Exhaustion Techniques in the Selection and Description of Phenolic Compounds in Jerez Wine Extracts Obtained by an Accelerated Aging Technique

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This paper explains the selection and description of phenolic compounds in macerated solutions of *sobretablas* wines and oak shavings. The aging technique proposed and studied allows a considerably shorter stay in barrels and represents a genuine alternative to the oxidative aging to which *oloroso* wines from the Jerez-Xérés-Sherry are usually subjected. The influence of factors such as heating, maceration, and exhaustion of oak shavings using water/alcohol mixtures on the extraction of polyphenolic compounds affecting the organoleptic, sensory, and technological characteristics of these wines was examined.

Keywords: *Accelerated aging; oxidative aging; oloroso wine; phenolic compounds; Jerez-Sherry*

INTRODUCTION

In Jerez (Spain) aging of wines is carried out in a unique fashion (Figure 1). Unlike nearly all other wine-producing regions of the world, the wine is moved several times from one barrel to another—a system known as *criaderas y soleras*—which allows the wine to maintain identical characteristics for an indefinite period regardless of the degree of consumption. Nonetheless, this procedure has the disadvantage of its low economic return, as only 20% of the wine stored in the cellars can be used annually. Together with the cost of the enormous amount of barrels required, the interest on capital tied up and loss by evaporation (up to 7% per year), this means it is impossible to lower the prices of these wines (Bravo Abad, 1984; Barbadillo et al., 1987; Díaz; Cano Muñoz, 1990).

Our technique, based on the traditional wood charring used in coopery, causes thermal degradation of the wood, leading to formation of different families of compounds. The effect on the polyosids is the formation of furanic aldehydes, whereas volatile phenols, aldehydes, and, to a lesser extent, phenolic acids and phenyl ketones result from degradation of lignin (Alonso et al., 1988; Chatonnet et al., 1993; Artajona Serrano, 1991; Sarni et al., 1990; Puech, 1992).

We studied the influence of factors such as heating, maceration, and exhaustion of oak shavings on the extraction of a group of phenolic substances affecting organoleptic, sensory (color, taste, etc.), and technological (oxidation, etc.) characteristics (Puech, 1988; Pinedo et al., 1994; Manga et al., 1996). Our aim was to obtain concentrations of these compounds and physical–chemical characteristics as close as possible to those of commercial *oloroso* wines (produced by oxidative aging) from the Jerez-Sherry district (Spain) in order to reduce aging time and thus improve commercial return.

Liquid chromatography is normally used as analytical technique to identify and determine the different phenolic compounds, the samples being subjected to different prior treatments.

Due to the diversity of phenolic compounds in must and wine, different methods, based on either conventional (discontinuous) or differential (continuous) extraction using different pH values, have been proposed for their preconcentration and extraction. The solvents normally used are ethyl ether and ethyl acetate (nonflavonoid phenols) or isoamylic alcohol (phenolic compounds with some degree of polymerization) (Díez and Gómez-Cordobés, 1980; García-Barroso et al., 1994; Guillén et al., 1994; Bertrand et al., 1994).

Jaworski and Lee (1987) and Oszmiauski et al. (1986) developed a fractionation technique for phenolic compounds using Sep-Pak C_{18} cartridges. This involves using a very small amount of sample, so that it is difficult to measure minority compounds of great importance such as phenolic acids. De la Presa et al. (1995) and Betés-Saura et al. (1996) achieve separation without any previous treatment to the sample, before injection in the HPLC.

In this paper we describe how we measured a total of 11 phenolic compounds including benzoic acids, cinnamic acids, and phenolic aldehydes using HPLC after concentration of the sample and extraction using organic solvent. We show that exhaustion of oak shavings causes a generalized decrease in the level of the main phenolic compounds, thus producing macerates with mean concentrations very similar in almost all cases to those of the samples of commercial wines subjected to oxidative aging (Laurichesse and Tricher, 1988; Chatonnet et al., 1989; Fernández de Simón et al., 1996).

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Table 1. Characteristics of Macerates Using the Rapid Aging System

macerate	charring time (h)	wood treatment
1	3	
2	6	
3	15	
4	3	exhaust. 60% alcohol
5	6	exhaust. 60% alcohol
6	15	exhaust. 60% alcohol
7	3	exhaust. 35% alcohol
8	6	exhaust. 35% alcohol
9	15	exhaust. 35% alcohol
10	3	exhaust. water washed
11	6	exhaust. water washed
12	15	exhaust. water washed

Table 2. Retention Times (t_R in Minutes) of the Phenolic Compounds Identified after 10 Injections of One of the Samples (over Several Work Sessions)

polyphenolic compd	$t_R \pm s_{n-1}$	polyphenolic compd	$t_R \pm s_{n-1}$
gallic acid	7.96 ± 0.07	*p*-coumaric acid	79.66 ± 0.31
protocatechic acid	14.93 ± 0.09	ferulic acid	91.23 ± 0.27
p-OH-benzoic acid	27.46 ± 0.43	syringaldehyde	86.95 ± 0.21
syringic acid	75.02 ± 0.18	vanillin	75.34 ± 0.05
vanillic acid	58.21 ± 0.15	sinapaldehyde	101.35 ± 0.12
caffeic acid	61.67 ± 0.39		

Table 3. Precision of HPLC Method after 10 Injections of One of the Samples (over Several Work Sessions)

	mean area	mean dev	std dev	rel error (%)	variation coeff (%)
gallic acid	93982718	46513.5	147988.6	1.11	0.15
protocatechuic acid	8242432.1	30211.1	95535.8	0.82	1.15
p-OH-benzoic acid	2917583.4	6854.2	21674.8	0.53	0.74
syringic acid	23606673	108666.2	343632.6	1.04	1.45
vanillic acid	8546172	13425	42453.5	0.35	0.49
p-coumaric acid	8831338.8	9709.4	30703.8	0.24	0.34
caffeic acid	8197048.8	39585.3	125179.7	1.09	1.57
ferulic acid	2157614.4	5334.1	16867.9	0.55	0.78
syringaldehyde	46054944	76038.9	240456.1	0.37	0.52
vanillin	24342421	83444	263873.1	0.77	1.08
sinapaldehyde	22426764	75663.2	239268	0.76	1.06

MATERIALS AND METHODS

Samples. *(a) Wines.* Eighteen samples of commercial oloroso wines from the Jerez-Xerez-Sherry region were used.

