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The phenolic composition of red wine vinegar produced in barrels made from different woods

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Abstract

The presence of phenolic compounds has been extensively studied in Sherry and Balsamic vinegars due to their impact on quality but little work has been done on red wine vinegars. Phenolic compounds were monitored during the acetification of red wine vinegars produced by surface culture in different wood barrels (oak, chestnut, acacia and cherry). A total of 166 samples were analysed for phenolic compounds using LC-DAD, the total phenol index (TPI) and the total monomeric anthocyanins (TA). Twelve phenolic compounds were identified corresponding to phenolic acids, flavanols and stilbens. Most phenolic acids did not significantly change their concentrations in the different acetifications. (+)-Catechin and resveratrol glycoside underwent significant decreases during acetification while gallic acid and gallic ethyl ester increased substantially for those vinegars produced in chestnut wood. The concentrations of phenolic compounds were used to build the functions for discriminant analysis. Samples belonging to two wine substrates (groups F and T) were correctly classified with 98.6% (group F) and 100% (group T) for the four types of wood barrels. During acetification a decrease (~50%) in the content of total monomeric anthocyanins was observed. According to the results of triangle difference test the panel was able to distinguish most of the vinegars according to the different woods they were made in. The results of descriptive sensory analysis show that oak and cherry gave the maximum scores for most of the descriptors.

Keywords: Red wine vinegar; Phenolic compounds; Wood barrels; Surface acetification; Sensory analysis

1. Introduction

Wine vinegar is largely produced in Mediterranean countries using different methods which give rise to products of greatly differing quality (Tesfaye, García-Parrilla, & Troncoso, 2002a). There are two methods of production: traditional slow methods in which the acetic acid bacteria is placed on the surface of the acetifying liquid and quick methods where acetic acid bacteria is submerged into the substrate in such a manner that oxygen demand is guaranteed. Traditional methods of production usually include the use of wood barrels and the vinegars obtained are highly valued due to their outstanding sensory properties (González-Viñas, Salvador, & Cabezudo, 1996).

Nowadays, the presence of diverse types of wine vinegars in the market and consumer demand for quality condiments stimulates the characterization and establishment of parameters for quality control. Phenolic compounds have been shown to be good markers of the quality and origin of vinegars. Thus, phenolic compounds of low molecular weight were useful to differentiate both aged vinegars from those which were not aged, and Sherry vinegars from other white wine vinegars (Gálvez, Barroso, & Pérez-Bustamante, 1995). García-Parrilla, González, Heredia, and Troncoso (1997) proved that phenolic compounds are useful for classifying and predicting the membership of samples according

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to the method applied in their elaboration or according to the geographical origin of the substrate wine. Using phenolic composition, the authors were also able to differentiate between Sherry vinegars according to their ageing period in wood (less than two years, more than two years) (García-Parrilla, Heredia, & Troncoso, 1999).

Sherry vinegars aged for two years in small American oak casks resulted in a considerable number of phenolic compounds, mainly aromatic aldehydes, being extracted (Tesfaye, Morales, García-Parrilla, & Troncoso, 2002b).

Accelerated ageing of wine vinegars using oak chips seems to be a good way of decreasing ageing time (Tesfaye, Morales, Benítez, García-Parrilla, & Troncoso, 2004). The concentration of gallic acid and above all aromatic aldehydes (siringaldehyde, coniferaldehyde, sinapaldehyde and vanillin) increased after 15 days.

In general, we can say that the phenolic composition of Sherry and white wine vinegars is well known (Alonso, Castro, Rodríguez, Guillen, & Barroso, 2004; García-Parrilla, León Camacho, Heredia, & Troncoso, 1994; García-Parrilla, Heredia, & Troncoso, 1996; García-Parrilla et al., 1997; García-Parrilla, Heredia, & Troncoso, 1998; García-Parrilla et al., 1999; Morales, Tesfaye, García-Parrilla, Casas, & Troncoso, 2001; Natera, Castro, García-Moreno, Hernández, & García-Barroso, 2003; Tesfaye et al., 2002b, 2004), but little is known about the phenolic composition of red wine vinegars (Andlauer, Stumpf, & Fürst, 2000; Natera et al., 2003).

The aim of this work is to study the different phenolic composition of red wine vinegars when produced by surface acetification in barrels made from four different types of wood: chestnut, acacia, cherry and oak. This is a novel approach since surface acetification is generally done in oak wood barrels. Oak is chosen for the majority of wooden barrels used in wine making because of its limited oxygen transfer and because some compounds (mainly phenols) are extracted into the wine. As for acetification, higher oxygen transfer is needed, therefore, in the present study we use more porous woods in order to test their suitability for wine vinegar production. We also analyze the sensory quality of the vinegars produced.

2. Materials and methods

2.1. Samples

We acetified two red wines (Grenache variety) in two different wineries (group F and T) using a surface culture system. Their characteristics are shown in Table 1. The barrels were constructed specifically for this study. We used a total of 48 barrels, 6 from each different type of wood; oak, chestnut, acacia and cherry. Samples (group F and T) were taken at different points of the acetification process; O (starting point; 0.8° acetic, $n = 24$), I (initial point; 2° acetic, $n = 48$), H (middle point; 4° acetic, $n = 48$) and *E* (finished vinegar; 6° acetic, $n = 46$). A total of 166 samples were analysed.

