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Journal of Chromatography A, 805 (1998) 259–268

JOURNAL OF
CHROMATOGRAPHY A

Fatty acid, tocopherol and sterol content of some hazelnut varieties (*Corylus avellana* L.) harvested in Oregon (USA)

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Received 14 October 1997; received in revised form 14 January 1998; accepted 16 January 1998

Abstract

We analysed the fatty acid, tocopherol and sterol composition of several hazelnut varieties of different geographical origins harvested in Oregon. Monounsaturated and polyunsaturated fatty acids were the most predominant fatty acids in hazelnut oil extracted from samples. A one-way analysis of variance revealed significant differences for fatty acid content between varieties. Discriminant analysis using individual fatty acids as variables revealed that hazelnut samples were grouped according to their origin. α -Tocopherol, campesterol, stigmasterol, β -sitosterol and Δ^5 -avenasterol were predominant in the unsaponifiable lipid fraction of hazelnut samples. A Kruskal Wallis nonparametric test revealed significant differences between hazelnut varieties for α -tocopherol and sterol content. However, no significant differences were found in relation to geographical origin. © 1998 Elsevier Science B.V.

Keywords: *Corylus avellana*; Hazelnut; Food analysis; Fatty acids; Tocopherols; Sterols; Vitamins

1. Introduction

Hazelnuts (*Corylus avellana* L.) are mainly produced in Turkey, Italy, Spain and the USA [1]. Washington and Oregon are the principal hazelnut producing states in the USA. Several hazelnut varieties cultivated in these states, i.e. Barcelona, Ennis, Halls Giant, Butler and Daviana, are originally from North America or were introduced a long time ago [2,3]; other varieties have recently been introduced from other producing countries, for example, the variety Negret from Spain, or the varieties Tonda gentile delle langhe and Tonda giffoni from

Italy, and Tomboul Ghiagli and Imperial de Trebizonde from Turkey. Hazelnuts are particularly valuable for their lipid composition that accounts for 60% of the hazelnut kernel. Several authors have published data on the lipid composition of hazelnut varieties cultivated in Turkey, Italy and Spain [4–11]. They are high in both monounsaturated (MUFAs) and polyunsaturated (PUFAs) fatty acids [4–7], as well as vitamin E (α -tocopherol) [12–14] and sterols [9–11].

Several authors have shown that monounsaturated and polyunsaturated fatty acids, as well as natural sterols, contribute to lowering serum cholesterol levels in humans [15–26]. Other workers have suggested that nuts protect against ischaemic car-

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diovascular diseases, possibly due to their high MUFA and PUFA content [27–30]. Thus, hazelnuts are not only a source of energy but they also provide certain compounds (MUFAs, PUFAs, vitamin E and natural sterols) that enhance the nutritional value of the human diet.

In this paper we show data on the lipid composition (fatty acids, vitamin E and sterols) of native and introduced hazelnut varieties cultivated in Oregon, focusing on nutritional quality which would encourage hazelnut consumption regardless of their high energetic value. Moreover, we want to estimate how the composition of hazelnut lipid fraction differs from hazelnut varieties that come from different countries after being harvested in the same orchard.

2. Experimental

2.1. Samples

Hazelnut samples were collected during the second half of September from 17 cultivar trees: Tonda gentile delle langhe (*T. gentile*), Tonda giffoni (*T. giffoni*), Tonda romana (*T. romana*), Mortarella, Daviana, Ennis, Willamette, Butler, Halls Giant, Montebello, Barcelona, Casina, Segorbe, Negret, Ribet, Tomboul, and Imperial de Trebizonde (*Imperial*). Hazelnut trees from the same variety were labelled; after maturity hazelnuts were picked up from under the trees and piled up. A final sample of 1 kg was taken from the whole collection, which was used for further analyses. The same procedure was followed for each variety included in our study. Cultivar trees were located in the same orchard at the Experimental Station of Oregon State University (Corvallis, OR, USA).

2.2. Oil extraction

Hazelnut oil was extracted from ground kernels following the procedure proposed by Folch et al. [31].

2.3. Analysis of fatty acids

Fatty acid methyl esters (FAMES) were prepared from oil samples according to a modified method of

Slover and Lanza [32]. Ca. 200 mg of hazelnut oil was saponified with 3 ml of sodium methoxide in methanol (0.5 mol l^{-1}) at 100°C in a water bath for 10 min; the solution was cooled to room temperature and 2 ml of 12% (w/w) boron trichloride in methanol was added. The solution was heated for a further 10 min in a boiling-water bath. After cooling, 1 ml of hexane was added and the mixture was shaken vigorously. Then 1 ml of 0.6% (w/v) of sodium chloride was added. The organic layer was transferred to a screw-capped test tube with a Pasteur pipette. The organic solution was dried with anhydrous sodium sulphate and filtered. Finally the filtrate was concentrated under a stream of nitrogen.