(b) Preparation of Macerates. The chosen macerates were prepared in duplicate with shavings of American oak (*Quercus alba*) at 2% in *sobretablas* wines. The shavings were 3−5 mm in size, since studies by Giménez et al. (1996) showed that this was the best size for maximum extraction of furanic and phenolic aldehydes from the wood by alcohol spirit. The shavings were sieved through an appropriately sized mesh and heated to 180 °C with a thermostatically controlled oven for 3, 6, and 15 h.

Before maceration, some shavings were subjected to an exhaustion treatment to reduce the concentrations of particular phenolic compounds. Twelve macerates were thus obtained, and their characteristics are summarized in Table 1. In all cases the shavings macerated in the sobretablas wine for 3 months. The samples were finally shaken for 24 h nonstop.

Analytical Determinations. *(a) Total Phenolic Compounds.* These were measured by external calibration and expressed as gallic acid equivalents (mg/L) following the Folin−Ciocalteu reference method (EEC Regulation 2676/90; CEE, 1990).

(b) Individual Phenolic Compounds. These determinations were carried out using HPLC, under the following conditions:

(1) Equipment. A Perkin-Elmer liquid chromatograph with a Waters model 717 plus automatic injector and a diode array 235 type UV−vis detector equipped with a Penelson 1020

Table 4. Statistical Study of the Straight Line Calibrations of the Different Phenolic Compounds

	gallic acid	protocatechuic acid	*p*-OH-benzoic acid	syringic acid	vanillic acid	caffeic acid	*p*-coumaric acid	ferulic acid	syringaldehyde	vanillin	sinapaldehyde
mean area	22595748.60	15662197	16352990	26873738.6	25082700.2	26076918.8	42471027.8	51167071.2	17345705	33924121.4	30168373.8
min value	4615484	3404241	3613424	6123424	4324521	5124425	80786288	10524383	3215412	6452315	5541312
max value	44355680	29821480	32034392	54855460	48514312	54601648	10134251	104525614	34524512	67524412	58344512
std dev	17895781.54	11824623.42	12320019.26	20355881.66	19792295.94	20759615.06	31195847.49	39427966.8	13663110.10	2499893.5	23214478.2
mean dev	7779630.01	5288132.35	5509680.11	9103427.03	8851383.83	9283982.09	13951207.12	17632722.81	6110328.59	11851112.67	10381830.2
95% conf	15248074.82	10364739.42	10798973.02	17842716.98	17348712.30	18196604.90	27344365.95	34560136.72	11976244.04	23228280.84	20348387.3
99% conf	20071445.43	13643381.48	14214974.69	23486841.74	22836570	23952673.8	35994114.3	45492424.86	15764647.77	30575870.7	26785122.12
a	159336.68	449952	452198.8	662143.3	−37447	−654472	2255816.1	341278.61	−286430.6	−279848.6	253629.05
b	1794912.95	1216979.6	1272063.2	2096927.6	2036971.8	2138511.3	3217216.9	4066063.4	1410570.8	2716317.6	2393179.8
r	0.999045	0.99651	0.999731	0.997422	0.996494	0.99742	0.998549	0.998517	0.999611	0.999788	0.998164

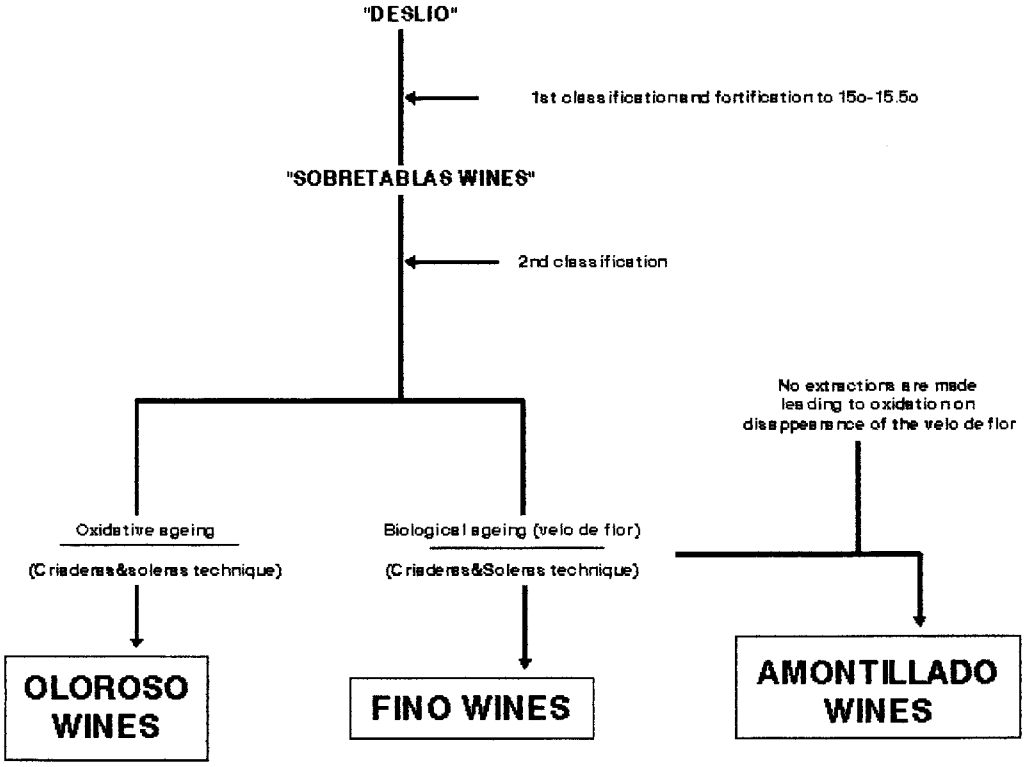

Figure 1. Scheme of biological and oxidative aging in Jerez wines.