Table 1
Characteristics of wine substrates

Group	Wine substrate
F	Alcohol (%v/v): 14.5 Acidity: 0.9 g/100 mL Glucose + fructose: 20.9 g/L + 43.4 g/L pH 3.4 Variety: 100% Grenache Acetification length: 45 days
T	Alcohol (%v/v): 13.6 Acidity: 0.9 g/100 mL Glucose + fructose: 0.36 g/L + 0.78 g/L pH 3.4 Variety: Grenache mostly Acetification length: 150 days

Four digital sample codes were used following this order: the first digit corresponds to group (F or T); the second digit corresponds to the point of acetification process (O, I, H, E); the third digit corresponds to the type of wood (A: acacia; C: cherry; S: chestnut; R: oak); and the fourth digit corresponds to the replica number of the barrel (1–6).

2.2. HPLC analysis of phenolic compounds

HPLC analysis of phenols was performed using an Agilent Serie 1100 system equipped with a quaternary pump (Serie 1100 G1311A), automatic injector (Serie 1100 G1313A) and degasser on line (Serie 1100 G1379A). Detection was done using a UV/Vis (Serie 1100 G1315B) coupled to a Chemstation HP A.10.02 (HP/Agilent). The column was a Reverse Phase Zorbax SB C18 particle size 3.5 μm (30 mm × 4.6 mm) protected by a Zorbax SB C18 guard cartridge and kept at 30 °C. Duplicate samples were filtered through a Millex-LCR 13 mm filter before injection. The sample volume injected was 20 μL (Ibern-Gómez, Andrés-Lacueva, Lamuela-Raventós, & Waterhouse, 2002). The flow rate was 4 mL/min couple with a UP microsplitter valve that limited the flow into the detector to 1 mL/min. The following solvents were used: solvent A, water with 0.2% trifluoroacetic acid (TFA); solvent B, acetonitrile with 0.2%TFA. Gradient elution profile was as follows: linear gradients from 0 min to 0.5 min (100% A); 0.5 min to 2 min (98% A), 2 min to 8 min (92% A), 8 min to 15 min (85% A), 15 min to 18 min (77% A). Identification was based both on retention time and on UV–Visible spectra matching of the corresponding standards. Quantification was performed by external calibration at 280 and 320 nm.

The standards of 28 phenolic compounds were purchased from Fluka, Sigma, Merck and Chromadex.

2.3. Other parameters

The total phenols index (TPI) was determined by the Folin–Ciocalteu micro-method proposed by Waterhouse (2001). Results were expressed as gallic acid equivalent (GAE).

The total monomeric anthocyanins (TA) were estimated by a pH differential method (Giusti & Wrolstad, 2001). Absorbance (A) was measured at 520 nm and at 700 nm in buffers at pH 1.0 and 4.5 using the following equation: $A = [(A_{\lambda vis\text{-}max} - A_{700})_{pH\,1.0} - (A_{\lambda vis\text{-}max} - A_{700})_{pH\,4.5}]$, with a molar extinction coefficient of malvidin-3-glucoside (M3G) of 20,200 L cm^{-1} mol^{-1}. Results were expressed as mg M3G/L.

2.4. Sensory analysis

An expert sensory panel composed of eight members previously trained in the sensory analysis of vinegar (Tesfaye et al., 2002a) made triangle difference and descriptive analyses according to international protocols (ISO 4120, 1983 and ISO 6658, 1985, respectively). Vinegar samples were tasted by direct olfaction as described in a previous paper (Tesfaye et al., 2002a).

Following methodology for descriptive analysis (Stonem & Sidel, 2004), ten attributes (ethyl acetate, pungent sensation, wine character, woody flavour, red fruit, sweet aroma, bitter almond, vanilla, raisin qualities and general impression) were formally selected by consensus to describe the wine vinegar samples.

2.5. Statistical analysis

Statistical analyses were performed by means of Statistica software (Statsoft, 2001). One-way analysis of variance (ANOVA) was used to test significant differences. Multivariate analysis of data included cluster analysis and standard discriminant analysis.

3. Results and discussion

3.1. Total polyphenol index

Generally the TPI did not show significant changes ($p < 0.05$) during the different acetifications, as seen in Table 2. Two exceptions to this tendency were seen. The first was a slight decrease of no more than 13% (group F: acacia and cherry; and group T: cherry). The second was a slight increase of no more than 20% in the group T samples acetified in chestnut. In fact, submerged culture acetification of red wine vinegars resulted in a 13% reduction in polyphenols (Andlauer et al., 2000).

Data reported in previous literature referred either to traditional surface culture or submerged culture. In general, traditional methods take longer with simultaneous extraction from wood also taking place. Evaporation and concentration is also considerable (Tesfaye et al., 2002b). Our results reveal that in our study these phenomena are unlikely to occur since acetification length is only 45 and 150 days for both groups (F and T, respectively).