FAMES were analysed by gas–liquid chromatography (GLC) with flame ionisation detection (FID). The sample (1 μl) was injected into the gas chromatograph, a Hewlett-Packard (HP) 5890 series II (Little Falls, Wilmington, DE, USA) equipped with a 60 m Supelcowax-10 capillary column (Supelco, Bellefonte, PA, USA) coated with poly(ethylene glycol) (0.25 mm I.D., 0.25 μm film thickness). The oven temperature was programmed as follows: 180°C for 2 min, then raised to 200°C at $2^\circ\text{C}/\text{min}$, held at 200°C for a further 10 min, then raised to 215°C at $2^\circ\text{C}/\text{min}$. The final oven temperature was maintained for 10 min. The injector and detector temperatures were 200 and 250°C , respectively. Grade 4.7 helium (Airco, Vancouver, WA, USA) was used as a carrier gas at a pressure of 210.9 kPa.

Samples were injected into the column inlet using a Hewlett-Packard 7673 automatic injector. FAMES were identified by comparison of their retention time and equivalent chain length with respect to standard FAMES [33]. Hazelnut FAMES were quantified according to their percentage area, obtained by integration of the peak as a semiquantitative method [7].

2.4. Analysis of unsaponifiable constituents

2.4.1. Saponification of hazelnut oil

Oil samples were saponified following the procedure described by Slover et al. [34]. Ca. 200 mg of oil was weighed in a 20 ml screw-capped glass test tube. Fifty μl of 5,7-dimethyltocol (5 mg ml^{-1} in isooctane) was mixed as internal standard (I.S.); then

8 ml of a solution of 3% (w/v) of ethanolic pyrogallol was added, followed by 0.5 ml of saturated potassium hydroxide in water. The sample was shaken vigorously in a mixer for 30 s, then heated in a water bath at 80°C for 8 min. The mixture was shaken vigorously again and cooled under running cold water. Then it was transferred into a separatory funnel. Twenty ml of cyclohexane and 12 ml of distilled water were added consecutively. The mixture was shaken gently and then centrifuged at 650g in a Meditronic centrifuge (J.P. Selecta, Abrera, Barcelona, Spain) for 10 min at 25°C. The upper layer was suctioned with a Pasteur pipette and dried with anhydrous sodium sulphate. Then it was filtered off and concentrated in a rotary vacuum pump. The concentrated solution was transferred to a 10 ml screw capped glass test tube.

2.4.2. Derivatization of the unsaponifiable constituents

The remaining cyclohexane was evaporated under a stream of nitrogen. Then 50 μ l of pure dry pyridine was added followed by 50 μ l of a mixture containing *N*, *O* - bis(trimethylsilyl)acetamide – trimethylsilylchlorosilane–trimethylsilylimidazole (3:2:3, v/v/v) (Sylon BTZ). The mixture was shaken gently for 1 min and left at room temperature for 15 min.

2.4.3. GLC–mass spectrometry (MS) conditions

The sample, 1 μ l, was injected into the GC system, a Hewlett-Packard 5890 Series II connected to a HP 5989A mass spectrometer. The GC system was equipped with a 30 m (0.25 mm I.D., and 0.25 μ m film thickness) HP-5 fused-silica capillary column (Anorsa, Barcelona, Spain) coated with a stationary phase of 5% crosslinked phenylmethylsilicone. The oven temperature was as follows: 210–250°C at a rate of 6°C/min, held at 250°C for 11 min, then 250–310°C at a rate of 3°C/min, then held at 310°C for 12 min. The injector temperature was 290°C, the detector temperature was 350°C. Grade 5.0 helium (Air Liquide España, Madrid, Spain) was used as a carrier gas at a pressure of 75.0 kPa. *O*-Trimethylsilyl ether derivatives, eluted from the column, passed into the mass spectrometer using electron impact (EI) with an ion source temperature of 350°C.

2.4.4. GLC–FID conditions

The sample, 1.5–2.0 μ l, was injected into the GC, a Sigma 2000 Perkin-Elmer (PE) GC system (Norwalk, CO, USA) with a FID, coupled to a PE 1010 integrator. The GC system was equipped with a 25 m (0.25 mm I.D., and 0.13 μ m film thickness) wall-coated open tubular (WCOT) fused silica capillary column coated with a stationary phase of CP-Sil 5CB (Chrompack, Middelburg, Netherlands). The oven was programmed as follows: 230–264°C at a rate of 2°C/min, held at 264°C for 5 min, then raised to 294°C at a rate of 2°C/min. The injector and detector temperatures were 290 and 350°C, respectively. Grade 4.7 helium (Air Liquide España) was used as a carrier gas at a pressure of 103.4 kPa.

