Chemical evaluation and thermal behavior of Chilean hazelnut oil (*Gevuina avellana Mol*) a comparative study with virgin extra Olive oil

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Abstract

There is a growing interest in the study of oils from native fruits, especially when the oil has high quality. In this sense it is mandatory to evaluate the oxidative stability and the relationship with the modifications of the fatty acid content, physicochemical parameters, the antioxidant capacity and its protection against the thermal deterioration processes. The fatty acid profiles of Chilean hazelnut oil showed a relevant presence of the omega series (ω-9, ω-5 and ω -9) with good stability across the thermal treatment. The physics-chemical parameters such as polar compounds and absorption coefficients K_{232} and K_{270} shown a similar behavior compared with olive oil oxidation in the range of 25 to 360°C. The antioxidant capacity and total phenolic content in olive oil is significatively higher than Chilean hazelnut oil at 25 ºC, however this antioxidant capacity decreases in the olive oil after 100°C until 247 ºC where the antioxidant capacities for both oils are equalized. Total phenolic content of olive oil diminish after 100°C until the final study temperature (360°C) where its concentration is very similar than Chilean hazelnut oil. The results of the thermogravimetric and differential analysis in the range of 100-700°C shown that the thermal oxidative decomposition processes occurred in both samples mainly in three steps with a total mass loss for olive oil and Chilean hazelnut oil of 99.7 and 99.9% respectively. It is important to note that hazelnut oil remains thermally stable up to 247 ºC just a few degrees lower than olive oil (252 ºC).

Introduction

Chilean hazelnut (*Gevuina avellana* Mol) is a native variety that grows mainly in the southern part of Chile and Argentina, is characterized by its high-oil content, around 50% [1]. Chilean Hazelnuts is high content in A and E vitamins, extracts from the hulls of hazelnuts showed high antioxidant activity and offered a great potential as a natural source of carotenoids for using in food technology [2].

The hazelnut oil can be extracted mainly by two methods: by pressing or solvent extraction. The solvent extraction is the most efficient method, however can change the properties of the oil obtained, in addition, presents an environmental risk due to the toxicology of the solvents used. Mechanical pressing oil extraction generally have better preserved native properties and is free of chemical substances being advantageous over the extraction solvent method, but the yield is very low between 10-12% of oil, wich make it unefficient method to industrial purpose [3,4].

The hazelnut oil has excellent cosmetic properties, because filtering the infrared and UV low spectrum radiation, which gives it application as a solar protection agent and skin regenerator. The oil is composed mainly of unsaturated fatty acids, which represent 93% of the total [5]. Its main components are oleic and palmitoleic acids, which represent 70% fatty acids and penetrates into skin faster than other fatty acids, being rapidly adsorbed [6]. This property has allowed its use as a carrier for pharmaceutical and cosmetic products. Often it is added to creams as solar UV filter [7,8].

The unsaturated fatty acid content of the hazelnut oil make it more susceptible to auto-oxidation process. On the other hand, phenolic compounds such as tocopherols and tocotrienols are very important in the antioxidant activity of oils [9] and contribute to their oxidative stability [9,10]. The antioxidant activity of tocopherols was reported to be in the order $\alpha > \beta > \gamma > \delta$ under low to mild temperatures and in the reverse order at higher temperatures [11]. Processes at

high temperature the loss of tocopherols generally becomes more rapid as the degree of oil unsaturation decreases [12].

It has been reported that α-tocotrienol was the main natural antioxidant present in this oil [6,9]. Also, the addition of α-tocopherol and α-tocotrienol improved the thermal stability and reduced the formation of polar compounds during thermal oxidation of hazelnut oil [9]. Similarly, it has been shown that the carotenoid-tocopherol interaction, through the addition of rosa mosqueta extract on Chilean hazelnut oil, can protect tocols against degradation at high temperature [13].

In processes that occur at high temperatures it is of primary interest to know the changes that suffer the compounds present in the oil to define their relationship with oil deterioration. There is a lack of information in the literature on the behavior of Chilean hazelnut oil at high temperatures and its chemical quality. This deepening in the changes suffered by this oil would be a contribution to knowledge if its behavior is compared with the widely studied extra virgin olive oil.