ANOVA analysis was also done to explore differences between finished vinegars. In most cases there were significant differences according to the type of wood used (Table 3).

3.2. Phenolic compounds

In our samples we identified twelve phenolic compounds derived from benzoic and cinnamic acids, together with the tartaric acid esters of these acids, and flavanols, stilbens and metabolic products of yeast, such as tyrosol. Caftaric

Table 2
Means and standard deviations (SD) for total phenol index (TPI) and total anthocyanins (TA) (in mg/L)

		Group F				Group T			
		TPI		TA		TPI		TA	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
A	O	1923.6^{a,c}	42.5^{a}	1.30^{a,c}	0.00^{a}	1393.3^{a}	130.8^{a}	0.42^{a,c}	0.00^{a}
	I	1853.9^{b}	38.6^{b}	1.05^{b}	0.08^{b}	1426.67^{b}	75.18^{b}	0.34^{b}	0.04^{b}
	H	1787.3^{b}	32.4^{b}	0.73^{b}	0.08^{b}	1447.9^{b}	111.3^{b}	0.33^{b}	0.02^{b}
	E	1817.58^{b,d}	47.14^{b}	0.71^{b,d}	0.10^{b}	1480.00^{b}	68.21^{b}	0.22^{b,d}	0.04^{b}
C	O	1781.2^{a,c}	20.4^{a}	1.23^{a,c}	0.00^{a}	1393.33^{a,c}	39.03^{a}	0.42^{a,c}	0.00^{a}
	I	1743.8^{b}	93.4^{b}	0.86^{b}	0.13^{b}	1357.0^{b}	30.0^{b}	0.35^{b}	0.02^{b}
	H	1744.85^{b}	64.11^{b}	0.69^{b}	0.07^{b}	1366.1^{b}	98.4^{b}	0.33^{b}	0.03^{b}
	E	1587.3^{b,d}	72.9^{b}	0.39^{b,d}	0.09^{b}	1006.19^{b,d}	20.20^{b}	0.16^{b,d}	0.02^{b}
S	O	1911.5^{a}	74.9^{a}	1.23^{a,c}	0.00^{a}	1338.8^{a,c}	31.7^{a}	0.49^{a,c}	0.00^{a}
	I	1817.6^{b}	55.7^{b}	0.90^{b}	0.08^{b}	1535.8^{b}	32.4^{b}	0.38^{b}	0.03^{b}
	H	1849.4^{b}	24.7^{b}	0.70^{b}	0.09^{b}	1596.4^{b}	51.4^{b}	0.35^{b}	0.05^{b}
	E	1882.7^{b}	70.7^{b}	0.49^{b,d}	0.06^{b}	1618.1^{b,d}	58.9^{b}	0.24^{b,d}	0.04^{b}
R	O	1847.9^{a}	32.4^{a}	1.21^{a,c}	0.06^{a}	1387.3^{a}	45.7^{a}	0.42^{a,c}	0.00^{a}
	I	1796.4^{b}	75.7^{b}	0.97^{b}	0.17^{b}	1417.58^{b}	47.14^{b}	0.36^{b}	0.03^{b}
	H	1775.2^{b}	60.5^{b}	0.80^{b}	0.21^{b}	1417.6^{b}	45.4^{b}	0.37^{b}	0.03^{b}
	E	1714.6^{b}	38.6^{b}	0.63^{b,d}	0.03^{b}	1411.0^{b}	36.7^{b}	0.23^{b,d}	0.04^{b}

[a] Means values for two barrels.
[b] Means values for six barrels.
[c,d] Starting and final concentration within acetification process with different letter as superscript are significantly different ($p < 0.05$).

Table 3
ANOVA

	P-level					
	A–C	A–S	A–R	C–S	C–R	S–R
Group F	0.0041	0.0729	0.1075	0.0069	0.2058	0.0298
Group T	0.0112	0.0231	0.0875	0.0045	0.0176	0.0026

A = acacia; C = cherry; S = chestnut; R = oak.
Significant differences (p-value < 0.05) in the TPI of the finished vinegars depending on type of wood barrel.

acid was a major phenolic, followed by gallic acid and tyrosol, which agreed with previously reported data for Sherry vinegars obtained by submerged culture (Morales et al., 2001). Moreover, resveratrol glucoside was only identified in samples from group F. Tables 4 and 5 show the phenolic composition of the finished vinegars.

We searched for natural groupings among the samples using unsupervised pattern recognition methods. Thus, the data matrix was subjected to a hierarchical agglomerative cluster analysis of cases. Taking the euclidean distance as metric and the Ward's method as amalgamation rule (Ward, 1963), we obtained the dendrogram. A simple inspection allows some observations to be easily made (Figs. 1 and 2):

- The first subcluster grouped almost all samples from chestnut barrels in both groups.
- A second subcluster grouped 83% of the samples from starting point (O) and 33% of initial point (I) in group F. This means that the samples are very similar between different woods during the first stages of the acetification process when using the same starting substrate.
- A second subcluster appeared for group T, which grouped 72% of the samples obtained from oak barrels.
- Finally, a third subcluster grouped almost all the finished vinegars for both groups F and T.

