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Study of the carbohydrate fraction of the principal varieties of Tarragona hazelnuts (*Corylus avellana L.*)

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The amounts of sugars, starch and fibre were determined in 22 samples of the main varieties of Tarragona hazelnuts (Negret, Pauetet, Gironell, Culplà, Morell and Grifoll). The main sugar identified by gas chromatography was sucrose, with small amounts of glucose, fructose, myo-inositol and raffinose. The typical mountain varieties (Culplà and Morell) showed the highest sucrose contents (7·90 g/100 g and 6·80 g/100 g of defatted material, d.m.). The amount of reducing sugars exceeded 0·40 g/100 g d.m. in only one sample. All varieties had similar contents of starch, neutral detergent fibre (NDF) and acid detergent fibre (ADF).

INTRODUCTION

In the hazelnut, soluble carbohydrates are fundamentally used for the synthesis of other components such as fibre (cell wall reserve polysaccharides), protein (amino acids) and lipids (fatty acids) or to supply the energy required in metabolic processes. Of the 'sugars' identified, only sucrose and myo-inositol are detected in the different stages of fruit maturity. Glucose, fructose and sorbitol disappear in the course of development, and raffinose appears towards the end of the nut maturation process. In most nuts, an overall increase in sucrose is detected throughout maturity, while glucose and fructose diminish to the point of disappearing (Saura *et al.*, 1984, 1988). Moreover, if the hazelnut is not preserved under suitable conditions (moisture $<$ 5 g/100 g; relative humidity $<$ 65%; temperature, 5–7°C), invertase may be activated (Keme *et al.*, 1983*a*,*b*), leading to the hydrolysis of sucrose to glucose and fructose. According to Keme *et al.* (1983*a*,*b*) satisfactory, fresh hazelnuts have glucose and fructose contents of less than 0·05 g/100 g. Increased values in excess of 0·1 g/100 g indicate old or badly-stored nuts which are not suitable for further storage, and sucrose values below 2 g/100 g indicate spoilage. Using these criteria, we can identify improperly stored hazelnuts.

In the 'carbohydrate' fraction myo-inositol is also detected. As there is an insignificant amount of myo-inositol in ripe nuts (Saura *et al.*, 1988) and its presence may be increased due to phosphoinositol hydrolysis, detecting myo-inositol in the carbohydrate fraction can indicate the storage life of the hazelnut (Loewus & Loewus, 1980).

From the nutritional standpoint there is an interest in food fibres. Fortunately, their importance in preventing certain cardiovascular and cancerous diseases has been established, especially colon cancer, which is very common in countries with a high socio-economic level. These facts have warranted studies which have led to a greater understanding of fibre in all its aspects (Roussel, 1981; Asp & Johansson, 1984). Every study of food composition must include fibre and fibre fractions. Therefore, we have determined the crude fibre and dietary fibre content of the hazelnut. We utilized the Southgate classification (1976) which consists of available carbohydrates (sugars, starch and dextrins) and unavailable carbohydrates, or crude fibre (pectins, hemicellulose, cellulose and lignin). In this context, we have identified and measured the sugar, fibre and

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phosphatide content of the main varieties of irrigated and dry-farmed Tarragona hazelnuts (Negret, Pauetet, Gironell, Culplà, Morell and Grifoll), representing more than 90% of domestic production.

MATERIALS AND METHODS

Materials

Twenty-two samples of hazelnuts of the main Tarragona varieties cultivated using dry-farming, irrigation and mixed methods (1989 season) (Table 1) were studied. The samples were collected in the stores of the principal producers, specifying origin, farming method, number of cultivated fields, gathering method, drying and storage conditions. Each sample was made up of 5 kg of hazelnuts in the shell. The samples were preserved in the dark at room temperature, with a hazelnut moisture of less than 5 g/100 g. All analyses were carried out in triplicate.

Physicochemical analyses

Sugar spectrum

The extraction of sugars was carried out on a sample of 1·5 g of defatted hazelnuts using mechanical agitation in about 40 ml of standard solution plus an oximation reagent (1 g of xylose and 15 g of hydroxylamine hydrochloride in 250 ml of pyridine), warming the solution slightly. Trimethylsilyloxime derivatives were then obtained; 1 ml of the extractant solution was mixed with 1 ml 1,1,1,3,3,3-hexamethyldisilazane and 0·1 ml trifluoroacetic acid in a teflon tube with a screw-on top. It was placed in a glycerine bath at 60–70°C for 1 h. It was left to cool and settle in order to proceed with the gas chromatography in accordance with Serra & Bosch (1989).