The principal aim of this research was to investigate the behavior of Chilean hazelnut oil at high temperature conditions and compare with the extra virgin olive oil behavior, through the analysis of antioxidant capacity, total polar compounds, spectrophotometric measurements, fatty acids profile and thermogravimetric analysis.

Experimental

Chemical and reagents

Methanol and hexane and other solvents were obtained from Arquimed (Santiago, Chile). Gallic acid, Folin-Ciocalteu, and 2,2-Diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma-Aldrich (St. Louis, MO, U.S.A). Other chemicals (analytical grade) used in this study were purchased from Merck (Santiago Chile), unless stated other wise.

Vegetable oils

The Chilean hazelnuts were collected from the Nahuelbuta mountain in Chile, the hazelnut oil was obtained by pressure according to previously published conditions with some modifications [3]. Approximately 50 g of ripe Chilean hazelnut were added in a mechanical press (Carver, Inc., Wabash, Indiana, USA), then the crude oil was filtered with filter paper (watman n°1) and finally the crude oil was centrifuged at 3500 rpm for 20 min (DLAB, DM04125) to eliminate any residual particles. The hazelnut oil was stored at 5 °C until analysis. Extra virgin Olive Oil was obtained from the local market.

Thermal oxidation assays

The oil samples were studied in a thermogravimetric analyzer (Netzsch, STA 409 PC/PG model), under the following conditions; constant heating ramp of 5°Cmin^{-1}. The heating range was from room temperature to 700°C, using air as reactive gas with a mass flow of 100 mL min^{-1}. In addition, He gas with a flow of 10 mL min^{-1} was used as protection gas in the electronic balance. the mass used for each sample was around 110 mg which was placed in a ceramic pan. Once the TG / DTG curves were obtained, 5 temperatures were selected to carry out a detailed follow-up of the sample degradation process. The selection criteria for temperatures were room temperature ($T_{25°C}$); temperature of the onset of degradation (T_0); intermediate temperature (T_{int}) between ($T_{25°C}$) and (T_0); the temperature that considers 5% of the degradation ($T_{5\%}$); the temperature that considers 10% of the degradation ($T_{10\%}$).

Fatty acid composition

Fatty acids were determined in the oils by gas chromatography FID detection, previous preparation of the fatty acid methyl esters derivatives. A Hewlett Packard model 5890 serie II chromatograph fitted with a FID detection (Hewlett-Packard, Palo Alto, CA, USA) equipped with a split-splitless injector, automatic autosampler, and coupled to a computerized Chroncard system for data acquisition was used. It was fitted with a capillary column SP-2380 capillary column (30 m length, 0.25 mm i.d., 0.20 μm film thickness). The carrier gas was hydrogen at a flow rate of 1mL/min. the temperatures of the injector and detector were held at 220, and 250, respectively. The initial oven temperature was 180 °C and a temperature gradient from 180 to 220 °C at 3 °C min^{-1} was applied. The sample size was 1 µL. Standard fatty acid methyl esters (FAME) from Merck (Merck, Darmstadt, Germany) [14]. The identification of the fatty acids was done by comparison of their retention times with those of standard FAME.

Heating of oils

At least 10 mL of each oil was added in 25 mL beaker and then heated through a hot plate with a thermometer to temperature control. Each oil was submitted to different heating temperatures ($T_{25°C}$, T_{int}, T_0, $T_{5\%}$, $T_{10\%}$) selected from TG/DTG survey for 15 min. The determination of total phenolic content, antioxidant activity, fatty acid profile, extinction coefficients and total polar compounds were performed for each temperature with the purpose of to understand the deterioration process applied for the two studied oils.

Total phenolic content (TPC)

The phenolic content of oil was extracted according to the protocol described by Ali Rehab & El Anany (2012) with slight modifications [15]. Approximately 5g of oil were weighed and placed in a Falcon tube, the oil was combined with an equal

amount of n-hexane. Then extraction with 5 mL of a methanol: water mixture (60:40) was performed. The mixture was stirred for 5 min and then centrifuged at 5500 rpm for 5 min. This procedure was performed at least 3 times. A small portion of hexane was used to wash the aqueous phase and extract oil residues. The TPC of the hydroalcoholic fraction of the oils were determined according to the Folin-Ciocalteu method [16].