Discriminant analysis was done to check the validity of phenolic compounds in order to classify samples according to the kind of wood used in their elaboration. Samples of starting point (O) were excluded because they had not been in contact with the wood. The classification function was created using the standard method plus eight variables (gallic acid, protocatechuic acid, tyrosol, caftaric acid, vanillic acid, (+)-catechin, syringic acid and gallic ethyl ester) which showed significant differences ($p < 0.05$) when pairs of woods were compared. With this function the samples were correctly classified at 98.6% (group F) and 100% (group T). The functions' roots in the discriminant space

Table 4
Means and standard deviations of the concentration (mg/L) of phenolic compounds in the different finished vinegars

Compounds	Acacia		Cherry	
	Group F	Group T	Group F	Group T
Gallic acid	28.51 ± 0.20	32.65 ± 0.06	28.59 ± 0.15	29.52 ± 0.04
Protocatechuic acid	6.7 ± 0.4	11.29 ± 0.08	5.10 ± 0.25	5.80 ± 0.02
Tyrosol	16.1 ± 0.7	19.7 ± 0.3	16.8 ± 0.5	20.08 ± 0.17
Caftaric acid	263.1 ± 3.3	156.8 ± 0.5	264.52 ± 5.03	165.15 ± 0.23
Vanillic acid	1.08 ± 0.08	1.31 ± 0.02	1.22 ± 0.05	1.78 ± 0.01
(+)-Catechin	–	–	2.35 ± 0.00	–
Caffeic acid	–	5.68 ± 0.00	5.40 ± 0.15	6.00 ± 0.01
Syringic acid	3.0 ± 0.3	2.66 ± 0.04	4.49 ± 0.19	4.31 ± 0.01
Gallic ethyl ester	12.98 ± 0.06	–	7.8 ± 0.5	–
(−)-Epicatechin	–	–	–	–
Resveratrol glucoside	3.44 ± 0.13	–	3.31 ± 0.22	–
Ellagic acid	2.8 ± 0.3	5.3 ± 0.6	1.54 ± 0.10	4.08 ± 0.03

Table 5
Means and standard deviations of the concentration (mg/L) of phenolic compounds in the different finished vinegars

Compounds	Chestnut		Oak	
	Group F	Group T	Group F	Group T
Gallic acid	77.9 ± 0.9	162.72 ± 0.07	30.25 ± 0.10	33.97 ± 0.06
Protocatechuic acid	6.5 ± 0.8	7.91 ± 0.07	5.78 ± 0.13	5.79 ± 0.01
Tyrosol	16.5 ± 0.3	14.18 ± 0.17	16.10 ± 0.07	13.30 ± 0.16
Caftaric acid	268.8 ± 0.6	186.17 ± 0.11	273.53 ± 2.22	176.61 ± 0.24
Vanillic acid	1.26 ± 0.04	1.55 ± 0.04	1.36 ± 0.05	1.67 ± 0.05
(+)-Catechin	2.80 ± 0.23	1.72 ± 0.02	7.61 ± 0.12	2.03 ± 0.07
Caffeic acid	5.79 ± 0.09	5.76 ± 0.03	6.14 ± 0.06	5.67 ± 0.02
Syringic acid	4.4 ± 0.6	4.14 ± 0.01	4.95 ± 0.10	4.21 ± 0.01
Gallic ethyl ester	10.74 ± 1.07	17.87 ± 0.11	9.3 ± 0.5	–
(−)-Epicatechin	–	3.53 ± 0.07	–	–
Resveratrol glucoside	3.39 ± 0.13	–	3.73 ± 0.06	–
Ellagic acid	3.86 ± 0.20	3.7 ± 0.6	4.44 ± 0.11	4.13 ± 0.00