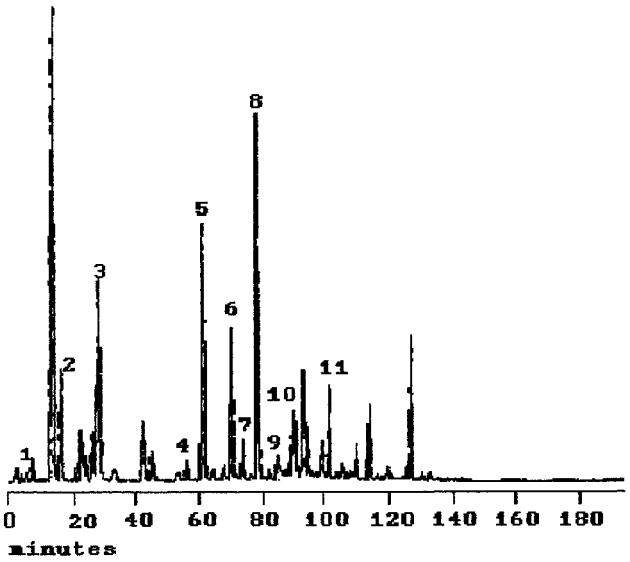

Figure 2. Chromatogram of polyphenolic compounds in one of the samples analyzed: gallic acid (1), protocatechuic acid (2), *p*-OH-benzoic acid (3), vanillic acid (4), caffeic acid (5), syringic acid (6), vanillin (7), *p*-coumaric acid (8), syringaldehyde (9), ferulic acid (10), and sinapaldehyde (11).

Table 5. Extraction Percentage of Polyphenolic Compounds after HPLC after Three Injections in Each of the Samples

polyphenol	initial concn (mg/L)	added concn (mg/L)	detected concn (mg/L)	recovery (%)
gallic acid	1.406	1.00	1.350	56.14
		2.00	1.821	53.48
protocatechuic acid	1.626	1.00	1.871	71.25
		2.00	2.723	75.12
p-OH-benzoic acid	1.625	1.00	2.060	78.48
		2.00	2.946	81.28
syringic acid	0.714	1.00	1.205	70.32
		2.00	1.958	71.48
vanillic acid	0.620	1.00	1.481	91.48
		2.00	2.486	94.92
caffeic acid	1.583	1.00	1.713	66.32
		2.00	2.443	68.20
p-coumaric acid	1.425	1.00	1.414	58.34
		2.00	2.094	61.15
ferulic acid	0.625	0.50	0.847	75.30
		1.00	1.175	72.35
syringaldehyde	2.825	2.00	4.816	99.82
		3.00	5.744	98.62
vanillin	1.925	1.00	2.958	101.15
		2.00	4.052	103.25
sinapaldehyde	2.870	2.00	3.894	79.96
		3.00	4.632	78.92

integrator was used. The column used was a C_{18} reversed phase Spherisorb (25 × 0.46 cm) with 5 mm internal particle size.

(2) Standards. Reference compounds were purchased from Fluka (protocatechuic, *p*-OH-benzoic, syringic, *p*-coumaric, and ferulic acids and synapaldehyde), Sigma (vanillic acid), and Merck (gallic, vanillic, and caffeic acids and syringaldehyde).

(3) Chromatographic Conditions. Mobile phase A was water/glacial acetic acid (98:2), and mobile phase B was methanol/water/glacial acetic acid (60:38:2) (García et al., 1985; Pinedo et al., 1994). Absorption wavelengths were 280 and 340 nm.

(4) Sample Preparation. We followed the conventional (discontinuous) extraction method, taking 100 mL of sample and concentrating it in a vacuum (T < 40 °C) to 25 mL. Ethyl ether was used as organic extraction solvent (four extractions), and anhydrous sodium sulfate was used as desiccant when necessary. The resulting residue was dissolved in 1 mL of methanol/water (1:1) mixture and filtered through a 0.45 mm Waters Millipore membrane (Diez et al., 1980).

(5) Identification and Measurement. Chromatographic peaks were identified by comparing their retention time (Table 2) and UV spectrum with those of the reference standards. Given the complexity of the sample, quantification was carried out by the external standard method. Three determinations were made on each wine sample. Figure 2 provides a graphic representation of the chromatogram of one of the samples analyzed.

Table 6. Statistical Summary of Concentrations (Milligrams per Liter) Detected in Commercial Oloroso Wines

	N	Xm	std dev	variation coeff(%)	range
Benzoic Acid					
gallic acid	18	1.691	1.039	61.460	3.330
protocatechuic acid	18	1.286	0.381	29.640	1.563
p-OH-benzoic acid	18	1.541	0.287	18.650	0.975
syringic acid	18	1.092	0.318	29.190	1.052
vanillic acid	18	0.624	0.165	26.470	0.613
Cinnamic Acid					
caffeic acid	18	1.473	0.268	18.250	0.888
p-coumaric acid	18	1.214	0.147	12.110	0.622
ferulic acid	18	0.546	0.111	20.370	0.398
Phenolic Aldehyde					
syringaldehyde	18	2.492	0.589	23.640	2.117
vanillin	18	1.349	0.392	29.100	1.438
sinapaldehyde	18	3.467	0.707	20.390	2.341

Table 7. Determination (by Folin−Ciocalteu Method) of Total Polyphenols in Selected Macerates

macerate	total polyphenols	macerate	total polyphenols
1	298.30	7	272.57
2	370.82	8	322.57
3	399.76	9	411.17
4	250.64	10	274.34
5	301.52	11	363.80
6	353.27	12	379.59

Table 8. Multiple Variance Analysis Applied to the Values Obtained after Determination of the Total Polyphenols According to Type of Treatment and Exhaustion Technique

Multiple Range Analysis for POLYPHEN.Polyphenol by POLYPHEN.Time Method: 95% LSD

level	count	LS mean	homogeneous groups
3	4	273.96250	X
6	4	339.67750	X
15	4	385.94750	X
contrast		difference	± limits
3−6		−65.7150	29.0769*
3−15		−111.985	29.0769*
6−15		−46.2700	29.0769*

Multiple Range Analysis for POLYPHEN.Polyphenol by POLYPHEN.Treatment Method: 95% LSD

level	count	LS mean	homogeneous groups
60% alcohol	3	301.81000	X
35% alcohol	3	335.43667	X
water	3	339.24333	X
charring	3	356.29333	X
contrast		difference	± limits
charring/60% alcohol		54.4833	33.5751*
charring/35% alcohol		20.8567	33.5751
charring/water		17.0500	33.5751
60% alcohol/35% alcohol		−33.6267	33.5751*
60% alcohol/water		−37.4333	33.5751*
35% alcohol/water		−3.80667	33.5751

*Denotes a statistically significant difference.

(6) Validation of the Method. To test the precision of the HPLC method, one of the samples to be analyzed was injected 10 times— over several sessions—under the chromatographic conditions described above (AOAC, 1990). Table 3 summarizes the results obtained.