Radical scavenging activity

Radical scavenging activity (RSA) of the different oil samples was determined as previously described with slight modifications [17]. An aliquot of 75 µL of each oil and control (80% methanol), respectively, were combined with 150 µL of DPPH. The mixture was shaken vigorously for 10s in a screw-capped test tube, and then incubated under dark conditions for 30 min at room temperature. The spectrophotometric measurements in the solutions were made at a wavelength of 515 nm. The DPPH radical-scavenging activity was calculated using the following formula:

DPPH radical – scavenging activity (%) = [(1 - AE/AD) x 100],

In the formula AE corresponds to the absorbance of the solution after adding the extract of fraction and AD corresponds to the absorbance of the blank DPPH solution. The compound used for quantification was quercetin.

Analysis of polar compounds (PC)

Testo 270 instrument was used to measure total polar compounds (PC). In accordance with the manufacturer's statement the results are showed in percentage. The sensor is based on parallel plate capacitor, this is immersed in hot oil at about 10 min after to reach the temperatures obtained from the TG/DTG study. the sensor was immersed at least 1 min until to get stable Reading. Value of TPC was showed in the screen of the monitor.

Statistical analysis

Results of most the experiment were expressed as mean ± standard deviation (SD). The statistical analysis ANOVA was used with the software SPSS 18.0 (Statistical Product and Service Solutions). The statistical significance level was set at $p<0.05$.

K_{232} and K_{270} Extinction Coefficients

Extinction coefficients (K_{232} and K_{270}) of the oil samples were calculated from absorption values measured at 232 and 270 nm. The UV analysis of the oil was performed on a scanning spectrophotometer (Helios Alpha Unicam, using 1 cm path length quartz cuvettes with hexane as a reference). The calculations were based on the formula, $K_\lambda = D_\lambda/C$ (eq 1), where K_λ is the specific extinction coefficient for each wavelength, D_λ is the absorption, and C is the oil concentration in g/100 mL [18].

RESULTS AND DISCUSSION

Table 1A shows the fatty acid composition of CHO. At the initial temperature of the thermal's study, CHO is a monounsaturated vegetable oil with a total of 85.16% of this kind of fatty acids. Represented meanly by oleic acid (36.8%) and palmitoleic acid (23.6%) with a total of 3 positions's isomers for this last fatty acid. Moreover, CHO showed a low content of polyunsaturated (7.95%) and saturated fatty acids (6.89%), represented mostly by linoleic (7.83%) and behenic (2.23%) fatty acids respectively. The CHO fatty acid profile is in agreement with data published previously [9]. On the other hand, the higher content of unsaturated fatty acids in CHO (U/S ratio start at 13.51 until 10.14) sample compare with OO sample (U/S

initial value = 5.77), would explain a less thermal stability for CHO. It has been reported that there is a relationship between the content of linoleic acid and oxidative stability, where linoleic acid is proposed as the main cause of the chemical rancidification of the hazelnut oil [19]. Additionally, Goncuoglu & Gokmen (2015) reported range of percentages of fatty acids of 7.65-10.75 for SFA, 89.1-91.1 for MUFA and 8.2-11.9 PUFA for fourteen Turkish hazelnut varieties harvested in the year 2013 [20]. Being the contribution of fatty acids in decreasing order; oleic acid > linoleic acid > palmitic acid > stearic acid. These total percentages for saturated, monounsaturated and polyunsaturated fatty acids are close to the obtained for Chilean Hazelnut according table 1. However, a different composition in fatty acid could be used for detection of adulterations or a tool to detect authenticity. In the OO case, see table 1B, at the initial temperature shows a high percentage of monounsaturated fatty acids represented mainly by oleic fatty acid (72.43%). Followed by saturated fatty acids with the palmitic fatty acid (12.34%) with the bigger concentration and finally polyunsaturated fatty acids represented mainly by the linoleic fatty acid (7.57%). Similar results for fatty acid composition were reported in other countries [21]. U/S ratio for OO is kept in a low range 5.77-4.02 during the thermal's study, suggesting that OO is less sensitive to thermal oxidation than CHO.