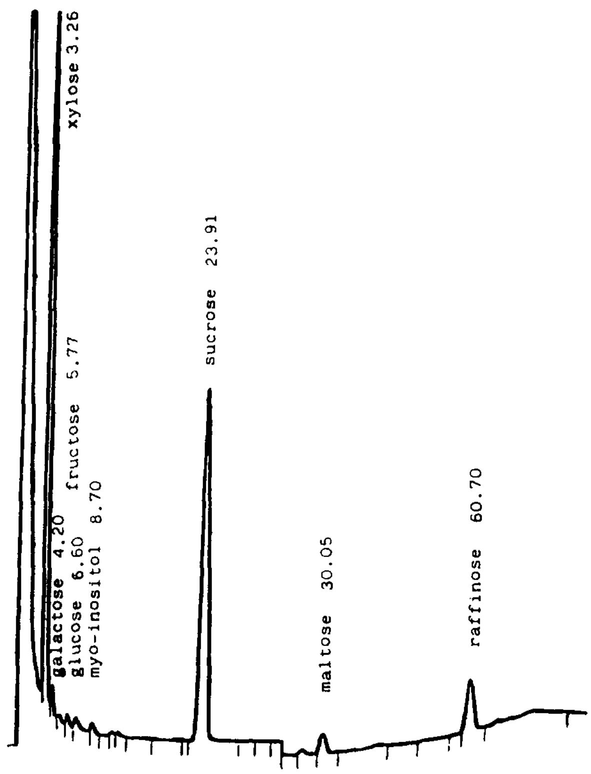

Fig. 1. Typical chromatogram of hazelnut sugars.

Table 1. Hazelnut sampling: site of origin

Sample No.	Variety	Geographical origin	Farming method
01	Morell	Falset	Dry-farmed
02	Culplà	Falset	Dry-farmed
03	Morell	Falset	Irrigated
04	Culplà	Falset	Irrigated
05	Negret	Vilaplana	Dry-farmed
06	Negret	Vilaplana	Irrigated
07	Grifoll	Vilaplana	Dry-farmed
08	Grifoll	Vilaplana	Irrigated
09	Pauetet	Vila-seca	Irrigated
10	Gironell	Vila-seca	Irrigated
11	Pauetet	Riudoms	Irrigated
12	Gironell	Riudoms	Irrigated
13	Negret	Riudoms	Irrigated
14	Gironell	Riudecols	Irrigated
15	Negret	Riudecols	Dry-farmed
16	Negret	Reus	Irrigated
17	Gironell	Vilallonga	Irrigated
18	Negret	Vilallonga	Irrigated
19	Gironell	El Morell	Irrigated
20	Negret	El Morell	Irrigated
21	Pauetet	Alcover	Irrigated
22	Culplà	Falset	Dry-farmed[a]

[a] Biological cultivation.

Starch

The starch percentage was determined using enzyme methods from the firm Boehringer Mannheim GmbH. About 0·5 g of ground hazelnuts (0·15 g defatted hazelnuts) were weighed. The starch was solubilized using 20 ml of dimethyl sulphoxide and 5 ml of 37% hydrochloric acid, incubated at 60°C for 30 min. The pH was adjusted to between 4 and 5 and the volume was levelled at 100 ml with double-distilled water. We used 0·1 ml to carry out the analysis.

Table 2. Influence of farming method on the sugars and phosphatides composition

Parameter	Farming method				
	Dry-farmed		Irrigated		Significant diff.
	$\bar{x}$	SD	$\bar{x}$	SD	($P = 0·1$)
Glucose	Tr.	—	Tr.	—	—
Fructose	Tr.	—	Tr.	—	—
Sucrose	6·40	1·06	5·20	1·43	x
myo-Inositol	Tr.	—	Tr.	—	—
Raffinose	Tr.	—	Tr.	—	—
Starch	2·06	0·38	1·84	0·33	—
NDF	9·25	1·33	9·24	1·16	—
ADF	6·43	0·96	6·39	0·63	—
Phosphatides	0·47	0·13	0·52	0·17	—

Carbohydrates (g/100 g defatted matter).
Phosphatides (g/100 g oil); $n = 6$, dry farmed; $n = 16$, irrigated.