The phenolic acids and aldehydes identified in the samples examined were measured by obtaining the corresponding calibration curves based on the injection of solutions with increasing concentrations of the different standards. Table 4 summarizes the characteristics of the curves obtained, which can be seen to have correlations coefficients invariably >0.99.

Likewise, we studied the accuracy (ACS, 1980) of the method by measuring the recovery percentage. This was done by choosing a sample with a known initial concentration of polyphenols, to which we added higher and lower concentrations of the same compounds. The results obtained after three injections in each sample are summarized in Table 5.

Table 9. Benzoic Acid Concentrations in Selected Macerates

macerate	gallic acid (mg/L)	protocatechuic acid (mg/L)	*p*-OH-benzoic acid (mg/L)	syringic acid (mg/L)	vanillic acid (mg/L)
1	3.16	1.31	1.28	1.57	0.96
2	2.79	1.40	1.21	3.29	1.52
3	2.53	1.45	1.19	11.00	5.37
4	1.75	1.22	1.18	1.29	0.76
5	1.47	1.25	0.94	2.99	1.26
6	1.21	1.27	0.90	10.10	4.50
7	1.85	1.28	1.20	1.32	0.80
8	1.52	1.35	1.10	3.15	1.40
9	1.38	1.31	0.93	10.21	4.63
10	2.04	1.28	1.18	1.44	0.84
11	1.56	1.35	1.19	3.14	1.42
12	1.20	1.43	1.16	10.30	5.24

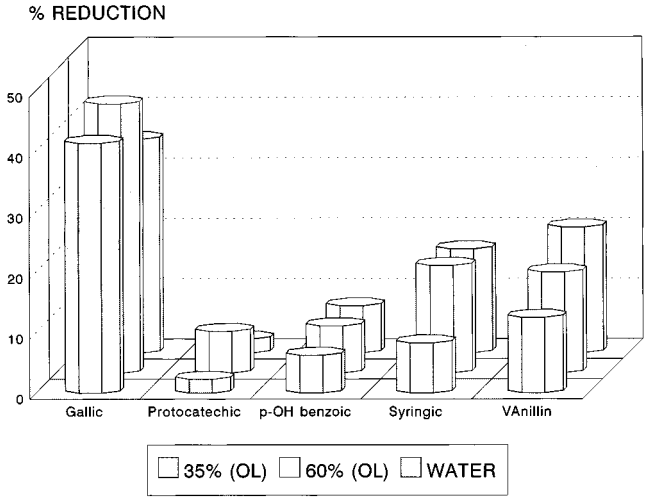

Figure 3. Percentage reduction of benzoic acids according to exhaustion treatment.

RESULTS AND DISCUSSION

When the macerates had been prepared according to the procedure described above, they were deposited for aging in a room with humidity and temperature similar to those of a wine cellar (*bodega*). They were kept in these conditions of static maceration for various periods.

In a previous study carried out by our research group we determined the phenolic compound levels in samples of commercial wines from the main producers of oloroso wines (subjected to oxidative aging) in the Jerez district. The results of this study were taken into account for reference purposes (Table 6).

The results obtained in previous studies (Giménez et al., 1996; Quesada et al., 1996) showed that macerates prepared with shavings charred at 180 °C for 3 h and aged for 3 months present concentrations of phenolic compounds closest to those of the commercial samples. However, some of these compounds, such as gallic acid, syringaldehyde, or sinapaldehyde, are found in higher concentrations in the macerates.

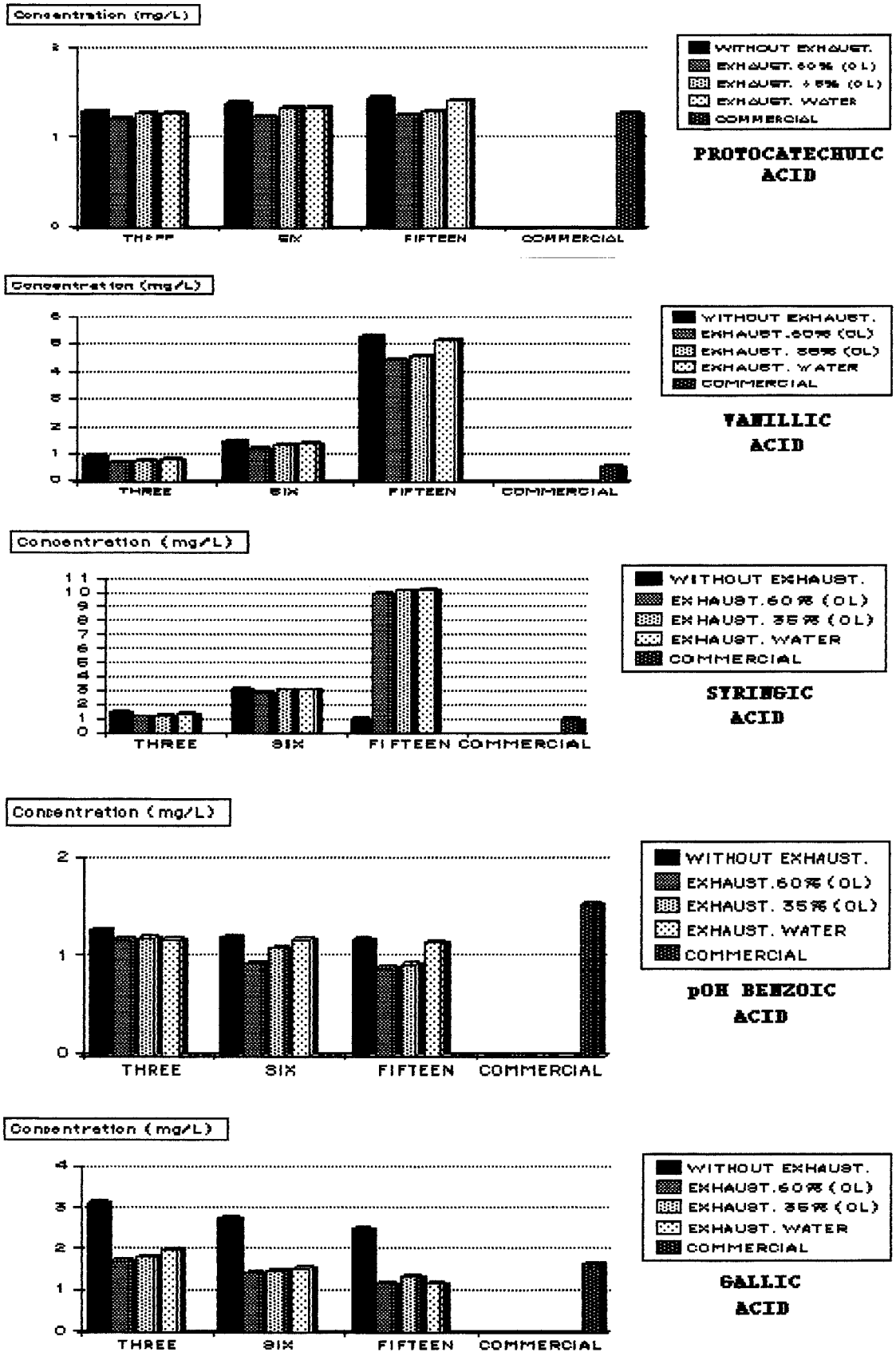

Figure 4. Benzoic acid content of the selected macerates according to assayed aging technique (average contents in commercial samples).