Table 1 also shows the changes in fatty acid composition, total saturated fatty acids, total monounsaturated fatty acids and total polyunsaturated fatty acids content in OO and CHO during termooxidation study. In general, the results show a change in every fatty acid present in both oils heated from 25 to 360ºC. This range is because over 360°C the mass of vegetable oils diminish considerably. There were decreases drastically in polyunsaturated (PUFAs) such as linoleic (C18:2) and linolenic (C18:3) acids including a total disappearance of the last fatty acid in both study oils at the 360ºC. Whereas total saturated fatty acids (SFAs) increased represented mainly by palmitic (C16:0), stearic (C18:0), arachidic (C20:0) and lignoceric acids (C24:0) for both oils. Sulieman et al. (2006) reported that when different vegetable oils are submitted to high temperatures at longer time (16h), the level of polyunsaturated fatty acids such as linoleic acid decreased in contrast to

saturated fatty acids such as palmitic acid increased [22]. The PUFA / SFA (P/S) ratio is known as the polyene index and is considered as a measure of the degree of polyunsaturation of an oil and its tendency to suffer autoxidation [23]. The difference in fatty acid profile resulted in a polyunsaturated fatty acid/saturated fatty acid (P/S) ratio from 0.6 to 0.03 for OO and 1.2 to 0.1 for CHO at the initial and final study temperatures. It should be noted that CHO reduce their P/S ratio proportionally less than OO demonstrating that CHO is stable during deterioration conditions.

In this heating study for both oils total polyunsaturated fatty acids decrease drastically, to less than 0.1%. Total monounsaturated fatty acids increased lightly and total saturated fatty acids increased notoriously, close to 25% with respect of the initial temperature condition. The behavior of vegetable oils submitted to termooxidation process have been related to degradation firstly to PUFAs, followed by the degradation of MUFAs and finally [24].

In the present study, a very low percentage of geometric isomers (trans fatty acid) for oleic and linoleic acids appeared in the range of temperatures of 247 and 340ºC respectively in both study oils. Tsuzuki (2010) show that heat induced double bond isomerization by radical species in unsaturated lipid modeling systems [25]. Also, at high temperatures (above 200°C) the double bond can also be shifted to adjacent positions when conjugated systems can be formed [26].

The absorbance ($E_{cm}^{\%}$) measurements at 232 nm (K_{232}) and 270 nm (K_{270}) contribute to the determination of the oxidation of fats. K_{232} has been associated to generation of primary oxidation products (conjugated dienes) and K_{270} secondary (conjugated trienes) oxidation products. The changes in $E_{cm}^{\%}$ at 232 and 270nm during heating study for OO and CHO are shown in fig. 1A and 1B respectively. The $E_{cm}^{\%}$ at 232 and 270 for all samples increased with increasing of the temperature, except for the final temperature (360°C) for K_{232} case in both samples. It can be observed that from room temperature until 180°C the slope of the curve of K_{232} and K_{270} are low compared with the slopes over 180°C. This situation can be related with the loss of protective compounds to oil oxidation process such as phenolic compounds due boiling point is close to this temperature.

The levels of conjugated dienes throughout heating time are lower in OO than CHO except for the final temperature. Similar behavior was observed for all temperatures for K_{270} on OO and CHO. Indicating less stability oxidative for CHO compared with OO. This situation can be correlated with a higher proportion of monounsaturated fatty acids in CHO than OO, and it's also complemented with higher content of saturated fatty acid in OO against CHO. These could be the reasons why CHO accumulated more conjugated dienes and trienes during all study temperatures.

Whereas the maximum permitted value of K_{232} and K_{270} for extra virgin olive oil (EVOO) in the European regulation limits are 2.5 and 0.2, respectively, in our case OO at 25ºC is below these values [27]. The OO exceed these limits over 180 ºC y 100 ºC for K_{232} y K_{270} respectively. For CHO there are no regulations.

The peroxides index is one of the parameters most used at the industrial level when it is required to measure the deterioration of fats and oils, however this indicator is not very robust because the peroxides are unstable at high temperatures. Some countries propose in their regulations to use the index of polar compounds (PC) to measure the quality of fats subjected to high temperatures, this index is widely used, since it considers the oxidative and hydrolytic deterioration suffered by fat [28]. In the case of our country, the permitted limit is 25% for oils subjected to frying processes, where a higher value is recommended to discard fat [29]. The Testo 270 measurements are based on changes in the dielectric constant of the heated oil and this measurement has been correlated highly with PC open-column conventional method [30]. In this study, the content of PC increased strongly starting from 180ºC in both vegetable oil, see fig. 2. In spite of the PC of CHO were significantly higher than OO in every study temperature. PC were less than 25% at least until 250ºC for both oils, confirming that CHO is stable to high temperatures and good alternative to cooking process.