O-Trimethylsilyl ether sterol and tocopherol derivatives were identified by their mass spectra and by comparison of their retention time, obtained by GLC–FID, to those of pure sterol and tocopherol standard *O*-trimethylsilyl ether derivatives. *O*-Trimethylsilyl ether derivatives were determined by a calibration curve using several solutions containing increasing amounts of α -tocopherol (15, 20, 25, 30, 35 and 40 μ g, respectively) and β -sitosterol (20, 50, 100, 150 and 200 μ g, respectively). To each solution 250 μ g of 5,7-dimethyltolcol was added as an internal standard. α -Tocopherol, campesterol, stigmaterol, β -sitosterol and Δ^5 -avenasterol content were determined five times. α -Tocopherol showed a mean value of 380.4 ± 37.9 mg kg⁻¹ with a relative standard deviation (R.S.D.) of 10.0%, campesterol showed a mean value of 50.0 ± 4.3 mg kg⁻¹ with a R.S.D. of 8.6%, stigmaterol showed a mean value of 6.3 ± 2.7 mg kg⁻¹ with a R.S.D. of 43.0%, β -sitosterol showed a mean value of 864.4 ± 20.8 mg kg⁻¹ with a R.S.D. of 2.4%, and Δ^5 -avenasterol showed a mean value of 61.9 ± 20.8 mg kg⁻¹ with a R.S.D. of 5.6%.

2.5. Reagents and standards

Hexane was purchased from Fisher (Pittsburgh, PA, USA), and isooctane and cyclohexane were purchased from Panreac (Montcada i Reixac, Barcelona, Spain). All were reagent grade. Anhydrous sodium sulphate was of analytical grade from both Fisher and Panreac, and potassium hydroxide was of analytical grade purchased from Panreac. Sodium

methoxide in methanol was purchased from Aldrich (Milwaukee, WI, USA), boron trichloride in methanol was purchased from Supelco, and pyrogallol was of analytical grade purchased from Sigma (Alcobendas, Madrid, Spain). Pure FAME standard was purchased from Sigma. This standard included: 8% of caprylic ($C_{8:0}$), 8% of capric ($C_{10:0}$), 8.0% of lauric ($C_{12:0}$), 8% of myristic ($C_{14:0}$), 11.0% of palmitic ($C_{16:0}$), 5.0% of palmitoleic ($C_{16:1, \text{cis-9}}$), 8.0% of stearic ($C_{18:0}$), 5.0% of oleic ($C_{18:1, \text{cis-9}}$), 5.0% of linoleic ($C_{18:2, \text{cis-9,12}}$), 5.0% of linolenic ($C_{18:3, \text{cis-9,12,15}}$), 8.0% of eicosanoic ($C_{20:0}$), 8.0% of behenic ($C_{22:0}$), 5.0% of erucic ($C_{22:1, \text{cis-13}}$), and 5.0% of lingnoceric ($C_{24:0}$) fatty acid methyl esters. Anhydrous pyridine was of analytical grade purchased from Merck (Darmstadt, Germany). Sylon BTZ was purchased from Supelco. α -Tocopherol, campesterol (24 α -methyl-5-cholesten-3 β -ol), stigmaterol (3 β -hydroxy-24-ethyl-5,22-cholestadiene), β -sitosterol (24 β -ethylcholesterol), Δ^5 -avenasterol and Δ^7 -stigmaterol were purchased from Sigma. The standard 5,7-dimethyltolcol was purchased from Matreya (Pleasant Gap, PA, USA).

2.6. Statistical analysis

Statistical calculations by one-way analysis of variance (one-way ANOVA), using the Tuckey multiple range test [35], were carried out on data obtained from triplicate determinations of each of the compounds. Discriminant analysis [35] was applied to hazelnut varieties using individual fatty acids as variables.

All statistical analyses were conducted using the Statistical Package for Social Sciences (SPSS/PC+, version 6.1) (Hispanoportuguesa, Madrid, Spain) for Microsoft Windows version 3.11 (Microsoft Ibérica, Madrid, Spain).

3. Results and discussion

3.1. Fatty acid composition

Table 1 shows the fatty acid content of the hazelnut varieties. The main fatty acids were oleic ($C_{18:1}$), linoleic ($C_{18:2}$), palmitic ($C_{16:0}$), stearic ($C_{18:0}$), linolenic ($C_{18:3}$), eicosanoic ($C_{20:0}$) and