To attempt to reduce the gallic acid concentration, we took as a basis the French method of *afranchissement*, or treatment of the wood prior to barrel construction. This technique is designed to eliminate tannic matter of an astringent nature, as well as any substance causing unpleasant smells that might later affect the wine. The wood is therefore washed with either steam or boiling water or macerated for at least 2 days in

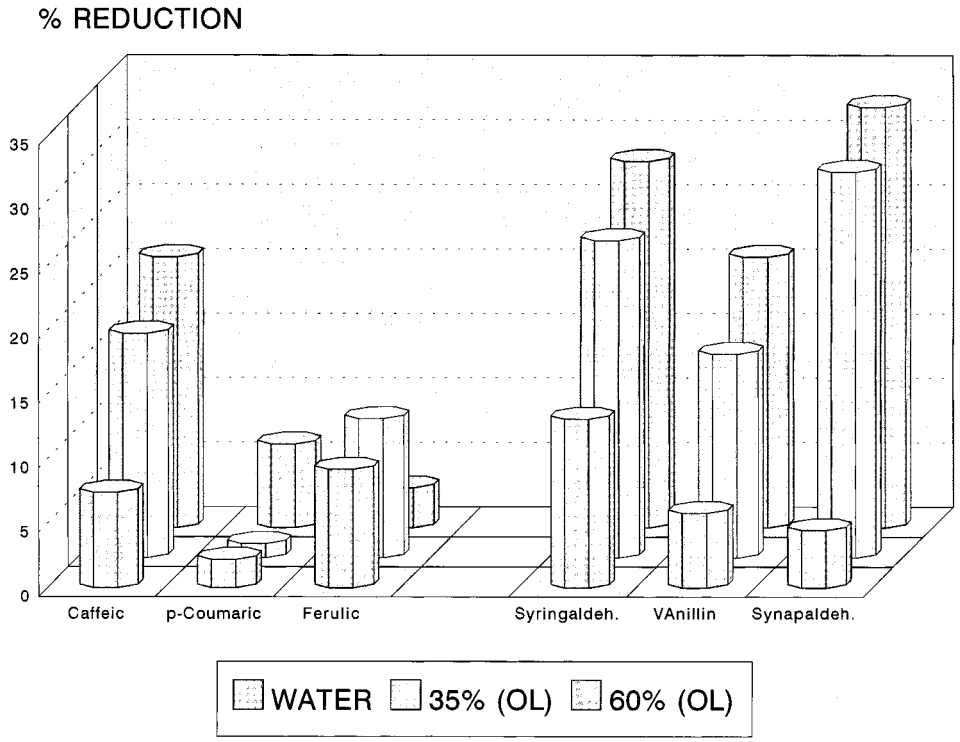

Figure 5. Percentage reduction of cinnamic acids and benzoic aldehydes according to exhaustion treatment.

slightly sulfited water (0.5−1 g/L). In the laboratory this process was reproduced by macerating the oak shavings in boiling water for 2 h.

In addition, we carried out an exhaustion treatment after charring of the shavings to reduce the syringaldehyde and sinapaldehyde concentrations to levels near those of the commercial samples. The treatment was based on studies by Puech et al. (1987a,b, 1988), who subjected the oak wood to heating in a water/alcohol mixture. We macerated the charred shavings in two water/alcohol mixtures at 60 and 35% (v/v). These macerates were then boiled for 2 h. This treatment involves exhaustion of the shavings, thus encouraging extraction of polyphenolic compounds by the water/alcohol mixture.

(A) Determination of Total Polyphenolic Compounds. Table 7 shows that both heat treatment and exhaustion of shavings have a considerable effect on the total content of phenolic compounds. In addition, Statgraphics was used to carry out a multiple variance study of the data obtained according to the type of treatment or exhaustion (Table 8). It was found that the longer the charring period, the higher the extraction of phenolic compounds and that the exhaustion process of the shavings reduces the total phenolic compound content.

Nonetheless, of the three exhaustion procedures tested, the most effective (statistically significant differences) regarding this parameter was that using a 60% (v/v) water/alcohol mix.

(B) Individual Measurement of Polyphenols. After individual measurement of the said phenolic compounds (Tables 9−11), it was observed that the exhaustion and washing techniques affected the resulting concentration in the macerates to varying degrees.

(1) Benzoic Acids. For all charring times, the exhaustion treatments of shavings tested considerably reduced the concentrations in the corresponding macerates. In particular, it can be seen from Table 9 that, in the case of gallic acid and *p*-OH-benzoic acid, an increase in charring time reduced the concentration of these compounds in the resulting macerate (very clearly, in the case of gallic acid). For the other benzoic acids the opposite is true (that is, concentration increased with increase in charring time), most particularly in the case of syringic acid, which increased by up to 7 times.

Individual examination of these treatments (Figure 3) showed that the water/alcohol mixture caused exhaustion proportional to the alcohol content, ranging from 44% (60% v/v alcohol) and 41.4% (30% v/v alcohol) in the case of gallic acid to 7.3 and 6.25% for *p*-OH-benzoic acid. We should point out that the greatest difference in exhaustion between the different alcohol concentrations occurred in the case of protocatechuic acid (up to 3 times as much).

Washing with water decreased extraction of gallic acid, syringic acid, and vanillic acid, similar to the effect of exhaustion with 35% (v/v) alcohol on protocatechuic acid and 60% (v/v) alcohol on *p*-OH-benzoic acid.