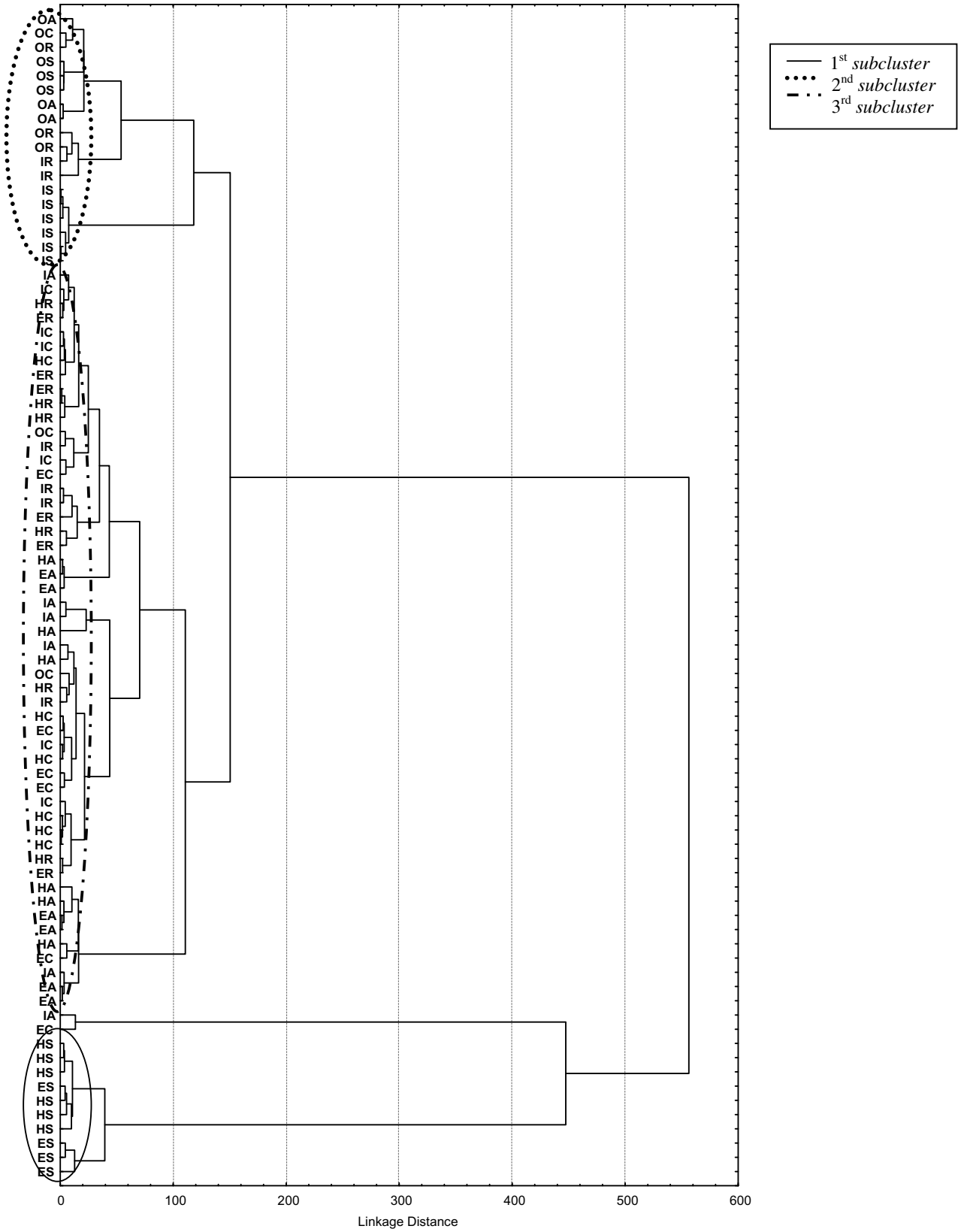

Fig. 1. Dendrogram obtained (Cluster analysis, Ward's method) with phenolic compounds as variables for samples from winery F ($n = 83$).

are shown in Figs. 3 and 4. As can be seen, samples are grouped according to the kind of wood.

Changes in phenolic compounds during eight acetifications seem to be discrete when analysed using LC-DAD