The thermogravimetric analysis was performed in a range from 100 to 700 °C, this wide range allows to study the oils from food cooking temperatures (100 °C), through frying temperatures (180 °C) reaching degradation total of all the components present in the oil.

Figure 3 shows the mass loss curves (TG) and the mass loss derivative (DTG) for OO and CHO in the temperature range previously discussed. A sequential oxidative thermal decomposition process of three stages occurs in both samples, where a total mass loss of 99.7% for OO and 99.9 for CHO occurs. According to figure 3 it is important to point out that the CHO remains without loss of mass and therefore thermally stable up to 247 °C. On the other hand, the temperature where the mass loss for OO begins was 252 °C.

The degradation onset temperatures for both oils is close, slightly the CHO was lower than OO. However, in the analysis of the first stage of thermal decomposition, it is observed that CHO loses less mass than OO, 84.0 versus 89.7% of mass loss. in the second decomposition stage, a drastic loss of mass was observed for both samples, with the mass loss for CHO being greater compared to OO, 13.4% versus 6.1%. The high loss of mass of the first stage in the heating of vegetable oils has been related to the degradation of polyunsaturated fatty acids (PUFA), which have a greater amount of carbon double bonds susceptible to deterioration, and then degraded monounsaturated fatty acids (MUFA) and lately, saturated fatty acids (SFA) [24].

Although the content of SFA, MUFA and PUFA for CHO and OO are different, the temperature at the beginning of the degradation is very similar for both oils, however the loss of mass of the first and second stages of decomposition follows a trend alternating for oils. this behavior can be understood because the thermal stability of an oil not only depends on the content of fatty acids, but also due to protective mechanisms against thermooxidation, in this sense the antioxidants that are found in the unsaponifiable fraction play an important role. Tabee et al. (2008) analyzed the thermal stability of vegetable oils with similar MUFA content, demonstrating that the results depended on the amounts of tocopherol and phytosterols present in the oils [31].

Arora et al. (2000) showed that sunflower oils with higher alpha-tocopherol content were more stable than those that did not [32]. Among the main antioxidants that olive oil presents are hydroxytyrosol, tyrosol and its derivatives (secoiridoids). Cheikhousman et al. (2005) showed that these antioxidants decrease drastically

when the olive oil is submitted to a heating process (180) for a short period of time (10 min) [33]. Berasategui et al. (2012) showed a similar thermal behavior between avocado and olive oil, although the former has more than twice as much phytosterols as the latter and this has a greater amount of tocopherols than the former [34]. In the case of hazelnut oil it has been published that it has high levels of vitamin E that protects it from thermal oxidation to a greater extent than olive oil [35].

At the initial temperature, OO showed 82.6% higher content of total phenols than CHO, which decrease as the temperature increases. (Fig. 4A).

For OO at 25ºC, there is a high phenolic content (80.5 ± 40 mg GAE L^{-1} of oil), which remains almost constant up to 100 ºC, after this temperature there is a decreasing of 45.16% from the initial total phenols content upon reaching the frying temperature (180 ºC) (Fig. 4A). From this temperature, a constant decline in the phenolic content was observed, until losing 83.11% of the initial value at 360 ºC. On the other hand, CHO showed a total phenolic concentration of 14 ± 15 mg GAE L^{-1} at 25 ºC, which it's almost constant during the entire temperature study, decreasing only 10.7% at the final temperature (340 ºC). in addition, at final temperature the total phenols content for both vegetable oils is very similar.

The difference in composition and polyphenol content between OO and CHO is primary due they are fruit that coming from different trees. This study it's a physico-chemical comparison during a thermal study for both oils. In olive oil highlights the presence of oleuropein, pinoresinol, tyrosol (b.p. 158 ºC), ferulic acid and hydroxytyrosol (b.p. 174 ºC) as the most abundant phenolic compounds [36]. Contrarily, the polyphenol content of CHO derived from the presence of flavonoids over phenolic acids demonstrating the presence of different chemical structure in both oils [2]. Is important to note that the concentration of the total phenolic compounds found in CHO was much lower than OO; in addition, the major compounds present in OO are not present in CHO.