eicosenoic ($C_{20:1}$) (Fig. 1). Traces of lauric ($C_{12:0}$) and myristic ($C_{14:0}$) fatty acids were also detected but not included in Table 1. The fatty acid profile of the hazelnut samples is consistent with results published by other workers [4–7]. Table 1 also shows results for saturated fatty acids (palmitic+stearic+eicosanoic), MUFAs (oleic+palmitoleic+eicosenoic) and PUFAs (linoleic+linolenic). Monounsaturated fatty acids were the main group of fatty acids in hazelnut oil (79.5%) ranging from 74.5 to 83.2%. The variety Tomboul showed the lowest value (74.5%), whereas the variety Tonda giffoni had the highest value (83.2%). PUFAs accounted for 12.6% of total fatty acids, ranging from 8.3 to 17.9%; the Italian varieties, Tonda gentile delle langhe (8.3%), Tonda giffoni (8.5%) and Tonda romana (8.7%) showed the lowest values for PUFAs, as found in a previous study [7]; in contrast, the varieties Ennis (15.7%) and Tomboul (17.9%) had the highest values for the PUFA fraction. Saturated fatty acids were minor compounds in hazelnut fatty acids (8.0%), ranging from 6.8 to 9.0%; the variety Ennis showed the lowest value for saturated fatty acids (6.9%), whereas the variety Tonda gentile delle langhe had the highest value (9.0%).

A one-way ANOVA showed significant differences ($p < 0.05$) between varieties for palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, and eicosenoic fatty acids. It also showed significant differences between varieties for saturated fatty acids, MUFAs and PUFAs. Taking into account the origin of the hazelnut samples, the one-way ANOVA revealed significant differences ($p < 0.05$) for oleic and linoleic as well as for monounsaturated and polyunsaturated fatty acid contents (Table 2).

Discriminant analysis using individual fatty acid content as the variables showed that hazelnut varieties harvested in Oregon are grouped according to their origin (Fig. 2): T. Romana, T. gentile, Mortarella and T.giffoni from Italy; Casina, Segorbe, Negret and Ribet from Spain; Tomboul and Imperial de Trebizonde from Turkey; and Barcelona, Daviana, Montebello, Butler, Ennis, Halls Giant and Willamette from the USA (Fig. 2). Hadorn and Zurcher [4,5], who studied the fatty acid composition of several hazelnut varieties from different origins, pointed out that there were significantly different levels of oleic and linoleic fatty acids in hazelnut

Table 1
 Percentages of fatty acids, SFAs (saturated fatty acids), MUFAs (monounsaturated fatty acids) and PUFAs (polyunsaturated fatty acids) of lipid fractions extracted from hazelnut samples