Initially we thought that washing the shavings with boiling water in an attempt to reproduce the afranchissement process would reduce gallic acid concentrations more than exhaustion with water/alcohol mixture. The results, however, showed that the opposite is true, as can be seen in Figure 4.

The mean value of gallic acid (1.89 mg/L) is very similar to that found in the commercial samples (1.69 mg/L), although the minimum value (1.20 mg/L) is rather higher than that of the commercial samples (0.38 mg/L) (Table 6).

The concentrations of protocatechuic acid and *p*-OH-benzoic acid were very similar to those of the commercial samples. Our macerates had a protocatechuic acid content of 1.22 mg/L (macerate 4) to 1.45 mg/l (macerate 3), which compares with a concentration range of 1−1.5 mg/L (average = 1.28 mg/L) for >50% of the samples of oloroso wine (Figure 4). The *p*-OH-benzoic acid concentrations of our macerates were, in

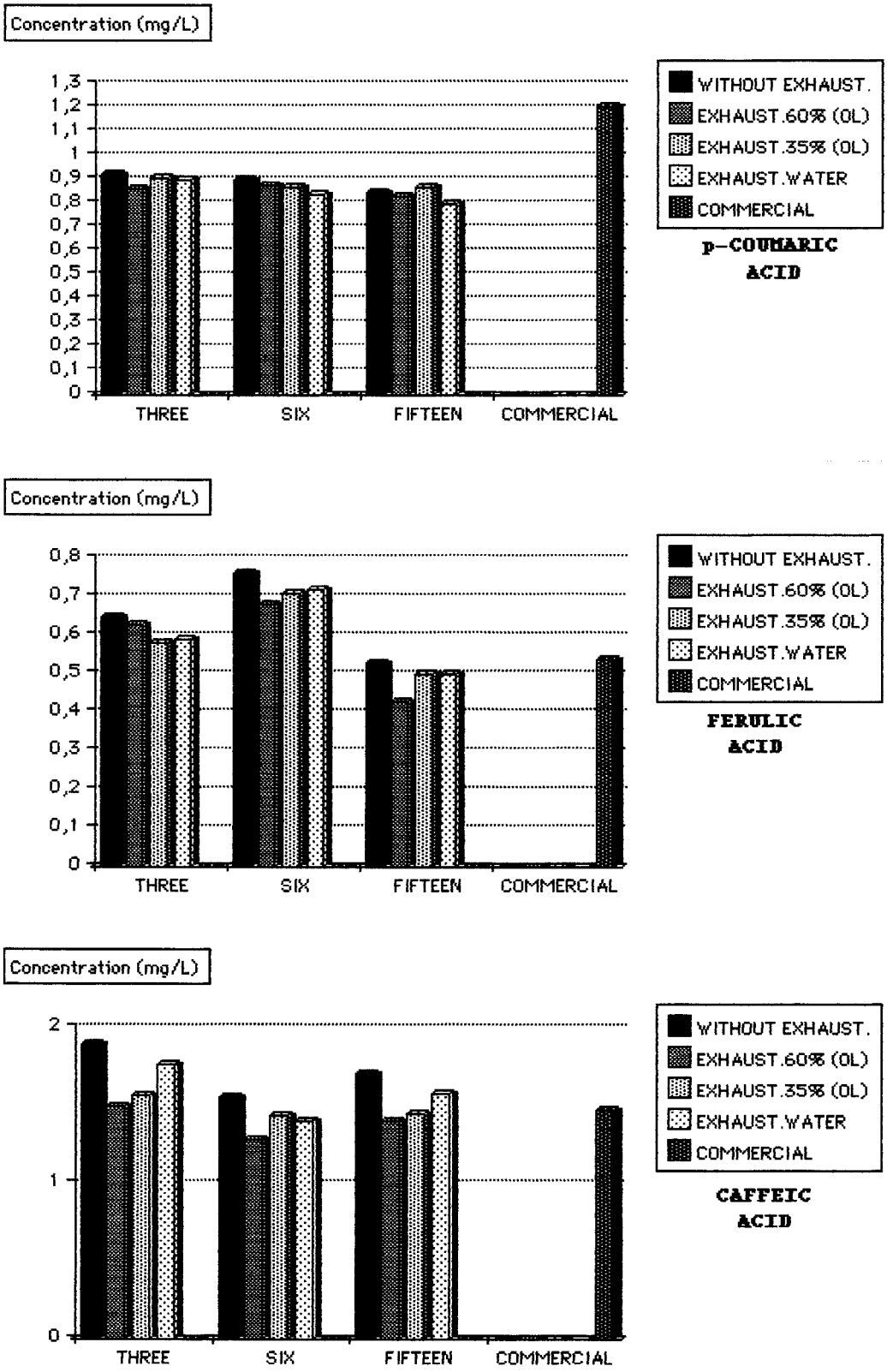

Figure 6. Cinnamic acid contents in selected macerates according to assayed aging technique (average content in commercial samples).

general, similar to but slightly lower than those of the commercial samples.

Comparison of the concentrations of syringic acid in the 12 macerates with the average value of the commercial oloroso wines (Figure 4) shows that the macerates prepared with shavings charred at 180 °C for 3 h and then exhausted with water/alcohol mix (macerates 4 and 7) were the most similar.

The final concentrations of vanillic acid after maceration were lower and closer to the mean value found in the commercial samples, in particular the macerates prepared with shavings charred at 180 °C for 3 h and then exhausted (macerates 4, 7, and 10).

(2) Cinnamic Acids. The behavior of these acids with regard to temperature was less uniform. The concentration of *p*-coumaric acid decreased with increase in