OO has an antioxidant capacity 43.16% higher than CHO at 25 ºC, this capacity decreases to 247 ºC where the antioxidant capacities for both oils are equalized. This situation is correlated by one hand with a greater amount of total

phenolic compounds present in OO than CHO at the initial temperature and also a similar content in these kind of compounds at final temperatures (Fig. 4B).

It is known that OO is low concentration in tocopherols. However, these compounds together to phenolic compounds contribute to the oxidative stability of oils [10]. Additionally, CHO present high amounts of tocotrienols, contributing to improve thermal oxidative stability and also this is a big difference compared other well-known nut oils [37].

Conclusions

This study shows that hazelnut oil is a good alternative for thermal processes. Chilean hazelnut oil showed a high degree of unsaturation represented mainly by oleic and palmitoleic fatty acids, 36 and 23% respectively. The follow-up of the change in fatty acid composition indicates a decrease in the indices P/S (polyunsaturated fatty acids / saturated fatty acids) and the U/S index (total unsaturated fatty acids / saturated fatty acids) for both oils. The ratio P/S and U/S for CHO remained close to twice that of OO in the temperature range studied. The thermogravimetric study (TG / DTG curves) shows that the degradation of both oils studied is carried out in a three-stage process in the temperature range studied. Hazelnut oil has a high temperature of resistance to mass loss, just 3 ° C below olive oil. Although the content of total phenols in hazelnut oil is much lower than that presented by olive oil at each temperature studied, the antioxidant capacity of both oils is similar from 247 ° C. in this sense it is demonstrated that this oil has a good behavior in thermal processes at high temperature.

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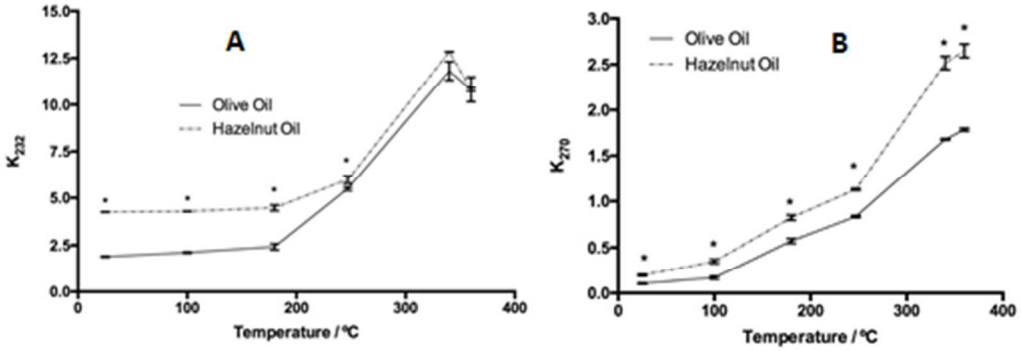

Fig.1 The absorbance ($E_{cm}^{\%}$) measurements at 232 nm (k_{232}) for CHO and OO. * p <0.05 (A) and the absorbance ($E_{cm}^{\%}$) measurements at 270 nm (K_{270}) for CHO and OO. * p <0.05 (B).

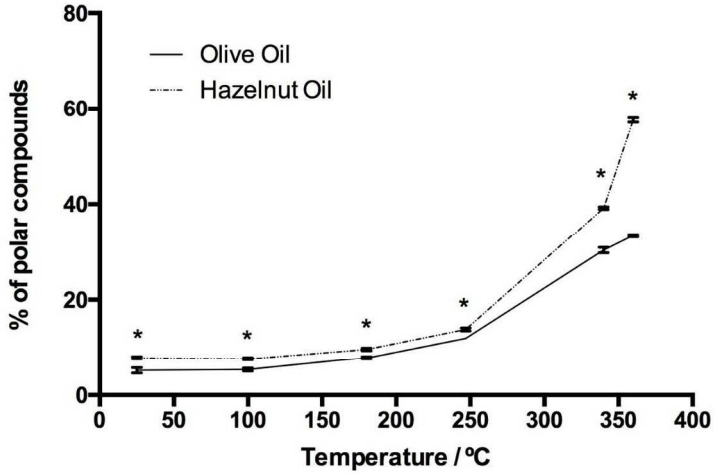

Fig. 2 Measurement of polar compounds in Olive and Hazelnut oils at each studied temperature. * p <0.05