Origin	Cultivar	Fatty acids (%)																					
		C _{16:0}		C _{16:1}		C _{18:0}		C _{18:1}		C _{18:2}		C _{18:3}		C _{20:0}		C _{20:1}		SFAs		MUFAs		PUFAs	
		x ¹	S.D. ^m	x	S.D.	x	S.D.	x	S.D.	x	S.D.	x	S.D.	x	S.D.	x	S.D.	x	S.D.	x	S.D.	x	S.D.
Italy	T. romana	5.78 ^f	0.01	0.22 ^c	0.00	2.50 ^f	0.01	82.55 ^d	0.01	8.59 ^b	0.00	0.10 ^a	0.00	0.01	0.01	0.14 ^a	0.00	8.41 ^e	0.01	82.91 ^j	0.01	8.68 ^b	0.000
	T.g.d.l.	6.04 ^g	0.02	0.30 ^f	0.01	2.81 ^h	0.01	82.29 ⁱ	0.01	8.17 ^a	0.00	0.10 ^a	0.01	0.01	0.03	0.14 ^a	0.01	9.00 ^f	0.00	82.72 ^j	0.01	8.27 ^a	0.005
	Mortarella	4.98 ^b	0.01	0.15 ^a	0.00	2.72 ^g	0.01	78.90 ^e	0.02	12.83 ^f	0.02	0.11 ^a	0.00	0.01	0.01	0.19 ^a	0.00	7.82 ^d	0.02	79.24 ^f	0.02	12.94 ^f	0.023
	T. giffoni	5.38 ^e	0.01	0.19 ^a	0.00	2.86 ^h	0.00	82.83 ⁱ	0.01	8.37 ^a	0.00	0.10 ^a	0.00	0.01	0.00	0.14 ^a	0.01	8.36 ^e	0.01	83.16 ^j	0.01	8.47 ^a	0.000
Spain	Casina	5.70 ^f	0.03	0.21 ^b	0.02	2.96 ⁱ	0.01	78.58 ^d	0.04	12.19 ^e	0.02	0.10 ^a	0.00	0.01	0.00	0.14 ^a	0.01	8.78 ^f	0.04	78.93 ^d	0.02	12.29 ^e	0.02
	Segorbe	4.66 ^a	0.03	0.17 ^a	0.00	2.58 ^f	0.01	79.85 ^g	0.04	12.34 ^e	0.01	0.12 ^b	0.00	0.01	0.01	0.16 ^a	0.01	7.36 ^b	0.05	80.18 ^h	0.03	12.46 ^e	0.01
	Negret	5.04 ^b	0.01	0.19 ^a	0.00	2.49 ^c	0.01	79.06 ^d	0.01	12.82 ⁱ	0.01	0.13 ^a	0.00	0.01	0.00	0.17 ^a	0.00	7.63 ^a	0.01	79.42 ^d	0.01	12.95 ⁱ	0.01
	Ribet	5.52 ^e	0.01	0.19 ^a	0.05	2.68 ^g	0.00	76.45 ^b	0.00	14.69 ⁱ	0.00	0.15 ^d	0.01	0.01	0.00	0.18 ^a	0.00	8.34 ^e	0.01	76.82 ^b	0.00	14.85 ^j	0.01
Turkey	Tomboul	5.48 ^e	0.05	0.21 ^b	0.00	2.04 ^b	0.02	74.13 ^a	0.17	17.78 ^j	0.04	0.11 ^a	0.01	0.01	0.01	0.16 ^a	0.01	7.61 ^c	0.16	74.50 ^a	0.13	17.89 ^j	0.03
	Imperial	5.07 ^b	0.00	0.18 ^a	0.00	3.36 ^j	0.02	76.42 ^b	0.05	14.52 ^j	0.02	0.13 ^c	0.00	0.01	0.01	0.18 ^a	0.01	8.58 ^e	0.07	76.77 ^b	0.06	14.65 ^j	0.01
USA	Barcelona	5.20 ^d	0.05	0.17 ^a	0.02	1.93 ^b	0.00	78.72 ^d	0.02	13.58 ^h	0.01	0.14 ^c	0.03	0.01	0.01	0.16 ^a	0.01	7.23 ^b	0.01	79.05 ^d	0.02	13.72 ^h	0.01
	Daviana	5.19 ^d	0.17	0.19 ^a	0.00	2.29 ^d	0.25	79.19 ^e	0.27	12.75 ^f	0.02	0.11 ^a	0.01	0.01	0.01	0.16 ^a	0.02	7.59 ^c	0.28	79.55 ^f	0.25	12.86 ^f	0.01
	Montebello	5.10 ^c	0.01	0.21 ^b	0.00	3.34 ^j	0.16	80.31 ^h	0.99	10.46 ^c	0.60	0.17 ^c	0.01	0.01	0.08	0.26 ^b	0.06	8.58 ^e	0.31	80.78 ⁱ	0.92	10.64 ^c	0.60
	Butler	5.77 ^f	0.01	0.24 ^c	0.00	2.68 ^g	0.01	79.55 ^f	0.09	11.26 ^d	0.01	0.11 ^a	0.00	0.02	0.10	0.15 ^a	0.02	8.68 ^e	0.08	79.95 ^g	0.08	11.37 ^d	0.01
	Ennis	5.41 ^e	0.03	0.23 ^d	0.00	1.38 ^a	0.01	77.08 ^c	0.02	15.55 ^k	0.01	0.11 ^a	0.02	0.01	0.02	0.16 ^a	0.02	6.87 ^a	0.04	77.47 ^c	0.03	15.66 ^k	0.01
	Halls giant	4.72 ^a	0.01	0.17 ^a	0.00	2.19 ^c	0.01	79.13 ^e	0.20	13.23 ^g	0.03	0.14 ^c	0.00	0.02	0.21	0.19 ^a	0.01	7.15 ^a	0.22	79.49 ^f	0.19	13.36 ^g	0.03
Willamette	5.20 ^d	0.01	0.18 ^a	0.00	2.43 ^e	0.01	80.76 ⁱ	0.02	11.04 ^d	0.00	0.11 ^a	0.00	0.01	0.02	0.15 ^a	0.03	7.75 ^d	0.02	81.10 ⁱ	0.02	11.15 ^d	0.00	

Data are means of triplicate results, SFAs (C_{16:0}+C_{18:0}+C_{20:0}), MUFAs (C_{16:1}+C_{18:1}+C_{20:1}), PUFAs (C_{18:2}+C_{18:3}).

T. romana (Tonda romana), T.g.d.g. (Tonda gentile delle langhe), T. giffoni (Tonda giffoni).

^{a-k} Denotes statistically significant differences.

¹ x, mean.

^m S.D., standard deviation.