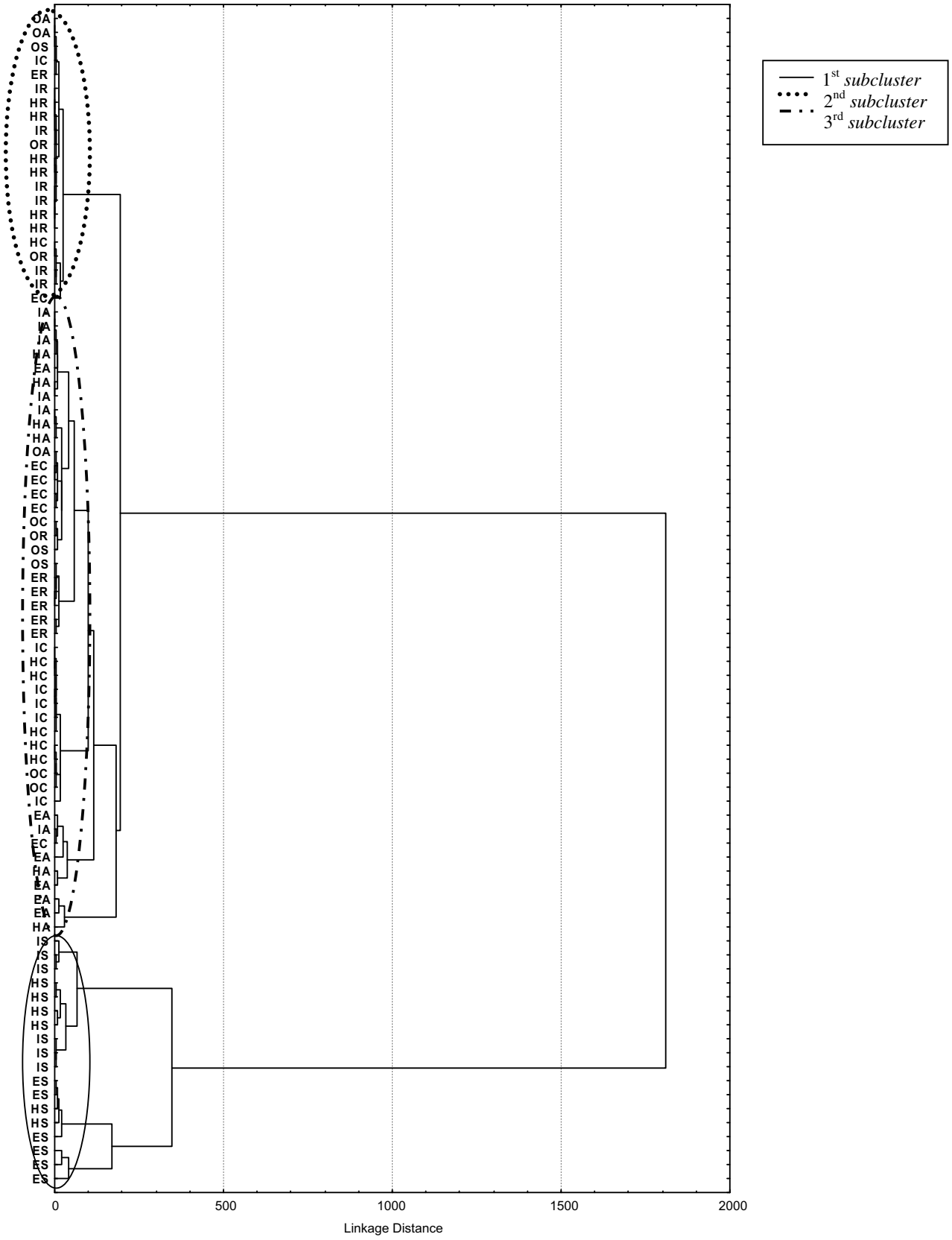

Fig. 2. Dendrogram obtained (Cluster analysis, Ward's method) with phenolic compounds as variables for samples from winery T ($n = 85$).

(data not shown), as reported above for the TPI. Gallic acid increased significantly in chestnut barrels in both groups F (30–78 mg/L) and T (31–163 mg/L), as can be seen in Fig. 5 In the other barrels it remained invariable

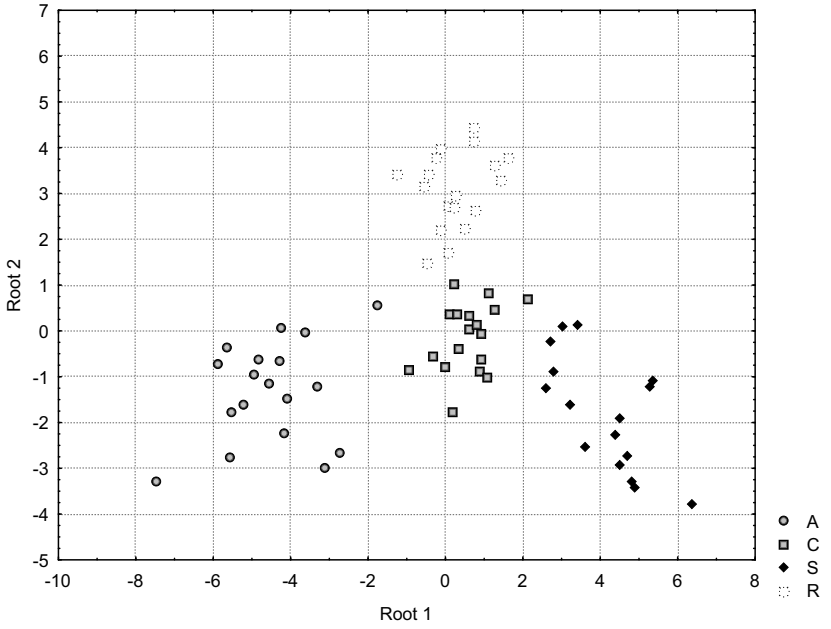

Fig. 3. Plot of the two first roots issued from discriminant analysis for group F of samples.

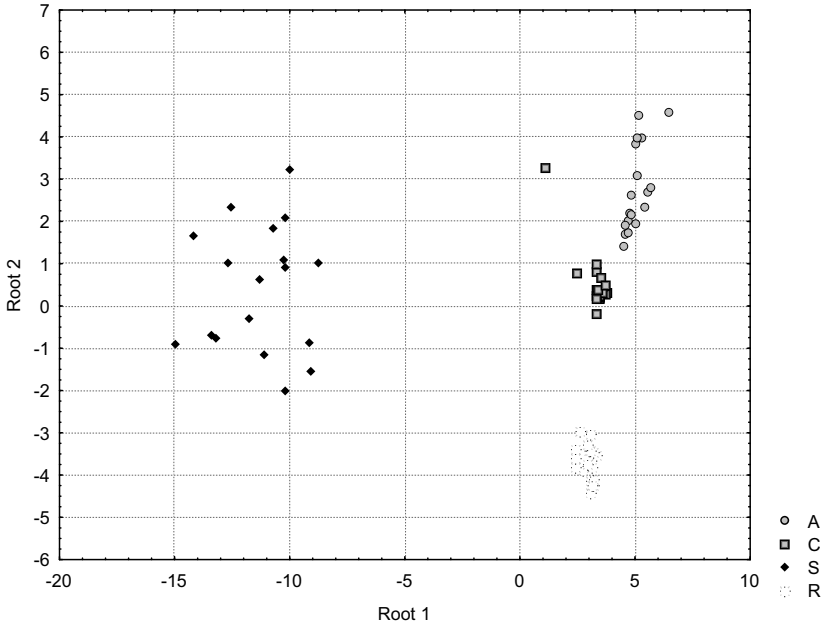

Fig. 4. Plot of the two first roots issued from discriminant analysis for group T of samples.