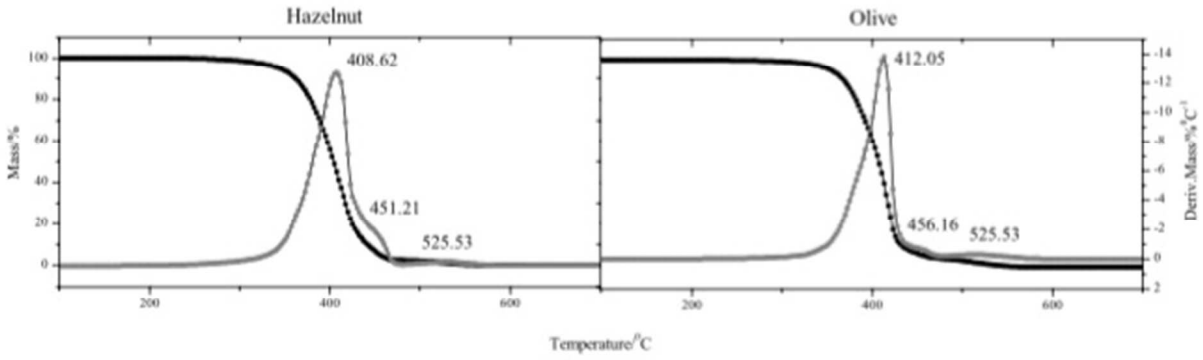

Fig. 3 TG/DTG curves of olive and hazelnut oil.

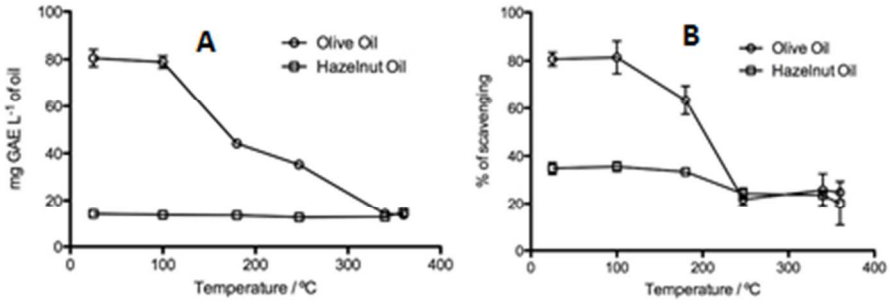

Fig. 4 Total phenolic content of the oils at each studied temperature (A) and antioxidant capacity of the oils at each studied temperature (B).

Table1A. Changes in fatty acid composition (%) of Chilean hazelnut oil (CHO) during thermal operation.