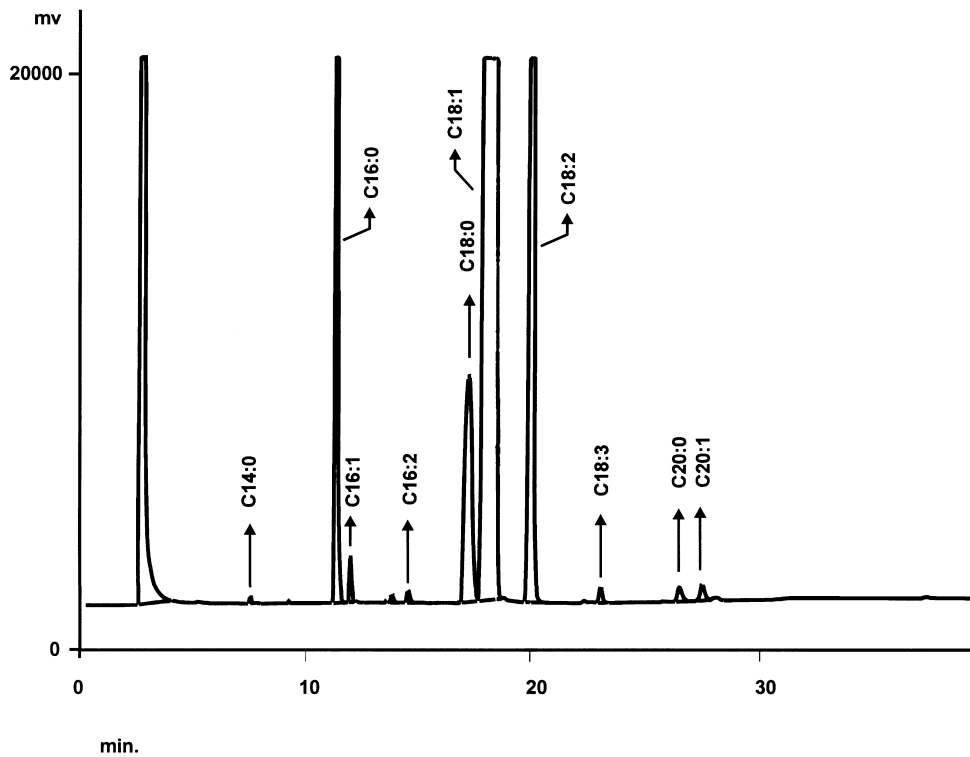


Fig. 1. Chromatogram of fatty acid methyl esters of the lipid fraction of a hazelnut sample ($C_{14:0}$, myristic; $C_{16:0}$, palmitic; $C_{16:1}$, palmitoleic, $C_{16:2}$, hexadecadienoic; $C_{18:0}$, stearic; $C_{18:1}$ oleic; $C_{18:2}$, linoleic; $C_{18:3}$, linolenic; $C_{20:0}$, eicosanoic; $C_{20:1}$, eicosenoic fatty acid methyl esters).

varieties according to their country of origin. Contini et al. [36,37] studied the fatty acid and triacylglycerol composition of hazelnut varieties harvested in Italy; although they did not show the influence of geographical origin on the fatty acid composition of these Italian varieties they reported a small influence

of geographical origin within Italy. Parcerisa et al. [38] reported that the oleic and linoleic content of hazelnut varieties harvested in Catalonia (Spain) were influenced by the area in which they were harvested. In our study we were unable to detect variability between harvesting seasons due to the fact

Table 2

One-way ANOVA results for oleic ($C_{18:1}$), linoleic ($C_{18:2}$), SFAs (saturated fatty acids), MUFAs (monounsaturated fatty acids) and PUFAs (polyunsaturated fatty acids) between origins ($p < 0.05$)

Origin	Fatty acids (%)							
	$C_{18:1}$		$C_{18:2}$		MUFAs		PUFAs	
	\bar{x}^e	S.E. ^f	\bar{x}	S.E.	\bar{x}	S.E.	\bar{x}	S.E.
Italy	81.6 ^a	0.9	9.5 ^b	1.1	82.0 ^a	0.9	9.6 ^c	1.1
Spain	78.5 ^b	0.7	13.0 ^b	0.6	78.8 ^b	0.7	13.1 ^b	0.6
Turkey	75.3 ^c	1.1	16.2 ^a	1.6	75.6 ^c	1.1	16.3 ^a	1.6
USA	79.2 ^d	0.4	12.6 ^b	0.7	79.6 ^b	0.5	12.7 ^b	0.7

^{a-d} Denotes statistically significant differences.

^e \bar{x} , mean.

^f S.E., standard error.

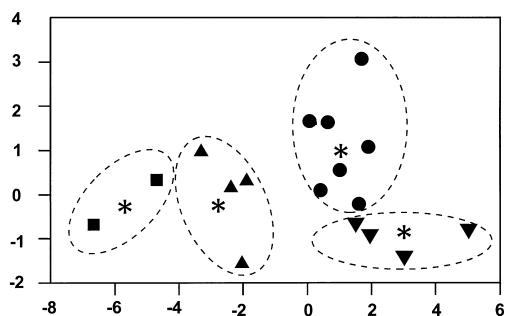


Fig. 2. Plot of the values of the two discriminant scores for each case (Discriminant analysis). Cases are identified by their origin: Turkey (■), USA (●), Spain (▲), Italy (▼). [Group centroids (*)].

that the research project only covered one harvesting year.

