW-treated corresponding to the three replicates were collected and allowed to cool to ambient temperature prior to the oil extraction by pressing. Hazelnut seed samples were oven-dried in a Memmert ULM 700 (Schwabach, Germany) to 50 °C for 6 h, and used as control treatment (untreated samples).

2.3. Oil extraction by pressing

Hazelnut oil was obtained by pressing 60 g of whole hazelnut shelled seed with a hydraulic laboratory press (Carver, Inc., Wabash, Indiana, USA) at 7.1 MPa by 5 min. With longer time there was not additional oil extraction. This operation was carried out three times and the extracted oil was quantified. Later, all the extracted oil was collected for its analysis. Fine particles in the expressed oil were separated by filtration. Additionally, these filtered crude oils were subsequently centrifuged in a centrifuge Hermle (model Z-320, Hermle AG, Tuttlingen, Germany) at 3500 rpm during 20 min to remove components that settled during storage, and stored at 1 °C under nitrogen. Oil extraction yield is defined as percentage of oil expelled at the pressing stage on a total oil extractable basis. Oil expelled is defined as the difference between total oil the original seed and the oil in residual cake.

2.4. Oil analysis

Analysis of the oil samples were determined according to AOCS (1993): specific gravity using a 10 mL pycnometer at 25 °C, refractive

index using Abbé refractometer at 25 °C, acid value expressed as mg KOH necessary to neutralise the free acids in 1 g of oil (Cd 3a–63), peroxide index expressed as milli-equivalents (meq) of peroxide per 1000 g of oil (Cd 8–53), saponification value expressed as mg KOH required to saponify 1 g of oil (Cd 3–25), iodine value by Wijs method, is expressed in terms of the number of g of iodine absorbed per 100 g of oil (Cd 1–25), and unsaponifiable matter expressed as percentage (Ca 6a–40).

Fatty acids composition in the oil samples were determined as methyl esters derivatives (AENOR, 1991) by gas chromatography (GLC) using a HP 5890 chromatograph (Hewlett-Packard, Palo Alto, CA, USA), with a fused silica capillary column BPX70 (50 m, 0.25 µm film, SGE, Incorporated Austin, TX, USA). Temperature programmed between 160 and 230 °C, rate 2 °C/min, with hydrogen as gas carrier with a column flow of 2.0 mL/min, using reference fatty acids methyl esters (FAME) from Merck (Merck, Darmstadt, Germany) for identification.

α-Tocotrienol content, were determined in the oil samples by high-performance liquid chromatography (HPLC) with fluorescence detection, following the AOCS standard method (AOCS Ce 8–89, 1993). The HPLC system consisted of a Merck-Hitachi L-6200A pump (Merck, Darmstadt, Germany), equipped with a Rheodyne 7725i injector with 20 µL sample loop, a Merck-Hitachi F-1050 fluorescence detector and a Merck-Hitachi D-2500 chromato-integrator. Peaks were detected at 290 nm and 330 nm, excitation and emission wavelengths respectively. A LiChroCART Superspher Si 60 column (25 cm×4 mm i.d., particle size 5 µm; Merck, Darmstadt, Germany) was used. The mobile phase was propan-2-ol in hexane (0.5:99.5 v/v) at a flow rate of 1 mL/min. α-Tocotrienol was quantified using external standard (Merck, Darmstadt, Germany).

2.5. Oxidative stability

The oxidation induction time was measured on a Rancimat Oxidative Stability Instrument (Metrohm Ltda, Herisau, Switzerland), according to AOCS (1993) standard method (Cd 12b-92). Standard Rancimat tubes containing 10 g of oil samples were heated at 100±1 °C and an air flow of 20 L/h was passed through the oil samples. The gases released during oxidation were led into a conductivimetric cell containing water, while the change of conductivity of the solution was plotted on a graph during the necessary time. The oxidative stability (OS) was measured as the time corresponding to the inflection point of the curve, named the induction time (IT).

2.6. Statistical analysis

Data were analyzed using ANOVA with microwave potency and time as factors. Statistical analysis was performed according to the Statgraphics Plus (Version 4.0). Statistical significance of the differences observed among mean values was assessed using Duncan's multiple range test. A probability of $p \leq 0.05$ was considered significant.

