Behavior of a Hyperoxidized Must During Biological Aging of Fino Sherry Wine

REMEDIOS CASTRO[1] and CARMELO GARCÍA BARROSO[2]*

Hyperoxidation treatment of wine must is a technique that has been used increasingly in recent years to obtain white wines with greater stability against undesirable oxidation phenomena. In the case of the typical "Fino" sherry wines, the problem of browning suffered by the finished wine has been studied for many years. Hence, in this study, the objective is to assess the viability of hyperoxidation of the must of the Palomino Fino grape variety, which is used in the production of these wines, as a means of giving the wine greater resistance to browning while preserving the particular organoleptic characteristics derived from the biological aging of the wine under the flor yeast film. For this assessment, musts from four consecutive harvests were subjected to hyperoxidation, and the resulting wines were kept in an experimental solera under biological aging conditions. This experimental wine was then compared with a control wine obtained by traditional winemaking methods from the same four harvests. It was observed that during the aging period the experimental wine showed similar behavior to the control, its sensory characteristics improving over the course of the period of aging in solera, while showing a reduced tendency towards browning.

KEY WORDS: hyperoxidation, sherry wine, biological aging

The typical Fino wines of the Jerez-Xérès-Sherry and Manzanilla of Sanlúcar Denomination of Origin (DO), as other white wines, are affected by the problem of browning that the wine undergoes after being bottled. It is known that this deterioration in the visual and flavor characteristics is due to the oxidation of the polyphenolic compounds present in the wine [12,19].

In our DO region, these wines are produced from the Palomino Fino grape variety. After vinification, they are submitted to a system of dynamic, biological aging under the surface layer of yeasts known as the flor yeast film, the creamy film or bloom. The aging system is very traditional and is termed aging in *solera*. The solera consists of rows of barrels (of American oak) stacked one upon the other; each level is a row of the system, being numbered from the ground up, so that the first row is that one of barrels resting on the ground in the wine cellar [6].

The new wine is introduced into the solera system at the top row, in the highest row number. The barrels are filled to about 5/6 of their maximum capacity, but the wine is protected from the action of the remaining air by a fine layer of mycodermic yeasts which grow on the wine's surface. It is this layer of yeasts that accounts for a large part of the wine's organoleptic and sensory characteristics.

Every four months or so, the barrels of each row are partially emptied in the *saque*, with a proportion of their content being added to that of the row immediately below, and lower in number. In their turn, they are replenished with younger wine from the row immediately above. The aged wine required for bottling is drawn from the lowest row, the first level of the solera. The average length of time that the wine remains under this dynamic aging is two to three years, after which it is prepared for bottling.

The *Fino* wine thus obtained, which was protected from oxidation during its aging by the layer of yeasts, then loses this protection and is exposed to the effects of environmental oxygen.

As has been the case with other types of white wine, a variety of techniques have been used to arrest or counter this detrimental evolution; these include bottling under an inert gas [8,17] and the addition of fining substances [1,2].

It is notable that in other winegrowing regions in recent years a technique known as hyperoxidation has been used; this consists of forcing the oxidation of the must by the pumping air or oxygen through it. The purpose of this is to oxidize in the must any polyphenolic compounds present that are susceptible to oxidation, transforming them into polymers of low solubility which can thus be easily eliminated. This technique is applied in the absence of sulfur dioxide, so that the must undergoes a rapid oxidation. This even encourages the self-clarification (settling) of the must [18]. The resulting precipitates are soluble in alcohol and must be removed from the must before the initiation of fermentation [15].

This enotechnical procedure has been used to date in these other wine-producing regions to obtain young white wines with good organoleptic characteristics and a greater resistance to browning [7,10,16]. For this reason, and taking these precedents into account, we undertook a study evaluating the effects of forced oxidation of the must of the Palomino Fino grape variety in order to answer whether a *Fino* sherry wine can be produced with a reduced tendency to browning whilst

[1,2]Analytical Chemistry Department, Faculty of Sciences, University of Cádiz, P.O. Box 40, E-11510, Pol. Río San Pedro, Puerto Real, Cádiz, Spain.

*Corresponding author [e-mail: carmelo.garcia@uca.es].

Acknowledgements: We gratefully acknowledge the collaboration from Bodegas Osborne & Cía, which allowed these experiments to take place.

This work was supported by Spanish CICYT (ALI94-0649).

Manuscript submitted for publication 30 June 1999; revised 13 December 1999.

retaining the sensory characteristics of this type of wine.

For this, one of the sherry wine-producing companies of the region, Bodegas Osborne & Cía., provided support and, in its installations, conducted experiments of controlled oxidation on an industrial scale for four consecutive vintages from 1992 to 1995. The behavior of hyperoxidized musts were monitored before the resulting wines were submitted to the solera aging system and were compared to control wines produced from non-hyperoxidized musts. From these hyperoxidized musts from successive grape harvests an experimental solera was created, consisting of barrels containing the wine produced. This wine was then aged biologically according to the typical system for producing Fino sherry wine. In parallel with this experimental solera another control solera, created and maintained under a conventional process of vinification, was monitored for three years. Both soleras were sampled periodically in order to determine both their organoleptic characteristics and their polyphenolic content and resistance to browning.

