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Influence of variety and geographical origin on the lipid fraction of hazelnuts (*Corylus avellana* L.) from Spain: (III) Oil stability, tocopherol content and some mineral contents (Mn, Fe, Cu)

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Induction time, acid value and α-tocopherol content of hazelnut oil and some mineral contents (manganese, iron and copper) of hazelnut kernels cultivated in Catalonia (Spain) are determined. Analysis of variance (ANOVA) showed that statistically significant differences existed for: α-tocopherol content, acid value and copper content in relation to the harvesting year of samples. Significant differences were also found for: induction time, manganese and copper contents in relation to the location of samples. On the other hand, no significant differences were found between varieties. In addition, a correlation study was performed between all parameters included in this work. A strong negative correlation was observed between linoleic acid and manganese content, and also copper content and oil stability (Rancimat).

INTRODUCTION

During three consecutive harvests (1990–1992) we studied the composition and stability of hazelnuts cultivated in Catalonia (Spain), in two geographical areas (Reus and Falset), and corresponding to the varieties Gironell, Negret, Pauetet and Tonda Romana. Previous works reported data on fatty acid composition (Parcerisa *et al.*, 1993*a*) and triglyceride composition (Parcerisa *et al.*, 1993*b*) and concluded that the most important factors in relation to the composition were geographical origin and harvesting year, not variety.

In order to follow the same scheme results are presented for stability of the lipidic fraction, i.e. induction time, α-tocopherol content and acid value. Mineral composition of nuts (manganese, iron and copper) is studied, in order to perform a correlation study between all parameters, and reveal fundamental aspects of the biochemistry and stability of hazelnuts.

MATERIALS AND METHODS

Samples

Four varieties of hazelnut were studied: Gironell, Negret, Pauetet and Tonda Romana (Italian variety). From 1990 to 1992, samples were taken from the same cultivar trees in each geographical origin (Reus, near the sea and Falset, in the mountains). The total number of samples for the analysis was 24, corresponding to 4 varieties × 3 years × 2 origins. All fruits were picked up from under the trees by (IRTA) trained workers during the second half of September. Samples were stored unshelled at 0°C until analysis.

The lipid fraction was obtained by pressing (300 kg/cm^2) from ground hazelnuts, in order to prevent alterations.

Induction time

The stability of oils extracted from hazelnut samples

was measured by the determination of the induction time (Frank *et al.*, 1982) (A.O.C.S. Cd 12b-92, 1992). A Rancimat 617 series 09 Methrom^R was used. The experimental conditions were as follows: air temperature 120°C and air flow 20 litre/h. The reproducibility of the method expressed as coefficient of variation was: 1·40%.

Tocopherol content

Determination of tocopherol content was performed in accordance with the method described by Slover *et al.* (1983). This method consists of an alkaline saponification of the oil, the extraction of the unsaponifiable matter and its derivatization with Sylon BTZ (SUPELCO), prior to the gas chromatographic determination.

Gas chromatography conditions:- Oven temperature program: 210–264°C at a rate of 2°C/min, 264– 290°C at a rate of 5°C/min and finally the oven temperature was kept at 290°C for 5 min. The injector temperature was 290°C and the detector temperature was 350°C. The carrier gas, He, was at 15 Psi. A 25 m × 0·25 mm WCOT fused silica column, coated with a stationary phase CP-Sil 5CB (CHROMPACK) was used.

All determinations were performed on a Perkin–Elmer Gas Chromatograph model 8700 Autosystem equipped with a flame ionization detector and coupled to a NELSON Perkin–Elmer integrator.

α-Tocopherol content was determined by a calibration curve using 5,7-dimethyltocol (MATREYA, INC.) as internal standard and a solution of 0·5 mg/ml of α-tocopherol (MERCK) in isooctane (PANREAC) as a reference standard. For the determination of the method precision, six replications of a same sample were measured for α-tocopherol content. The average value was 353 ppm, the standard deviation was 23·0. The reproducibility of the method expressed as coefficient of variation was: 6·51%.

Acid value

The acid value was determined in accordance with the AOAC method 16239 (AOAC, 1984).

Manganese, iron and copper contents

All these metals were determined by flame air acetylene spectroscopy according to the AOAC method 975·03 (AOAC, 1990) by dry ashing of hazelnut kernels and dissolving the ash in hydrochloric acid.

All determinations were performed on a Varian SpectrAA-40 Spectrometer. The reproducibilities of the method expressed as coefficients of variation for Fe, Cu and Mn contents were: 1·71%, 1·48% and 2·65%, respectively. The sensitivities of the method for Fe, Cu and Mn contents were: 0·12 mg/l, 0·09 mg/l and 0·06 mg/l, respectively.