3. Results and discussion

3.1. Effect of MW pretreatment on oil yield extraction and substrate microstructure

To investigate the effect of MW pretreatment on oil extraction yield by pressing, extractions were carried out by using hazelnut seeds with MW pretreatment and untreated samples. Hazelnut seeds had a moisture of 7.9 g H₂O/100 g sample (d.b.) and oil content of 46.53 g oil/100 g sample (d.b.). Table 1 shows the oil extraction yield expressed as the percentage of oil extracted regarding the initial oil content in the sample. Oil extraction yield from hazelnut seed increased according to the application of MW radiation. MW pretreatment under 400 W and 240 s enabled 45.3% of the initial oil content to be extracted, clearly superior to the untreated sample (6.1%). Of both variables studied, only time had a significant effect on oil extraction yield ($p < 0.05$).

Table 1
Oil extraction yield from Chilean hazelnut seeds

Potency	Time (s)	Extraction yield (%)	Moisture (%)
Control		6.1±1.5	6.5±0.1
400 W	180	35.6±3.2	5.6±0.4
	210	42.2±3.7	5.3±0.2
	240	45.3±3.4	5.3±0.4
600 W	180	41.6±0.8	4.7±0.1
	210	42.4±2.6	4.4±0.2
	240	43.5±0.7	4.2±0.1

Using Duncan's test ($p=0.05$), 240 s and 400 W were selected as conditions of MW pretreatment.

The low moisture in the MW-treated samples (Table 1) can make them more brittle and therefore can achieve a greater rupture of tissue and increase the extraction of oil during the mechanical pressing. However, observations under light microscopy help to explain the better extraction yield of MW-treated hazelnut seeds compared to untreated samples. Even in the literature, when the use of MW has been reported on with respect to the treatment of oilseeds (Ramesh, Rao, & Ramadoss, 1995; Takagi et al., 1999; Valentová, Novotná, Svoboda, Schwarz, & Káš, 2000; Yoshida, Hirakawa, Tomiyama, & Mizushina, 2003; Yoshida, Hirakawa, Tomiyama, Nagamizua, Mizushina, 2005; Anjum, Anwar, Jamil, & Iqbal, 2006; Yoshida, Tomiyama, Hirakawa, & Mizushina, 2006), the information on microscopic evidence of the effect of MW treatment on the substrate microstructure is limited.

Fig. 1 shows that hazelnut seeds contain oil-bearing structures. Fig. 1A shows the intact cellular walls and the oil in the form of globules at different locations in the untreated hazelnut seed. In this case, the original structure in the vegetable substrate is not adequate for the extraction, because the intact cell wall and adhering membranes constitute a major resistance to extraction by pressing (Aguilera & Stanley, 1999). Fig. 1B shows the microstructural effect of MW pretreatment on vegetable tissue from hazelnut seed (treated sample to 400 W and 240 s), clearly showing the modification of the cellular wall, which results in greater porosity. This microwave heating vaporizes the water of the vegetable substrate microstructure, increasing the pressure in its interior; its release causes the disintegration of the material (Starmans & Nijhuis, 1996; Aguilera & Stanley, 1999), cell membrane rupture and improving the efficiency of the pressing extraction of oil from oilseeds, enabling the passage of oil from the cell membrane. There are two types of lipids in oilseeds: storage lipids, which are mainly triacylglycerols and which are high in quantity and localised in oil bodies of the tissues; and membrane lipids, which are mainly phospholipids (Liu & Brown, 1996). Takagi et al. (1999), found that the MW pretreatment of soya bean, dramatically diminished the phospholipid content than triacylglycerol content. In our study, MW pretreatment affected both cell walls and the membrane cell (bilayers of lipids and proteins acting as biological barriers) and the largest extraction yield of oils was obtained.

3.2. Effect of MW pretreatment on fatty indices and functional components

Table 2 shows the physicochemical characteristics of Chilean hazelnut oil. Each value is the mean of three repetitions. Specific gravity (SG) is an important characteristic of vegetable oil and corresponds to the ratio of the weight of the substance's given volume to the weight of an equal volume of water. SG values (Table 2) were 0.912 for both cases, which is within the range reported in the literature for vegetable oils: olive oil (0.910–0.916), rapeseed oil (0.910–0.920), sunflower seed oil (0.918–0.923) and pumpkin seed oil (0.923–0.926) (Nichols & Sanderson, 2003). The refractive index (RI) is often used as a criterion for purity. The RI of saturated FA reveals a linear increase with escalating chain length when measured at a temperature above 40 °C, whereas the IR of unsaturated FA increases with the degree of unsaturation. In both cases, the RI was 1.470, which is within the range reported in the literature for