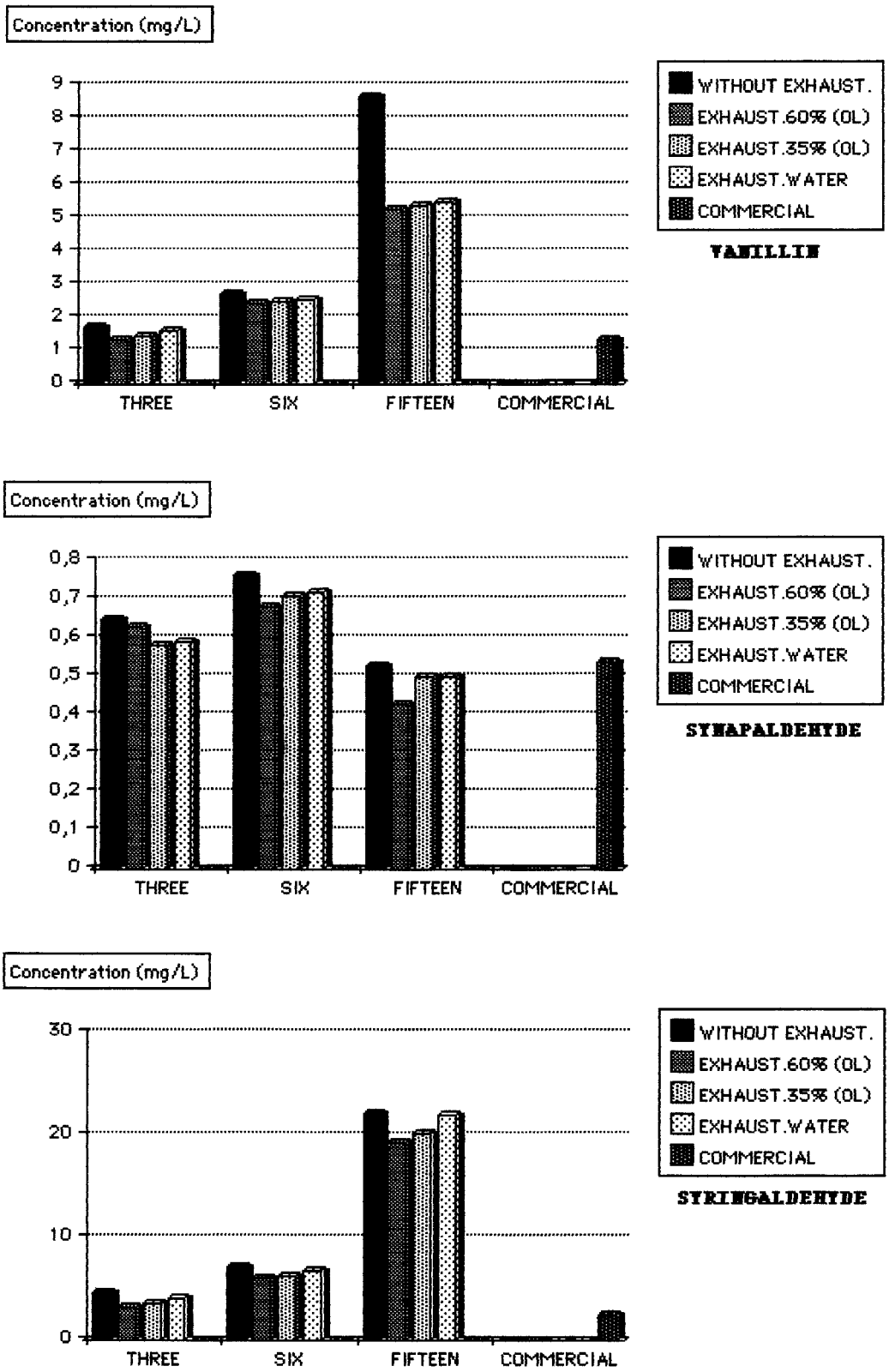

Figure 7. Benzoic aldehyde contents in selected macerates according to assayed aging technique (average content in commercial samples).

temperature, whereas extraction of caffeic acid decreased after 3−6 h and then increased after 15 h (although always below the levels reached after 3 h) and extraction of ferulic acid increased after 3−6 h and then decreased after 15 h of charring, again below the levels reached after 3 h.

Washing with alcohol reduced the concentration of these acids, and, as in the case of the phenolic acids, this reduction was more significant with 60% (v/v) alcohol than with 30% (v/v) alcohol, except in the case of ferulic acid, when the extracts obtained after treatment of the shavings with 30% (v/v) alcohol had lower concentrations (Figure 5). On the other hand, washing with water led to clearly higher concentrations of caffeic acid and results similar to those obtained with 35% (v/v) alcohol in the case of *p*-coumaric and ferulic acid.