during acetification (29–30 mg/L). This result agrees with that obtained by other authors (Salagoity-Auguste, Tricard, Marsal, & Sudraud, 1986) who observed a greater ratio of gallic acid extraction from commercial chestnut than from oak. Chestnut releases a higher concentration of gallic acid and, as a consequence, the formation of gallic ethyl ester is more likely in chestnut barrels (Fig. 6).

Most phenolic acids did not significantly change their concentrations in the different acetifications. This is in agreement with previous studies on submerged culture acetifications of Sherry wine (Morales et al., 2001). However, a significant decrease of (+)-catechin concentration (group F and T) and resveratrol glucoside (group F) was observed during the acetification process in each wood we studied. This could be due either to polimerization, precipitation or oxidation phenomena (Escribano-Bailón, Dangles, & Brouillard, 1996; Saucier, Bourgeois, Vitry, Roux, & Glories, 1997).

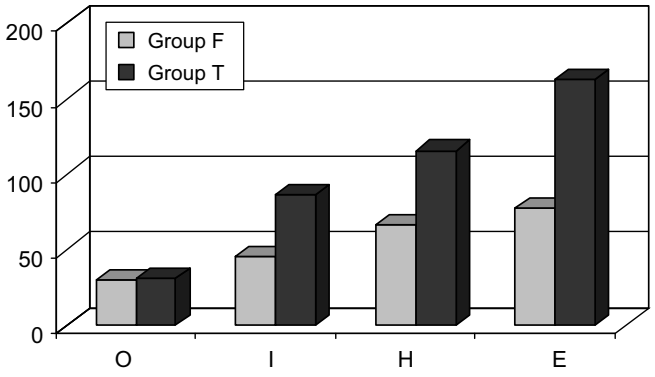

Fig. 5. Evolution of gallic acid concentration (mg/L) during the acetification in chestnut barrels.

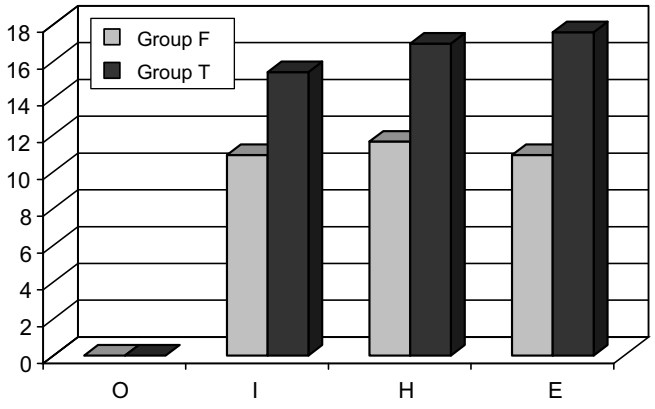

Fig. 6. Evolution of gallic ethyl ester concentration (mg/L) during the acetification in chestnut barrels.

3.3. Total anthocyanins

The total anthocyanins content in the starting red wines ranged between 1.20 mg of M3G/L (group F) and 0.45 mg M3G/L (group T). These values seem very low when compared with the usual figures for these parameters in red wine, which range between 50 mg/L and 170 mg/L (Sánchez-Moreno, Cao, Ou, & Prior, 2003). It can probably be assumed that these red wines had a degree of high evolution and warm-up. The vinegar winery usually employs them because they favour acetification.

Table 6
Probability levels of triangle difference tests for finished vinegars acetified in different woods (group F; A = acacia; C = cherry; R = oak; S = chestnut)

	FEA	FEC (%)	FER (%)	FES (%)
FEA	–	5	0.1	0.1
FEC		–	0.1	0.1
FER			–	0.1
FES				–

Table 7
Probability levels of triangle difference tests for finished vinegars acetified in different woods (group T; A = acacia; C = cherry; R = oak; S = chestnut)