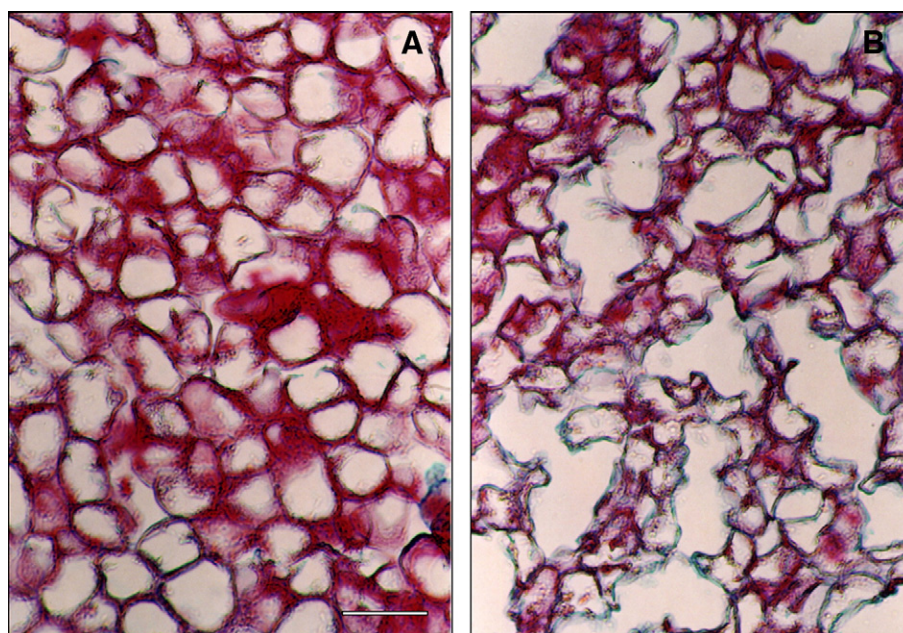


Fig. 1. Light photomicrographs of Chilean hazelnut seeds: (A) untreated hazelnut seed; (B) MW pretreatment hazelnut seed. bar=200 μ m.

vegetable oils: olive oil (1.468–1.471), rapeseed oil (1.465–1.469), sunflower seed oil (1.467–1.469) and pumpkin seed oil (1.466–1.474) (Nichols & Sanderson, 2003).

Acid value can be used for a purity check of oil and may have already started decomposition reactions. Although refined oils are largely devoid of free fatty acids, considerable amounts may be present in crude oils. Acid values stayed relatively constant, untreated seeds was 1.56 mg KOH/g oil and MW pretreatment seeds was 1.83 mg KOH/g oil. The increase in the acid value of oil might be attributed to hydrolysis of triacylglycerols by MW to produce free fatty acids (Anjum et al., 2006).

The peroxide value (PV) measures the quantity of peroxides in the oil; these are important intermediates of oxidative reactions since they decompose via transition metal irradiation and elevated temperatures to form free radicals (Decker, 1998). PV were 0.89 meq O₂/kg oil and 0.92 meq O₂/kg oil for untreated seeds and MW pretreatment seeds, respectively. PV has shown good correlation with organoleptic flavor scores. For example, for soybean oil, a PV of 1.0 or less indicates freshness (O'Brien, 2004). Farag, Hewedi, Abu-Raiia, and Elbaroty (1992) reported acceleration of cottonseed oil oxidation during microwave heating observed by an increase in PV, due to the presence of reactive radicals that might be formed by exposure to microwaves. Similar behavior was observed by Albi, Lanzón, Guinda, Leon, and Pérez-Camino (1997) and Vieira and Regitano-d'Arce (2001) for olive and sunflower oil respectively.

The saponification value (SV) is a measure of the alkali-reactive groups in fats and oils and is useful in predicting the type of glycerides in a sample. Glycerides containing short-chain fatty acids have higher SV than those with longer chain fatty acids. SV of the analyzed

hazelnut oils (Table 2) were 193.0 and 168.0 for untreated seeds and MW pretreatment seeds, respectively, which are within the range reported in the literature for vegetable oils: olive oil (184–196), rapeseed oil (168–181), sunflower seed oil (188–194) and pumpkin seed oil (174–197) (Nichols & Sanderson, 2003).