3.2. Tocopherol and sterol composition

MS data for trimethylsilyl ether derivatives of sterols were assigned according to published data [39–41].

O-Trimethylsilyl ether (TMS) derivatives were determined by GLC–FID. Fig. 3 shows a typical chromatogram of the unsaponifiable fraction of TMS derivatives of hazelnut oil. Table 3 shows α -tocopherol, campesterol, stigmasterol, β -sitosterol

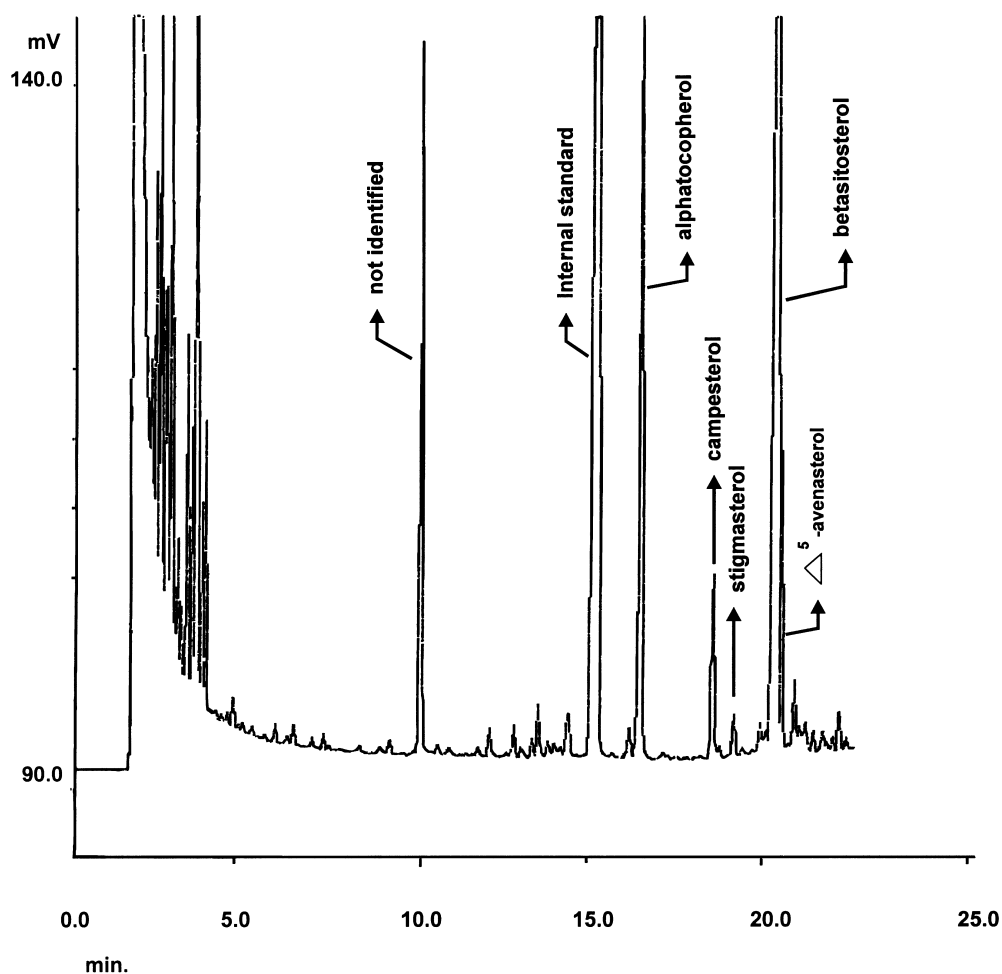


Fig. 3. Chromatogram of the identified O-trimethylsilyl ether derivatives of the unsaponifiable lipid fraction of a hazelnut sample.

Table 3
 α -Tocopherol and sterol contents of lipid fractions extracted from hazelnut samples