	TEA	TEC	TER (%)	TES (%)
TEA	–	n.s.	0.1	0.1
TEC		–	0.1	1
TER			–	0.1
TES				–

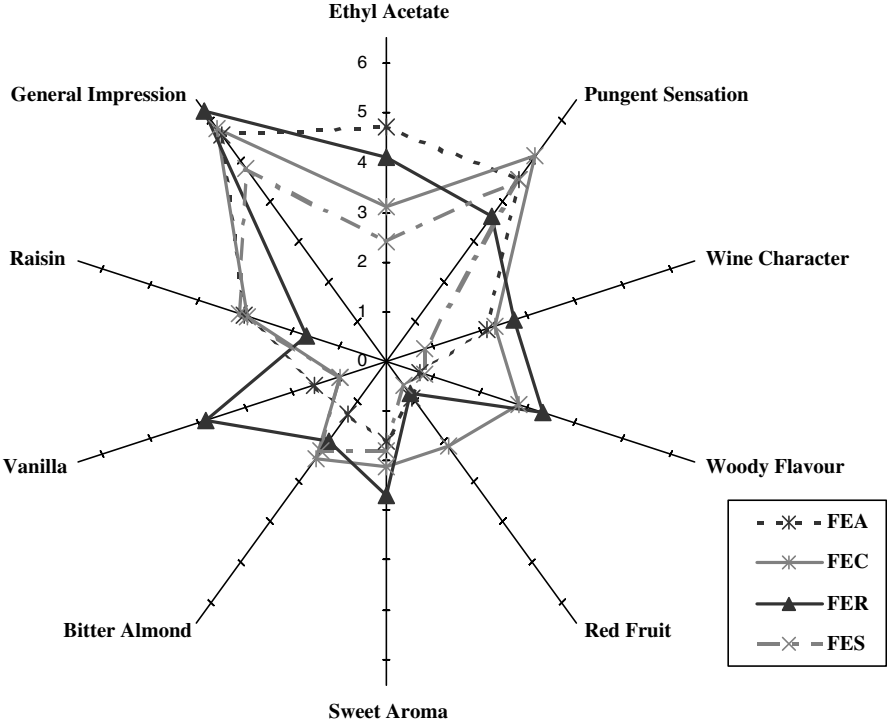

Fig. 7. Sensory analysis. Spider chart of finished vinegars from group F elaborated in the different woods (A = acacia, R = oak, S = chestnut, C = cherry).

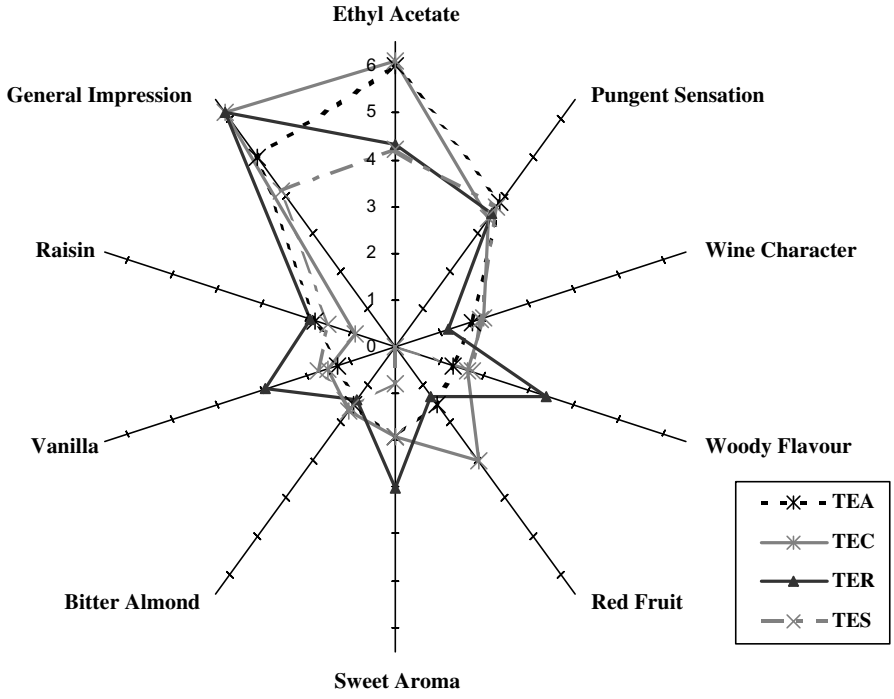

Fig. 8. Sensory analysis. Spider chart of finished vinegars from group T elaborated in different woods (A = acacia, R = oak, S = chestnut, C = cherry).

Analysis of variance showed significant decreases during the acetification process in each wood for both groups F and T ($p < 0.05$). The average decrease was 56% in group F and 51.6% in group T as reported by Andlauer et al. (2000) for red wine vinegars obtained by submerged culture.

3.4. Sensory analysis

The panel carried out triangle tests in order to differentiate which vinegars had been made in which wood. The results showed that the panel was able to differentiate most of the vinegars with different significance levels (Tables 6 and 7).

In order to obtain more information, the vinegars' sensory profile was built up according to the marks given for each attribute by the whole panel. Figs. 7 and 8 show the spider charts for vinegars from different woods. As can be seen, vinegars' sensory profiles were similar within either group but different between groups F and T. Nevertheless, woody aroma and vanilla perception accounts for higher marks in vinegars from oak wood. The red fruit attribute note was higher for vinegars obtained from cherry woods. In addition, higher scores for general impression were given to the vinegars from cherry and oak woods.

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