Statistical calculations

The statistical data calculations were performed on an IBM P/N 33G4578 PS/1 computer using the STATGRAPHICS 5·0 statistical software.

RESULTS AND DISCUSSION

The results for induction time, α-tocopherol content, acid value, manganese, iron and copper contents, corresponding to 24 hazelnut samples are shown in Table 1. In addition, the linoleic acid contents from a former paper (Parcerisa *et al.*, 1993*a*) are also included in Table 1.

The statistical analysis of data results was performed by two-way ANOVA for every parameter described above. The variables for ANOVA were the variety, the geographical origin and harvesting year of samples. Means, standard error for mean and significance level for every parameter are shown in Table 2. Data of varieties are not given since significant differences were not found. In relation to the geographical origin, significant differences were found for the following parameters: induction time, manganese content and copper content, and in relation to the harvesting year significant differences were found for the following parameters: α-tocopherol content, acid value and copper content. It should be pointed out that no statistical differences were found for any parameter between the four varieties studied, in agreement with previous findings for fatty acids (Parcerisa *et al.*, 1993*a*) and triglyceride composition (Parcerisa *et al.*, 1993*b*) in the same hazelnut samples.

Furthermore, a correlation study was performed between linoleic acid content, induction time, α-tocopherol content, acid value, and manganese, iron and copper contents. Results for the correlation coefficient (r) and significance level (P) are shown in Table 3.

The average minimum induction time corresponds to samples harvested in Reus, which agrees with the average higher linoleic acid content of these samples (Parcerisa *et al.*, 1993*a*). This is supported by the negative correlation found between linoleic acid content and induction time ($P<0·0001$) (Fig. 1). Similar results were reported by Zurcher *et al.* (1975) and Allen (1989).

In relation to the tocopherol content, the only isomer present in our samples was α-tocopherol, which showed a mean value of 394 mg/kg of oil (SD = 66·34). Contents reported by other authors for α-tocopherol in hazelnut oils are similar (Lambertsen *et al.*, 1962; Hotellier *et al.*, 1972; Beringer *et al.*, 1976; Gertz *et al.*, 1982, Hogarty *et al.*, 1989).

Significant differences were found for α-tocopherol content between the harvests but not between geographical origins (Table 2). Moreover, there was no correlation between α-tocopherol content and the rest of the parameters included in this work.

The acid value (x = 0·51, SD = 0·59) shows significant differences in relation to the harvesting year (Table 2). Moreover, this parameter is positively correlated with linoleic acid content (P = 0·04) and negatively correlated with copper contents (P = 0·04).

Table 1. Rancimat (induction time in hours), α-tocopherol content, acid value, linoleic acid content and manganese, iron and copper contents of hazelnut samples

Variety	Location	Harvest	Rancimat	Tocopherol	Acidity	C18:2	Mn	Fe	Cu
Gironell	REUS	1990	2·9	311	—	16·9	11·0	29·4	12·4
		1991	4·8	473	0·2	17·3	13·5	45·0	15·1
		1992	3·1	341	2·5	22·2	13·1	28·9	12·1
	FALSET	1990	6·0	293	0·3	7·4	34·6	40·8	21·4
		1991	8·8	435	0·2	8·1	42·3	43·2	25·2
		1992	4·4	375	0·1	17·5	51·5	36·1	17·4
Negret	REUS	1990	5·2	304	0·8	15·1	13·2	25·9	14·3
		1991	2·8	463	0·2	18·0	16·3	33·3	15·3
		1992	3·2	368	0·6	20·4	16·3	39·8	13·5
	FALSET	1990	8·5	296	0·2	9·0	45·0	38·2	19·2
		1991	4·5	476	0·1	10·1	20·0	32·0	20·0
		1992	3·7	444	0·1	15·0	13·8	35·3	16·9
Pauetet	REUS	1990	4·3	295	0·3	17·6	11·5	25·0	12·0
		1991	4·5	405	0·2	17·4	12·6	35·1	14·9
		1992	2·6	370	1·6	18·1	11·9	27·9	11·1
	FALSET	1990	9·6	—	0·3	7·9	27·8	41·2	21·2
		1991	5·1	458	0·8	8·9	29·3	40·1	21·9
		1992	4·9	419	0·8	14·6	36·1	40·0	15·3
Tonda Romana	REUS	1990	3·3	416	0·2	16·0	7·3	29·4	12·4
		1991	8·1	478	0·1	10·0	12·7	35·4	13·8
		1992	6·9	408	1·2	17·5	11·0	43·0	10·0
	FALSET	1990	—	331	—	5·7	18·7	26·2	12·8
		1991	10·0	490	0·1	6·4	58·0	38·1	22·8
		1992	9·2	413	0·6	6·9	36·7	28·6	13·7

Rancimat in hours, tocopherol, manganese, iron and copper contents in mg/kg.