The iodine value (IV) is a measure of the unsaturation of fats and oils; it is based on the ability of an unsaturated carbon to carbon bond to add halogen atoms and provides a measure of the degree of unsaturation of a lipid IV of the analyzed hazelnut oils (Table 2) were 86.79 g I/100 g oil and 89.40 g I/100 g oil for untreated seeds and MW pretreatment seeds, respectively, which are within the range reported in the literature for vegetable oils: olive oil (75–94), rapeseed oil (94–120), sunflower seed oil (118–145) and pumpkin seed oil (116–133) (Nichols & Sanderson, 2003). The reduction of IV with MW treatment may be attributable to reductions in the number of unsaturation sites as a result of oxidation, polymerization, or breakage of the long-chain fatty acid (Anjum et al., 2006).

Unsaponifiable matter of the analyzed hazelnut oils were 1.47% and 1.80% for untreated seeds and MW pretreatment seeds, respectively. This oil content higher of unsaponifiable matter in pressed pretreatment seed may be due to high content of hydrocarbons, sterols, triterpenols, carotenoids and tocopherols (Barnes, 1983).

Table 3 shows the fatty acids composition in oils from Chilean hazelnut seed. The fatty acid composition of hazelnut oil (Table 3) is very similar to what can be found in previous reports (Bertoli et al., 1998; Karabulut, Topcu, Yorulmaz, Tekin, & Ozay, 2005). However, differences in the fatty acid composition of hazelnut oil are observed between an untreated oil sample and a MW-treated sample. Takagi et al. (1999), Yoshida et al. (2005), Anjum et al. (2006) and Yoshida et al. (2006), studied the effect of microwave treatment on soya bean (*Glycine max*), peanut seeds (*Arachis hypogaea* L.), sunflower seed (*Heliantus annuus* L.) and pumpkin seeds (*Cucurbita* spp.), respectively. These authors reported a change in the fatty acid composition of vegetable oils through the effect of microwave treatment, but they don't inform about the change in extraction yield. Ramesh et al. 1995 studied the effect of microwave treatment on extractability and quality of oil groundnut (*A. hypogaea*). Microwave treatment of groundnut increased oil recovery by pressing.

Oleic acid was the most abundant fatty acid in hazelnut oil, 36.3% and 33.3% for untreated seeds and MW pretreatment seeds,

Table 2
Physicochemical characteristics of Chilean hazelnut oil

Property	Control treatment	MW pretreatment
Specific gravity	0.912±0.000	0.912±0.000
Refractive index (25 °C)	1.470±0.001	1.470±0.001
Acid value (mg KOH/g oil)	1.56±0.11	1.83±0.12
Peroxide value (meq O ₂ /kg oil)	0.89±0.01	0.92±0.02
Saponification value (mg KOH/g oil)	193.0±4.6	168.0±3.2
Iodine value (g I/100 g oil)	86.79±3.65	89.40±2.93
Unsaponifiable matter (%)	1.47±0.01	1.80±0.01

respectively. Among the nuts and other vegetable oils, hazelnut oil has been reported to contain the highest proportion of oleic acid (Ebrahim, Richardson, Tetley & Mehlenbacher, 1994). Palmitoleic acid was the second most abundant fatty acid in the samples and its range was between 29.1% and 24.5%, for untreated seeds and MW pretreatment seeds, respectively. Moreover, the highest concentration of unsaturated fatty acids (oleic, palmitoleic and linoleic acid) in untreated oil sample (U/S=13.574) allows oxidative rancidity to occur (Kinderlerer & Johnson, 1992). The results shown in Table 3 demonstrate that the MW pretreatment affected the fatty acid compositions of Chilean hazelnut oil. Changes in the fatty acid composition after MW pretreatment of oilseeds have been reported by Takagi et al. (1999) and Yoshida et al. (2003).

The lipid, in the form of oil globules, is present in the cells of the oilseed at different locations along with other constituents such as proteins, globoids and nucleus. Liu & Brown (1996), point out that in these different locations can exist two types of lipids: storage lipids (mainly triacylglycerols) and membrane lipids (mainly phospholipids). Takagi et al. (1999), Yoshida et al. (2003, 2005, 2006), have reported different fatty acid distribution between triacylglycerols and phospholipids in oilseeds. The different fatty acids distribution of oils between MW-treated seed and untreated samples, would be due to the partial destruction of microstructural barriers in MW treated samples, which enhanced the oil recovery, and can be extracting oils that come from the different compartments of the seed, contrary to the untreated seed, where the fatty acids distribution correspond to the oil that in quantity minor was recovered by pressing.