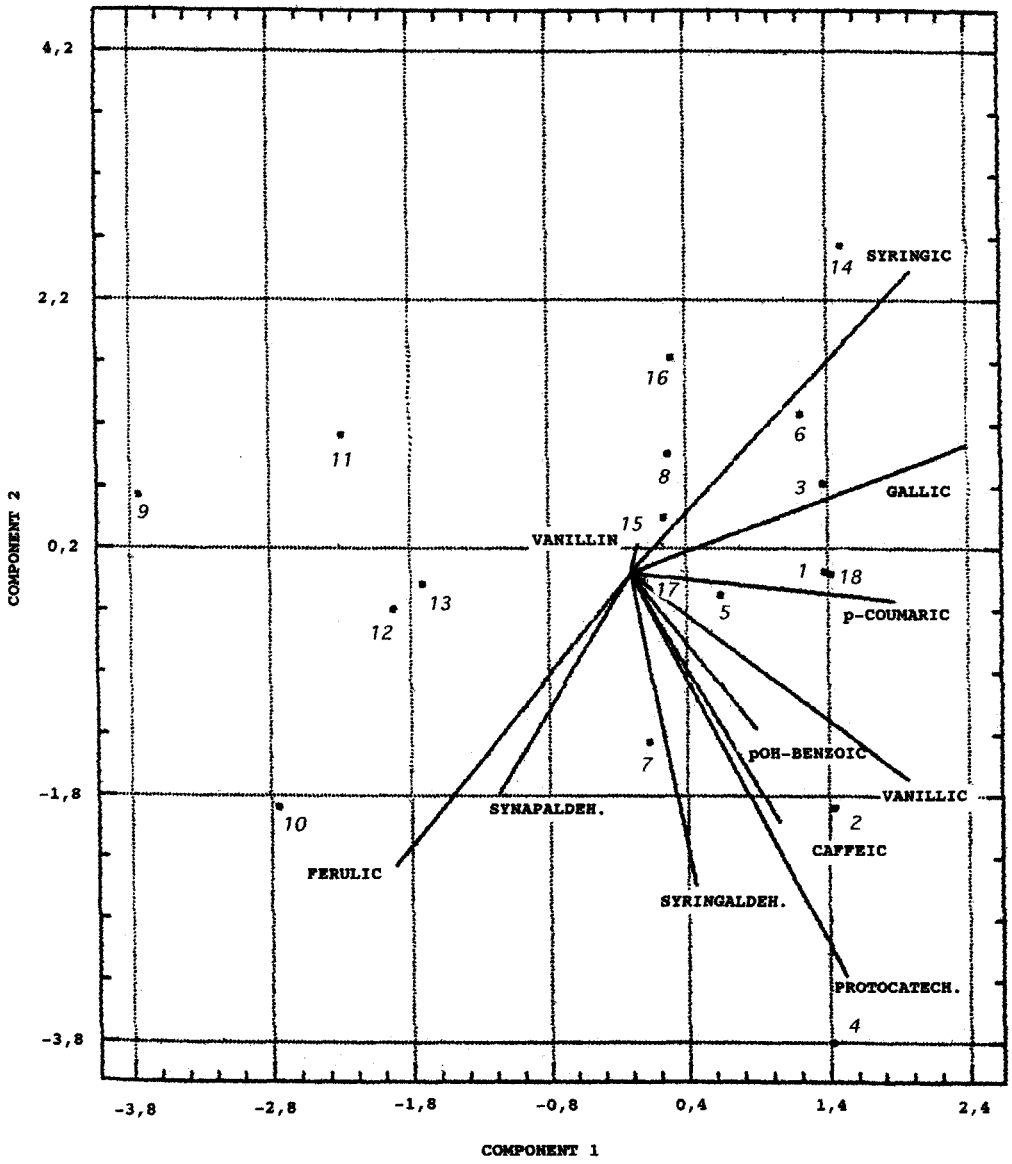

Figure 8. PCA of selected macerates.

Table 10. Cinnamic Acid Concentrations in Selected Macerates

macerate	caffeic acid (mg/L)	*p*-coumaric acid (mg/L)	ferulic acid (mg/L)
1	1.90	0.92	0.65
2	1.55	0.90	0.76
3	1.71	0.85	0.53
4	1.50	0.86	0.63
5	1.28	0.88	0.68
6	1.40	0.83	0.43
7	1.57	0.91	0.58
8	1.44	0.87	0.71
9	1.45	0.87	0.50
10	1.76	0.90	0.59
11	1.40	0.84	0.72
12	1.58	0.80	0.50

Table 11. Benzoic Aldehyde Concentrations in Selected Macerates

macerate	syringaldehyde (mg/L)	vanillin (mg/L)	sinapaldehyde (mg/L)
1	4.64	1.71	6.48
2	7.07	2.75	9.59
3	22.20	8.64	14.35
4	3.32	1.35	4.37
5	6.00	2.46	6.24
6	19.34	5.29	11.84
7	3.50	1.44	4.54
8	6.25	2.50	6.75
9	20.15	5.40	12.30
10	4.03	1.61	6.19
11	6.80	2.58	9.43
12	21.90	5.50	14.22

Generally speaking, all of the macerates analyzed showed caffeic acid concentrations very similar to the average value of this compound detected in the commercials samples (Table 10). The values were, moreover, inside the 1−2 mg/L interval found in all of the commercial samples (Table 6).

On the other hand, the macerates had lower *p*-coumaric acid concentrations than the mean value of the commercial samples (Figure 6) and ferulic acid values very similar to those of the commercial samples.

(3) Benzoic Aldehydes. Increase in charring time results in an increase in concentration in all cases, the increase being 6-fold for syringaldehyde and 5-fold for vanillin after 15 h. The same is true to a lesser extent for sinapaldehyde.

These concentrations were greatly reduced after exhaustion with alcohol (32% for sinapaldehyde, 21% for vanillin, and 28.4% for syringaldehyde), which are

Table 12. Factorial Analysis Results of Selected Macerates (Polyphenolic Compounds)

variable	commun-ality	factor	eigen-value	% var	cum %
gallic acid	0.72031	1	2.52748	50.5	50.5
protocatechuic acid	0.70221	2	1.63468	32.7	83.2
p-OH-benzoic acid	0.81416	3	0.52557	10.5	93.8
p-coumaric acid	0.74532	4	0.25003	5.0	98.8
syringaldehyde	0.85154	5	0.06224	1.2	100.0

Variable Rotated Factor Matrix

/FACTOR	1	2
gallic acid	0.87785	−0.21411
protocatechuic acid	0.53788	0.78328
p-OH-benzoic acid	0.89062	−0.10999
p-coumaric acid	0.41106	−0.77543
syringaldehyde	−0.29693	0.88268

Variable est Communality

gallic acid	0.81647
protocatechic acid	0.90285
p-OH-benzoic acid	0.80530
p-coumaric acid	0.77026
syringaldehyde	0.86729

much more significant decreases than when water was used (Figure 5). Nonetheless, these concentrations are still above the average value of the commercial samples, even though they are similar to the values detected in some of the latter (Figure 7).

Figures 5 and 7 show that after exhaustion of the wood with water/alcohol mixtures, macerates 4 and 7 had practically the same vanillin concentrations as the commercial samples. Likewise, regardless of charring time, exhaustion of the wood with alcohol led to lower sinapaldehyde concentrations, closer to the mean value and the concentration interval of the commercial samples.

We should point out that, of all the processes examined, the macerates prepared with wood shavings heated at 180 °C for 3 h and then exhausted with a water/alcohol mixture of 35 or 60% (v/v) (particularly the latter) produced the polyphenolic content closest to that of the commercial samples (Table 11).

To establish a comparison with the commercial samples and apply other types of analysis (for example, sensory analysis), the results were subjected to principal component analysis (PCA) and factorial analysis (FA) statistical analyses using the Statgraphics program (v. 6.0). Both studies were meant to assist interpretation of the complex multivariant data, taking all of the observations as a single group and attempting to establish which variables had more weight, to arrange the observations in the same groups while preserving the maximum information (variance) (Tapias et al., 1987; Armanino et al., 1990; Casp et al., 1992).

Both analyses allowed us to establish the matrices (linear equations) giving a linear correlation for each factor according to the different variables, as well as representing the samples by a point (two coordinates) on the space (Figure 8). FA differs from PCA in that it also estimates the weight of the factors (Table 12).

After elimination of polyphenols with a correlation coefficient <0.8, we obtained comparable results in each study, resulting in a classification and description of the macerates studied. Protocatechuic acid and syringic acid were the polyphenols with highest variability.

The components and factors determined by us coincide almost entirely with those obtained after a thorough examination of samples of commercial oloroso wines from the Jerez-Xérés-Sherry district (Monedero, 1995). These results will therefore be of use in future organoleptic analyses of the macerates examined in this paper and proposed as alternatives to the traditional aging process.

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