Table 3. Sugars, starch, fibre and phosphatide compositions

Parameters (g/100 g d.m.)	Sample No. 01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22
Glucose	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	0·10	Tr.	0·22	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.
Fructose	0·15	0·23	0·19	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	0·11	0·15	0·20	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.
Sucrose	6.80	7·60	6·70	8·20	6·40	4·90	7·30	5·10	5·00	4·44	6·70	4·20	4·19	6·20	4·90	5·00	3·60	7·10	4 80	2·60	4·50	5·40
myo-Inositol	0·12	0·10	Tr.	Tr.	Tr.	Tr.	Tr.	0·16	Tr.	Tr.	Tr.	0·14	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.
Raffinose	0·26	Tr.	0·12	0·19	0·19	0·26	0·32	0·22	Tr.	0·31	Tr.	0·19	0·24	0·12	Tr.	Tr.	Tr.	0·27	Tr.	Tr.	Tr.	Tr.
Starch	1·86	2·14	1·91	1·94	2·22	2·00	2·68	2·34	2·42	1·80	2·00	1·74	1·51	1·80	1·63	2·06	1·94	1·71	1·60	1·00	1·63	1·80
NDF	7·94	8·10	7·60	7·90	8·80	9·29	11·1	10·8	9·70	10·5	10·3	9·30	9·10	10·9	8·86	7·50	8·10	10·1	7 80	9·10	9·89	10·7
ADF	5·26	5·50	5·10	5·91	6·10	6·69	7·40	7·20	6·90	6·51	6·30	6·20	6·40	7·50	6·83	5·70	6·40	6·20	5 50	7·10	6·57	7·50
Hemicellulose	2·68	2·60	2·50	1·99	2·70	2·60	3·70	3·57	2·80	3·98	4·00	3·10	2·70	3·40	2·03	1·80	1·70	3·86	2 30	2·00	3·32	3·20
Phosphatides[a]	0·58	0·49	0·45	0·92	0·64	0·61	0·30	0·59	0·31	0·40	0·57	0·55	0·77	0·37	0·34	0·57	0·51	0·38	0 35	0·64	0·36	0·48

d.m., defatted matter; NDF, neutral detergent fibre; ADF, acid detergent fibre.
[a] P = 26·5 (g/100 g oil).

Fibre
The acid detergent fibre (ADF) and neutral detergent fibre (NDF) levels were determined using the Van Soest & Wine (1967) method. About 2 g of defatted hazelnuts were weighed and 100 ml of neutral detergent (sodium lauryl sulphate, 30 g; ethylenediaminetetraacetic acid, 14·6 g, NaOH, 4 g; decahydrated sodium borate, 6·8 g; anhydrous disodium phosphate, 4·6 g; ethylene glycol monoethyl ether, 10 ml in 1 litre of distilled water; the solution was adjusted to a pH of between 6·9 and 7·1) was added and set to boil with reflux for 1 h. The solution was filtered under vacuum, the residue being washed several times with boiling distilled water, ethanol and acetone. It was dried at 105°C at constant weight to obtain the dietary fibre or detergent fibre plus ash. It was normally considered to be the sum of cellulose, lignin and hemicellulose.

The previous residue was treated with 100 ml of acid detergent solution (1 M sulphuric acid, 1 litre; cetyltrimethylammonium bromide, 20 g) and the same procedure was followed. The crude fibre or acid detergent fibre was obtained plus ash. Finally, the residual material was calcined in a muffle furnace at 500–550°C for 3 h. The loss of weight gives us the cellulose and lignin quantity in the sample, as fundamental components of crude fibre.

Phosphorus
The Misson reaction was used, reading the vanadium phosphomolybdate yellow-orange complex at 400 nm in 2 g of hazelnut oil. The standards were prepared using anhydrous KH_2PO_4. The phosphatide percentage was determined as percentage phosphorus, F (conversion factor F = 26·5).

Statistical analyses

Analysis of variance between varieties and sugars, farming methods and sugars, and multiple range LSD test between varieties are done using the statistical packet Statgraphics version 4.0.

RESULTS AND DISCUSSION

Table 1 indicates the variety, geographic origin and type of cultivation. We have identified and confirmed the peaks corresponding to ribose, galactose, sorbitol,

Table 4. Carbohydrate (g/100 g defatted matter) and phosphatide (g/100 g oil) compositions of the different varieties