The α -tocotrienol content in the hazelnut oil ($\mu\text{g/g}$) is a measure of antioxidant quantity in the oil that was extracted by pressing (Table 4). A smaller concentration of α -tocotrienol is observed in the sample with MW pretreatment (92.2 $\mu\text{g/g}$ oil) with respect to the untreated sample (104.3 $\mu\text{g/g}$ oil). However, this is compensated with the higher oil yield extraction (20.11 g oil/100 g sample dried) for the MW-treated sample in comparison with the untreated sample (2.84 g/100 g substrate dried). This content of α -tocotrienol is according to that reported by Bertoli et al. (1998) of 130 mg/kg, identified as the major antioxidant in this oil.

The α -tocotrienol is a tocol. Tocols are important liposoluble metabolites synthesized by plant cells and in humans they act as Vitamin E precursors. The α -tocotrienol is well recognized for its antioxidative effect, which retards the oxidation of unsaturated fatty acids in foods and biological systems (Uppström, 1995). In general, antioxidants are supposed to reduce cardiovascular disease and

Table 3
Fatty acids compositions (%) of Chilean hazelnut oil

Fatty acids		Control	MW pretreatment
Lauric	C12:0	0.04±0.00	0.05±0.01
Myristic	C14:0	0.13±0.01	0.13±0.01
Myristoleic	C14:1n5	0.04±0.00	0.03±0.00
Palmitic	C16:0	1.92±0.01	1.55±0.01
Palmitoleic	C16:1n7	29.08±1.16	24.48±1.12
Stearic	C18:0	0.57±0.01	0.54±0.01
Oleic	C18:1n9	36.30±1.10	33.34±1.15
Vaccenic	C18:1n7	7.24±0.11	7.63±0.08
Linoleic	C18:2 n6	7.16±0.02	5.84±0.03
α -Linolenic	C18:3 n3	1.33±0.03	1.40±0.01
Arachidic	C20:0	2.62±0.01	3.08±0.11
Gondoic	C20:1n9	5.60±0.11	6.89±1.01
Behenic	C22:0	1.40±0.01	2.52±0.05
Erucic	C22:1n9	6.34±0.32	11.75±0.76
Lignoceric	C24:0	0.18±0.01	0.55±0.01
Nervonic	C24:1n9	0.07±0.01	0.21±0.01
Saturated fatty acids (S)		6.86±0.63	8.42±0.32
Polyunsaturated fatty acids (P)		8.48±0.44	7.24±0.54
Unsaturated fatty acids (U)		93.14±1.18	91.58±1.37
P/S		1.24	0.86
U/S		13.57	10.88

Table 4
Content of α -tocotrienol in oil from Chilean hazelnut seed

Type of oil	α -tocotrienol ($\mu\text{g/g}$ oil)	Extraction yield (g oil/100 g substrate)	α -tocotrienol yield ($\mu\text{g}/100$ g substrate)
Control treatment	104.3±1.02	2.84±0.67	295.37
MW pretreatment	92.2±0.41	20.11±1.82	1853.68

cancer. In the field of cancer chemotherapy, tocotrienols have been shown to display better anti-tumor activity than α -tocopherols. Hence, the role of α -tocotrienol in the prevention of cardiovascular disease and cancer may have significant implications (Therault & Chao, 1999).

3.3. Effect of MW pretreatment on oil stability

The OSI characterizes the ability of the oil to resist oxidation and is an important parameter in identifying conditions that preserve oil quality (Holser, 2003). The induction time (IT) were 8.8±0.7 h for oil from untreated seeds and 23.9±0.9 h for oil from MW pretreatment seeds, with this last value being considered of good oxidative stability. This IT value is close to that reported by Bertoli et al. (1998) for hazelnut oil extracted with petroleum benzene (IT=20 h at 110 °C). Romero et al. (2007) found an IT value of 19.6 h for rapeseed oil (*Brassica* sp.), which was considered a high IT.

The higher oil stability was possibly due to the inactivation of oxidative enzymes such as lipase, peroxidase and lipoxigenase (Veldsink et al., 1999; Valentová, Novotná, Svoboda, Pejchar, and Káš, 2002). Lipase and peroxidase are found to be responsible for the development of rancidity in almond and hazelnut (Metwalli, El-Sebaiy, & Noaman, 1983; Bonvehí & Coll, 1993; Pershern, Breene, & Lulai, 1995; Zacheo, Cappello, Perrone, & Gnoni, 1998) have reported that lipoxigenase activity in hazelnuts influences lipid oxidation and that it is inversely related with the shelf-life. Inactivation of these enzymes, for example by heating, has been shown to increase the shelf-life of oilseeds (Vetrimani, Jyothirmayi, Rao, & Ramadoss, 1992; Ponne et al., 1996).