Table 2. Statistical data: mean ($\bar{x}$), standard error of mean (SE) and significance level (P) for Rancimat, α-tocopherol, acid value and manganese, iron and copper contents

	1990	1991	1992		Reus	Falset			
	$\bar{x}$	$\bar{x}$	$\bar{x}$	SE	P	$\bar{x}$	$\bar{x}$	SE	p
Rancimat	5·865	6·075	4·75	0·7415	ns	4·3083	6·8183	0·6054	0·01
Tocopherol	321·62	459·76	392·14	12·610	<0·0001	386·01	396·34	10·29	ns
Acidity	0·3533	0·2125	0·9263	0·1759	0·0255	0·6878	0·3069	0·1507	ns
Mn	21·1375	25·250	23·800	3·5004	ns	12·3083	34·4833	2·858	<0·0001
Fe	32·0125	37·775	34·950	2·0258	ns	33·175	36·650	1·654	ns
Cu	15·7125	18·625	13·750	0·7698	<0·0009	13·075	18·9833	0·6285	<0·0001

Table 3. Correlations between linoleic acid, rancimat, tocopherol and manganese, iron and copper contents

		Rancimat	Tocopherol	Mn	Fe	Cu	Acidity
Linoleic	r	–0·7928	–0·2204	–0·6244	–0·2384	–0·7202	0·4483
	P	<0·0001	ns	0·0025	ns	0·0002	0·0415
Rancimat	r		0·1509	0·633	0·3224	0·4622	–0·2957
	P		ns	0·0021	ns	0·0349	ns
Tocopherol	r			0·0245	0·3391	0·2341	–0·3208
	P			ns	ns	ns	ns
Mn	r				0·3602	0·7056	–0·2737
	P				ns	0·0004	ns
Fe	r					0·4682	–0·2648
	P					0·0323	ns
Cu	r						–0·4512
	P						0·0401

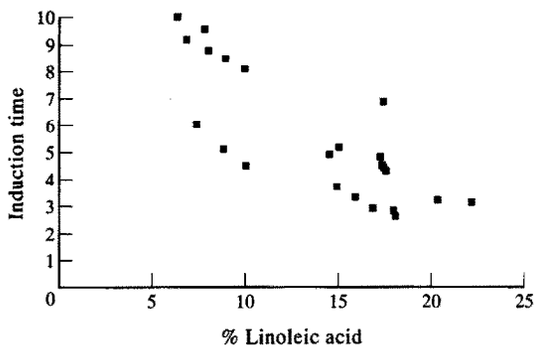

Fig. 1. Distribution of Rancimat values versus % linoleic acid.

The values obtained for manganese, iron and copper contents are of the same order of magnitude as the values published by other authors for hazelnuts (Díaz *et al.*, 1980; Ozdemir 1985; Shresta *et al.*, 1987; Holland *et al.*, 1992).

In relation to the metal contents determined (Cu, Mn, Fe) we can conclude that copper and manganese contents showed a similar distribution. So, manganese and copper contents are positively correlated (P = 0·0004). Furthermore, significantly higher values of both elements were found in Falset samples, with respect to the Reus samples. In contrast, iron content did not show these differences, and the only correlation observed for iron is with the copper content (P = 0·03). Among these three elements, copper content is the only one that shows significant differences between the three harvesting years.

From our correlation study we can conclude that linoleic acid shows a strong negative correlation with both manganese and copper (Table 3) (Fig. 2). Such correlations have not yet been described in hazelnuts.

These metals might play an important role in the linoleic acid biosynthesis pathway (Marschner, 1986). Moreover, the correlations observed between copper and iron and between copper and manganese suggest that the composition of soils and cultural practices (fertilizers spreading, irrigation) all affect the composition of hazelnuts and, in consequence, all these factors have an important role in the stability and global quality of the hazelnuts. However, the variety of hazelnuts has only a minor influence on these characteristics.

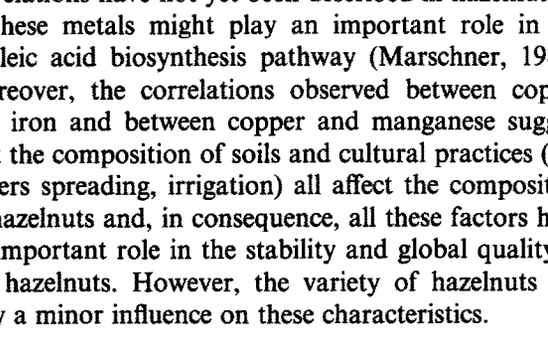

Fig. 2. Distribution of copper contents versus % linoleic acid content.

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