Variety	Glu $\bar{x}$	Glu SD	Fru $\bar{x}$	Fru SD	Suc $\bar{x}$	Suc SD	Ino $\bar{x}$	Ino SD	Raf $\bar{x}$	Raf SD	Star $\bar{x}$	Star SD	NDF $\bar{x}$	NDF SD	ADF $\bar{x}$	ADF SD	Hem $\bar{x}$	Hem SD	Phos $\bar{x}$	Phos SD
Culplà	Tr.	—	0·12	—	7·90	1·47[a]	Tr.	—	Tr.	—	1·96	0·17[b]	8·90	1·56[b]	6·30	1·06[b]	2·60	0·61[a]	0·63	0·25[a]
Morell	Tr.	—	0·17	—	6·80	0·07[b]	Tr.	—	Tr.	—	1·89	0·04[b]	7·77	0·24[a]	5·18	0·11[a]	2·59	0·13[a]	0·52	0·09[a]
Grifoll	Tr.	—	Tr.	—	6·20	1·56[b]	Tr.	—	Tr.	—	2·51	0·24[a]	10·95	0·21[a]	7·30	0·14[a]	3·64	0·09[a]	0·45	0·21[a]
Pauetet	Tr.	—	Tr.	—	5·40	1·15[b]	Tr.	—	Tr.	—	2·02	0·40[b]	9·96	0·31[b]	6·59	0·30[a]	3·37	0·60[a]	0·41	0·14[a]
Negret	Tr.	—	Tr.	—	5·01	1·46[a]	Tr.	—	Tr.	—	1·73	0·41[a]	8·96	0·78[b]	6·43	0·48[a]	2·53	0·69[a]	0·56	0·15[a]
Gironell	Tr.	—	Tr.	—	4·65	0·97[a]	Tr.	—	Tr.	—	1·78	0·12[a]	9·32	1·39[c]	6·42	0·72[a]	2·90	0·90[a]	0·44	0·09[a]
Anova[d]	—		—		—		—		—			x		x	x		—		—	

Glu, glucose; Fru, fructose; Suc, sucrose; Ino, myo-inositol; Raf, raffinose; Star, starch; NDF, neutral detergent fibre; ADF, acid detergent fibre; Hemi, hemicellulose; Phos, phosphatides; n = 3 (culplà), n = 2 (Morell), n = 2 (Grifoll), n = 3 (Pauetet), n = 7 (Negret), n = 5 (Gironell).
a,b,c Homogeneous groups (rank test LSD).
d P = 0·1.

fructose, glucose, myo-inositol and raffinose. Sucrose is the predominant sugar, while fructose, glucose, myo-inositol and raffinose were detected in all the samples (Fig. 1), coinciding with Zürcher & Hadorn (1976), Vidal *et al.* (1979). Ribose, galactose, sorbitol and maltose are generally not detected. Most of these sugars are also found in the almond (Saura *et al.*, 1980). We have found significant differences ($P = 0{\cdot}1$) between farming method and sucrose only (Table 2). The typical mountain varieties (Culplà and Morell) present the most significant percentages of sucrose (7·90 g/100 g defatted matter and 6·80 g/100 g d.m.). In dry-farmed crops the percentage of sucrose is also greater, while in irrigated crops the minimum value for well-developed hazelnuts is not reached (5·7 g/100 g d.m.) (Keme *et al.*, 1983*a*) (Table 2). Thus, hazelnut samples 6, 9, 10, 12, 13, 16, 17, 19, 20 and 21, cultivated using irrigation, and sample 15, cultivated using dry farming methods, are below this minimum value (Table 3). We detected significant variations among the samples from one place and between the cultivation methods, a maximum sucrose difference of 3·53 g/100 g d.m. being reached.

No. 12 was the only sample in which the reducing sugars exceeded 0·10 g/100, the maximum value in recently collected hazelnuts (Keme *et al.*, 1983*a*, *b*). Myo-inositol did not exceed 0·15 g/100 g d.m. in any sample. Table 4 shows the percentages of sugars and phosphatides, with a significant difference ($P = 0{\cdot}1$) between varieties and starch, NDF and ADF fractions using the Anova test. In every sugar, varieties have been classified into homogeneous groups according to the LSD range test. The quantity of glucose, fructose, myo-inositol and raffinose was minimal in all varieties. The Gironell, Negret and Pauetet varieties do not reach the minimum sucrose level recommended for hazelnuts (Keme *et al.*, 1983*a*). The hemicellulose content is the difference between the neutral detergent fibre (NDF) and acid detergent fibre (ADF) contents (Table 3). The starch, NDF and ADF contents of hazelnuts and almonds are similar (Saura *et al.*, 1983*a,b*; Esteban, 1985). In order to obtain an orientational reference of the state of the hazelnut, the myo-inositol and phosphatide results were compared for the different varieties. These values appear to indicate that the sugar fraction undergoes significant quantitative variations based on variety, origin and even crop and that they are not the result of hazelnut spoilage. Likewise, the free acid level, peroxide index and stability to oxidation did not show values which might reflect hazelnut rancidity (Serra & Ventura, 1992).

CONCLUSION

The fructose, glucose, myo-inositol and raffinose contents are not significant, while sucrose is the most prevalent sugar. The mountain varieties, Culplà and Morell, have the highest sucrose contents. The reducing sugar content can help determine hazelnut quality.

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