Origin	Cultivar	α -Tocopherol		Sterols (mg kg ⁻¹)							
		(mg kg ⁻¹)		Campesterol		Stigmasterol		β -Sitosterol		Δ^5 -Avenasterol	
		<i>x</i> ^a	S.D. ^b	<i>x</i>	S.D.	<i>x</i>	S.D.	<i>x</i>	S.D.	<i>x</i>	S.D.
Italy	T. romana	285.4	10.3	76.3	6.2	15.3	6.8	1060.1	100.0	tr ^c	–
	T. gentile	515.6	33.1	82.1	9.8	27.6	6.3	1166.0	48.8	105.34	4.9
	Mortarella	363.7	9.9	73.9	3.8	17.2	6.4	928.6	17.5	66.87	5.3
	T. giffoni	381.5	27.6	77.5	8.8	tr	–	1181.2	113.7	101.64	19.7
Spain	Casina	404.7	14.3	66.9	1.6	tr	–	1095.6	56.7	72.06	6.9
	Segorbe	654.9	22.6	93.2	4.2	13.3	6.5	1312.6	59.7	118.9	8.7
	Negret	409.8	18.1	81.1	8.2			1088.8	4.2	94.27	39.4
	Ribet	93.9	10.9	64.7	32.9	16.4	8.5	1223.3	60.2	93.79	3.1
Turkey	Tomboul	303.8	4.1	89.6	2.4	53.3	18.6	1128.5	13.7	122.34	1.3
	Imperial	516.7	11.1	113.9	22.0	6.6	1.7	1394.5	14.7	105.7	0.7
USA	Barcelona	386.6	39.0	52.7	6.3	tr	–	825.8	121.3	60.24	10.0
	Daviana	443.5	38.1	88.3	6.8	7.8	2.6	1306.1	14.8	71.58	1.3
	Montebello	211.4	1.3	78.3	1.8	8.9	1.7	1053.5	7.1	67.7	2.7
	Butler	376.4	17.5	54.3	1.5	1.6	1.1	1120.2	21.29	58.05	1.8
	Ennis	359.4	4.2	51.3	1.7	1.9	0.6	972.2	15.9	60.85	2.4
	Halls giant	243.6	9.9	94.5	5.8	9.5	0.8	1134.9	11.0	73.82	2.4
	Willamette	325.7	8.3	56.4	8.4	33.2	40.8	935.0	13.8	55.34	4.6

Data are means of triplicate results.

T. romana (Tonda romana), T.g.d.g. (Tonda gentile delle langhe), T. giffoni (Tonda giffoni).

^a *x*, mean.

^b S.D., standard deviation.

^c tr, traces.

and Δ^5 -avenasterol mean contents (mg kg⁻¹ of hazelnut oil) for hazelnut varieties. The Kruskal Wallis nonparametric test [35] revealed statistically significant differences between varieties for α -tocopherol, campesterol, stigmasterol, β -sitosterol and Δ^5 -avenasterol content. In relation to the α -tocopherol content, the varieties T. Gentile, Segorbe, and Imperial de Trebizonde showed the highest values. Although α -tocopherol was the most predominant tocopherol isomer, traces of β -tocopherol and γ -tocopherol were also detected, as found by other workers [12–14,42]. The varieties Daviana, T. giffoni, Negret and T. romana have the highest α -tocopherol/PUFA ratio (40, 48, 45 and 43, respectively), whereas the varieties Tomboul, Imperial de Trebizonde and Halls Giant have the lowest values

for this ratio (13, 14 and 7, respectively). In relation to this ratio, the statistical analysis did not reveal any significant correlation between α -tocopherol and PUFA content.

In relation to the sterol content, β -sitosterol is the most predominant sterol in all hazelnut varieties, followed by campesterol, Δ^5 -avenasterol and stigmasterol, which is consistent with results published by other workers [8–11]. The varieties T. gentile, T. giffoni, Segorbe, Ribet, Imperial de Trebizonde and Halls Giant have the highest β -sitosterol content. The varieties Imperial de Trebizonde, Ennis and Tomboul have the highest campesterol content. The varieties Tomboul and T. giffoni showed the highest Δ^5 -avenasterol content. Tomboul and Willamette have the highest stigmasterol content. Correlation

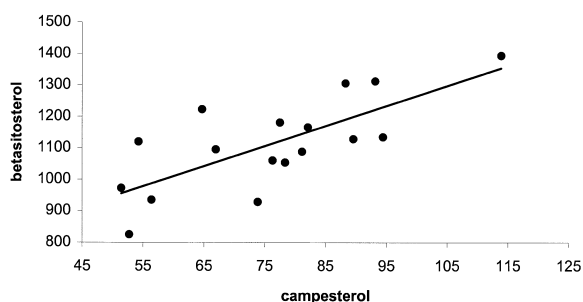


Fig. 4. Correlation between campesterol and betasitosterol contents.

analysis showed a positive correlation between β -sitosterol and campesterol content ($r=0.7382$, $p=0.001$) (Fig. 4).

There was no significant difference between origins for α -tocopherol or sterol content.

Acknowledgements

We thank S. Mehlenbacher (Department of Horticulture, Oregon State University, Corvallis, OR, USA) for providing hazelnut samples, D. Thomas (Statistical Department, Oregon State University, Corvallis, OR, USA) for statistical advice, S. Garver (Department of Horticulture, Oregon State University, Corvallis, OR, USA), S. Silvestre and A. Marín (Serveis Científicotècnics, Universitat de Barcelona, Barcelona, Spain) for technical assistance. This work was supported in part by a research grant from the Comissió Interdepartamental de Recerca i Innovació Tecnològica (1995BEAI30000A, CIRIT) (Catalonia, Spain).

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