On the other hand, the higher content of unsaturated fatty acids, mainly oleic, palmitoleic and linoleic, in untreated oil sample (U/S=13.57) with respect to oil from MW pretreatment oil (U/S=10.88) would explain the lowest oxidative stability in oil from pressed control seed. It has been reported that a relationship exists between the content of linoleic acid and oxidative stability, where linoleic acid is the main cause of the chemical rancidification of the hazelnut oil (Kermasha, Van Voort, & Metche, 1986; Bonvehí & Coll, 1993).

4. Conclusions

In this study, the effect of microwave (MW) pretreatment on extraction oil yield and oil quality from Chilean hazelnut was investigated. The conclusion reached was that a MW pretreatment could be applied to Chilean hazelnut oil extraction prior to pressing to improve the oil recovery and its quality. Pretreatment at 240 s and 400 W as conditions of MW pretreatment enabled up to 45.3% of the oil to be extracted. MW pretreatment methods can help to the microstructural modification of substrate tissue and on the increase in mass transfer of oils and other lipids minor, as it is demonstrated in the increase of unsaponifiable matter in the extracted oil, improving the extraction oil yield. Observations with light microscopy can be applied to evaluate the impact of MW pretreatment on the substrate microstructure. MW pretreatment would help in the rupture of the cell wall making cell permeabilization possible and enabling the oil to move through the permeable cell walls. Finally, the data also indicate the possibility that microwave radiation has a positive effect on oil quality. In effect, the oils obtained from MW pretreatment seeds have higher stability to the oxidative deterioration (IT=23.9 h) with respect

to untreated seed (IT=8.8 h), possibly due to the inactivation of the oxidative enzyme, and to the higher content of unsaturated fatty acids in untreated oil sample (linoleic acid=7.16%; P/S=1.24; U/S=13.57) compared to MW pretreatment seeds (linoleic acid=5.84%; P/S=0.86; U/S=10.88).

Acknowledgments

This study was financed by the Universidad de La Frontera (DIDUFRO project 120526). We wish to thank Mr. A. Campomanes (Cooperativa La Ñochas, Temuco, Chile) for kindly supplying hazelnut seed samples and the Agri Aquaculture Nutritional Genomic Center, Technology and Process Unit (UFRO, Temuco, Chile).