	Temperatures (°C)					
Fatty acid*	**25**	**100**	**180**	**247**	**340**	**360**
Myristic, C14:0	0.05	0.05	-	0.06	0.09	0.13
Palmitic,C16:0	1.96	1.94	1.93	1.97	2.21	2.54
Palmitoleic, C16:1,n-9	0.12	0.12	0	0.14	0.59	1.36
Palmitoleic C16:1, n-7	0.07	0.08	0	0.07	0.1	-
Palmitoleic C16:1,n-5	23.36	23.32	23.02	23.27	22.79	22.75
Margaric, C17:0	-	-	-	-	-	-
Margaroleic, C17:1	0.03	0.02	0.02	-	-	-
Stearic, C18:0	0.69	0.58	0.57	0.58	0.63	0.77
Oleic C18:1,*trans*	-	-	-	0.08	0.85	1.91
Oleic C18:1,n-9	36.8	36.8	36.43	36.71	36.53	36.64
Vaccenic Cis-C18:1, n-7	0.55	0.53	0.56	0.54	0.55	0.68
Vaccenic Cis C18:1 n-5	5.85	5.86	5.76	5.84	5.69	5.63
Linoleic□C18:2-*trans*	□	□	□	□	□□□	□□□□
Linoleic C18:2,n-9,n-12	7.83	7.11	7.27	6.99	4.62	0.03
Arachidic, C20:0	1.47	1.56	1.51	1.58	1.77	1.94
Linolenic C18:3-*trans*	□	□	□	□	□	□
Linolenic18:3,ccc,9,12,15	0.12	0.11	0.11	0.09	0.07	-
Eicosenoic, C20:1 n-9	3.07	3.11	3.01	3.12	3.29	3.6
Eicosenoic, C20:1 n-5	6.17	6.27	6.11	6.26	6.18	6.15
Behenic, C22:0	2.23	2.36	2.27	2.39	2.65	2.93
Docosenoic, C22:1 n-9	1.59	1.66	1.53	1.66	1.98	2.48
Docosenoic, C22:1 n-5	7.39	7.7	7.39	7.72	7.6	7.52
Lignoceric, C24:0	0.49	0.53	0.5	0.54	0.59	0.67
Nervonic, C24:1 n-9	0	0.05	0	0.12	0.51	0.83
Nervonic, C24:1 n-5	0.16	0.24	2.01	0.27	0.51	0.51
Total saturated	6.89	7.02	6.78	7.12	7.94	8.98
Total monounsaturated	85.16	85.76	85.84	85.8	87.17	90.06
Total polyunsaturated	7.95	7.22	7.38	7.08	4.89	0.96
P/S	1.15	1.03	1.09	0.99	0.62	0.1
U/S	13.51	13.25	13.75	13.04	11.59	10.14

* As the methyl ester

Table1B. Changes in fatty acid composition (%) of olive oil (OO) during thermal operation.

	Temperatures (°C)					
Fatty acid*	**25**	**100**	**180**	**247**	**340**	**360**
Myristic, C14:0	0.02	-	-	-	-	-

Palmitic,C16:0	12.34	12.27	12.28	12.92	15.76	17.03
Palmitoleic, C16:1,n-9	0.15	0.15	0.15	0.15	0.15	0.17
Palmitoleic, C16:1, n-7	0,77	0.77	0.78	0.79	0.85	0.92
Palmitoleic, C16:1,n-5	-	-	-	-	-	-
Margaric, C17:0	0.08	0.08	0.08	0.08	0.15	0.15
Margaroleic, C17:1	0.17	0.17	0.17	0.17	0.19	0.23
Stearic, C18:0	1.82	1.84	1.88	1.9	2.23	2.16
Oleic, C18:1,*trans*	-	-	-	0.24	3.14	2.8
Oleic, C18:1,n-9	72.43	72.2	75.57	75.33	70.99	70.25
Vaccenic, Cis-C18:1, n-7	3.03	3.28	-	-	3.38	3.25
Vaccenic, Cis C18:1 n-5	-	-	-	-	-	0
Linoleic,□C18:2-*trans*	□	□	□	□	0.32	□□□□
Linoleic, C18:2,n-9,n-12	7.67	7.69	7.5	6.94	0.3	0.23
Arachidic, C20:0	0.35	0.37	0.38	0.37	0.45	0.37
Linolenic, C18:3-*trans*	□	□	□	□	□	□
Linolenic,18:3,ccc,9,12,15	0.67	0.65	0.67	0.53	0.07	-
Eicosenoic, C20:1 n-9	0.33	0.35	0.35	0.34	0.37	0.31
Eicosenoic, C20:1 n-5	-	-	-		-	
Behenic, C22:0	0.11	0.13	0.13	0.12	0.14	0.1
Docosenoic, C22:1 n-9	-	-	-	-	-	-
Docosenoic, C22:1 n-5	-	-	-	-	-	-
Lignoceric, C24:0	0.06	0.05	0.06	0.12	0.08	0.1
Nervonic, C24:1 n-9	-	-	-	-	1	1.16
Nervonic, C24:1 n-5	-	-	-	-	0.43	0.49
Total saturated	14.78	14.74	14.81	15.51	18.81	19.91
Total monounsaturated	76.88	76.92	77.02	77.02	80.5	79.58
Total polyunsaturated	8.34	8.34	8.17	7.47	0.69	0.51
P/S	0.56	0.56	0.55	0.48	0.04	0.03
U/S	5.77	5.78	5.75	5.45	4.31	4.02

* As the methyl ester