References

- AENOR (1991). Asociación Española de Normalización. Norma UNE 55037-73 Madrid: Catálogo de Normas UNE.
- Aguilera, J. M., & Stanley, D. W. (1999). *Microstructural principles of food processing and engineering* (pp. 325–372). 2nd ed. Gaithersburg, MD: Aspen Publishers Inc.
- Albi, T., Lanzón, A., Guinda, A., Leon, M., & Pérez-Camino, M. C. (1997). Microwave and conventional heating effects on thermoxidative degradation of edible fats. *Journal of Agricultural and Food Chemistry*, 45, 3795–3798.
- American Oil Chemists Society (1993). *Official methods and recommended practices of the American Oil Chemists Society*, 4th ed. Champaign, IL: AOCS Press.
- Anjum, F., Anwar, F., Jamil, A., & Iqbal, M. (2006). Microwave roasting effects on the physico-chemical composition and oxidative stability of sunflower seed oil. *Journal of American Oils Chemists Society*, 83, 777–784.
- Ayappa, K. G., Davis, H. T., Davis, E. A., & Gordon, J. (1991). Analysis of microwave heating of materials with temperature-dependent properties. *AIChE Journal*, 37, 313–321.
- Barnes, P. J. (1983). Non-saponifiable lipids in cereals. In P. J. Barnes (Ed.), *Lipids in cereal technology* (pp. 33–55). New York: Academic Press.
- Bertoli, C., Fay, L. B., Stancanelli, M., Gumy, D., & Lambelet, P. (1998). Characterization of Chilean hazelnut (*Gevuina avellana* Mol) seed oil. *Journal of the American Oil Chemists Society*, 75, 1037–1040.
- Bonvehí, J. S., & Coll, F. V. (1993). Oil content stability and fatty acid composition of the main varieties of Catalan hazelnuts (*Corylus avellana* L.). *Food Chemistry*, 48, 237–241.
- Buenrostro, M., & López-Munguía, C. (1986). Enzymatic extraction of avocado oil. *Biotechnology Letters*, 8, 505–506.
- Datta, A. K. (1990). Heat and mass transfer in the microwave processing of food. *Chemical Engineering Progress*, 84, 47–53.
- Decareau, R. V. (1985). *Microwaves in the food processing industry* (pp. 28–32). London, UK: Academic Press.
- Decker, E. A. (1998). Antioxidant mechanisms. In C. C. Akoh, & D. B. Min (Eds.), *Food lipids, chemistry, nutrition, and biotechnology* (pp. 397–401). New York: Marcel Dekker.
- del Valle, J. M., & Aguilera, J. M. (1999). Extracción con CO₂ a alta presión. Fundamentos y aplicaciones en la industria de alimentos. *Food Science and Technology International*, 5, 1–24.
- Ebrahem, K. S., Richardson, D. G., Tetley, R. M., & Mehlenbacher, S. A. (1994). Oil content, fatty composition, and vitamin E concentration of 17 hazelnut varieties, compared to other types of nuts and oil seeds. *Acta Horticulturae*, 351, 685–692.
- Farag, R. S., Hewedi, F. M., Abu-Raiia, S. H., & Elbaroty, G. S. (1992). Comparative study on the deterioration of oils by microwave and conventional heating. *Journal of Food Protection*, 55, 722–727.
- Frankel, E. N. (1991). Recent advances in lipid oxidation. *Journal of the Science of Food and Agriculture*, 54, 489–511.
- Galloway, G. P. (1976). Cleaning, cracking, dehulling, decorticating and flaking of oil bearing materials. *Journal of American Oils Chemists Society*, 53, 271–274.
- Holser, R. A. (2003). Properties of refined milkweed press oil. *Industrial crops and products*, 18, 133–138.
- Karabulut, I., Topcu, A., Yorulmaz, A., Tekin, A., & Ozay, D. S. (2005). Effects of the industrial refining process on some properties of hazelnut oil. *European Journal of Lipid Science and Technology*, 107, 476–480.
- Kermasha, S., Van Voort, F. R., & Metche, M. (1986). Conversion of linoleic and hydroperoxide by French bean hydroperoxide isomerase. *Journal of Food Biochemistry*, 10, 285–303.
- Khan, L. M., & Hanna, M. A. (1983). Expression of oil from oilseed: A review. *Journal of Agricultural Engineering Research*, 28, 495–503.
- Kinderlerer, J. L., & Johnson, S. (1992). Rancidity in hazelnuts due to volatile aliphatic aldehydes. *Journal of the Science of Food Agriculture*, 58, 89–93.
- Liu, K., & Brown, E. A. (1996). Fatty acid compositions in newly differentiated tissues of soybean seedlings. *Journal of Agricultural Food Chemistry*, 44, 1395–1398.
- Metwalli, S. M., El-Sebaiy, L. A., & Noaman, M. A. (1983). Effect of roasting on lipase activity and organoleptic quality of sweet almond and hazelnut. *Journal of Agricultural Research*, 9, 1115–1125 Tanta University.
- Moure, A., Franco, D., Santamaria, R. I., Soto, C., Sineiro, J., & Domínguez, H. (2001). Enzyme-aided alternative processes for the extraction of oil from *Rosa rubiginosa* seeds. *Journal of American Oils Chemists Society*, 78, 437–440.
- Nichols, D. S., & Sanderson, K. (2003). The nomenclature, structure, and properties of food lipids. In Sikorski, & Kolakowska (Eds.), *Chemical and functional properties of foods lipids* (pp. 29–59). Boca Raton, FL: CRC Press LLC.
- O'Brien, R. D. (2004). *Fats and oils: Formulating and processing for applications* (pp. 174–233). 2nd ed. Boca Raton, FL: CRC Press LLC.
- Oyinlola, A., Ojo, A., & Adekoya, L. O. (2004). Development of a laboratory model screw press for peanut oil expression. *Journal of Food Engineering*, 64, 221–227.
- Pershern, A. S., Breene, W. M., & Lulai, E. C. (1995). Analysis of factors influencing lipid oxidation in hazelnuts (*Corylus* spp.). *Journal of Food Processing and Preservation*, 19, 9–26.
- Ponne, C., Möller, A. C., Pelkmans, Tijkens, L. M. M., Bartels, P. V., & Meijer, M. M. T. (1996). Influence of microwave and steam heating on lipase activity and microstructure of rapeseed (*Brassica napus*). *Journal of Agriculture and Food Chemistry*, 44, 2818–2824.
- Ramesh, M., Rao, P. H., & Ramadoss, C. S. (1995). Microwave treatment of groundnut (*Arachis hypogaea*): extractability and quality of oil and its relation to lipase and lipoxygenase activity. *Lebensmittel Wissenschaft und Technologie*, 28, 96–99.
- Romero, N., Robert, P., Masson, L., Ortiz, J., González, K., Tapia, K., et al. (2007). Effect of α -tocopherol, α -tocotrienol and *Rosa mosqueta* shell extract on the performance of antioxidant-stripped canola oil (*Brassica* sp.) at high temperature. *Food Chemistry*, 104, 383–389.
- Singh, J., & Bargale, P. C. (2000). Development of a small capacity double stage compression screw press for oil expression. *Journal of Food Engineering*, 43, 75–82.
- Starman, D. A. J., & Nijhuis, H. H. (1996). Extraction of secondary metabolites from plant material: A review. *Trends in Food Science and Technology*, 7, 191–197.
- Takagi, S., Ienaga, H., Tsuchiya, C., & Yoshida, H. (1999). Microwave roasting effects on the composition of tocopherols and acyl lipids within each structural part and section of a soya bean. *Journal of the Science of Food and Agriculture*, 79, 1155–1162.
- Theriault, A., & Chao, J. (1999). Tocotrienol: Review of its therapeutic potential. *Clinical Biochemistry*, 32, 309–319.
- Thostenson, E. T., & Chou, T. W. (1999). Microwave processing: Fundamentals and applications. *Composites. Part A, Applied Science and Manufacturing*, 30, 1055–1071.
- Uppström, B. (1995). Seed chemistry. In D. S. Kimber, & D. I. McGregor (Eds.), *Brassica oils production and utilization* (pp. 223). Wallingford, UK: Cab International.
- Uquiche, E., del Valle, J. M., & Ortiz, J. (2004). Supercritical carbon dioxide extraction of red pepper (*Capsicum annuum* L.) oleoresin. *Journal of Food Engineering*, 65, 55–66.
- Valentová, O., Novotná, Z., Svoboda, Z., Pejchar, P., & Káš, J. (2002). Influence of microwave treatment on the quality of rapeseed oil. *Journal of American Oils Chemists Society*, 79, 1271–1272.
- Valentová, O., Novotná, Z., Svoboda, Z., Schwarz, W., & Káš, J. (2000). Microwave heating and γ -irradiation treatment of rapeseed (*Brassica napus*). *Journal of Food Lipids*, 7, 237–245.
- Veldsink, J. W., Muuse, B. G., Meijer, M. M. T., Cuperus, F. P., van Sande, R. L. K. M., & van Putte, K. P. A. M. (1999). Heat pretreatment of oilseeds: Effects on oil quality. *European Journal of Lipid Science and Technology*, 101, 244–248.
- Venkatesh, M. S., & Raghavan, S. V. (2004). An overview of microwave processing and dielectric properties of agri-food materials. *Biosystems Engineering*, 88, 1–18.
- Vetrimani, R., Jyothirmayi, N., Rao, P. H., & Ramadoss, C. S. (1992). Inactivation of lipase and lipoxygenase in cereal bran, germ and soybean by microwave treatment. *Lebensmittel Wissenschaft und Technologie*, 25, 532–535.
- Vieira, T., & Regitano-d' Arce, M. (2001). Canola oil thermal oxidation during oven test and microwave heating. *Lebensmittel Wissenschaft und Technologie*, 34, 215–221.
- Yoshida, H., Hirakawa, Y., Tomiyama, Y., & Mizushima, Y. (2003). Effects of microwave treatment on the oxidative stability of peanut (*Arachis hypogaea*) oils and the molecular species of their triacylglycerols. *European Journal of Lipid Science and Technology*, 105, 351–358.
- Yoshida, H., Hirakawa, Y., Tomiyama, Y., Nagamizua, T., & Mizushima, Y. (2005). Fatty acid distributions of triacylglycerols and phospholipids in peanut seeds (*Arachis hypogaea* L.) following microwave treatment. *Journal of Food Composition and Analysis*, 18, 3–14.
- Yoshida, H., Tomiyama, Y., Hirakawa, Y., & Mizushima, Y. (2006). Microwave roasting effects on the oxidative stability of oils and molecular species of triacylglycerols in the kernels of pumpkin (*Cucurbita* spp.) seeds. *Journal of Food Composition and Analysis*, 19, 330–339.
- Zacheo, G., Cappello, A. R., Perrone, L. M., & Gnoni, G. V. (1998). Analysis of factors influencing lipid oxidation of almond seeds during accelerated ageing. *Lebensmittel Wissenschaft und Technologie*, 31, 6–9.