Since many studies exist in the field of enology in which chemometric techniques are employed as a means of discriminating between wines of different regions [14], of different grape varieties [13], and of different aging or vinification systems [20], and even between the different row of one solera system [3], it was decided to use statistical techniques to compare the two soleras and to determine reliably whether the hyperoxidation of the must altered the behavior of the wine while in the solera. The objective was to observe the evolution undergone by the wine obtained from the hyperoxidized must during aging under the flor yeast film, to determine the applicability of this technique which is still novel for our DO and to our specialized process of white wine production.

Material and Methods

The industrial-scale oxidation tests were conducted over four wine vintages. The musts from each harvest were dosed with calcium carbonate (2 g/L) and tartaric acid (up to pH 3.25). Oxygen was added in a vessel filled with 32 000 L of must, while this was pumped from the bottom to the top of the tank. The oxygen was supplied through the outlet of the recirculation pump, at a rate of 50 mg/L.

After the addition of the O_2, the must was left for one hour while the oxidation took place and then was clarified with 0.05 mL/L of liquid gelatine (GELSOL™, AEB Ibérica; Barcelona, Spain, E-08100) and 0.5 mL/L of silica sol (BAYKISOL™, AEB Ibérica; Barcelona, Spain, E-08100). After letting the must decant for 10 hours, the clean fraction (16 000 L) was racked into the fermentation tank, where SO_2 (100 mg/L) and the inoculum (1000 L) were added. The fermentation and subsequent processes were carried out according to the conventional process of vinification.

Taking the wine obtained from the first hyperoxidation test, an experimental solera was established. This was then periodically replenished with the wines obtained after subsequent oxidation tests.

In each vintage, another batch of must of identical characteristics was monitored as a control and followed a conventional processing and aging. Thus over the course of the four years of the experiment, a parallel control solera was maintained.

It was ensured that the times of sampling and rackings in the two soleras (every 4 months) coincided. The parameters monitored and the analytical techniques employed were as follows:

Polyphenolic profile — by means of HPLC [11], after first using a continuous rotatory liquid-liquid extraction phase [5]. The polyphenolic data were treated using Statistica 4.5, the statistical package for Windows; specifically, variance analysis was used to compare the two types of wine, both prior to and during the biological aging. Linear discriminant analysis (LDA) was used as the descriptive technique.

General analyses — parameters of enological interest (pH, total and volatile acidity, alcohol content, *etc.*), total phenolic content, by means of the Folin-Ciocalteu method; acetaldehyde, ethyl acetate, methanol and higher alcohols, by GC [9]; and organic acids by HPLC [9].

Tastings of the wines — performed by a group of experts from Bodegas Osborne & Cía.

Resistance of the wines produced to browning — checked by studying the evolution of the color (absorbance at 490 nm) of the wine drawn from the first row of the solera, monthly over the course of one year in bottle.

Results and Discussion

The chromatogram resulting from the application of the methods of preparation and HPLC analysis of the samples is shown in Figure 1; the polyphenolic compounds which we were able to identify are indicated.

With respect to the polyphenolic content of the oxidized and control wines before being introduced into

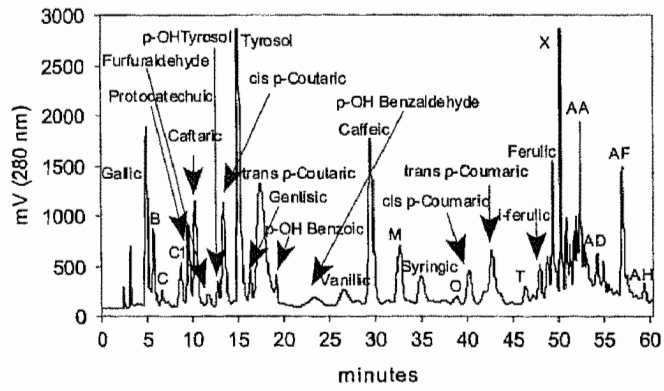


Fig. 1. Chromatogram of a Fino sherry wine. Polyphenolic variables submitted to statistical treatment.

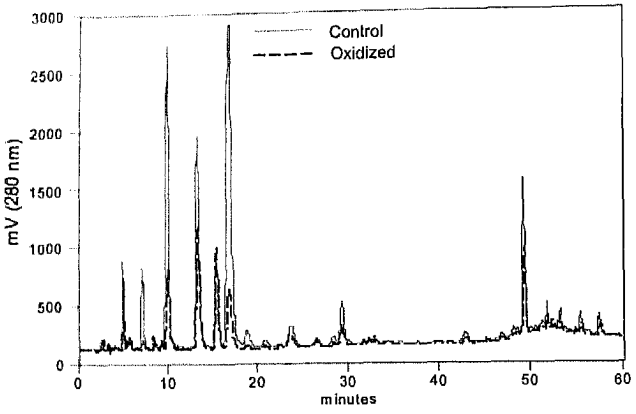


Fig. 2. Comparison of chromatograms (280 nm). Oxidized and control wines before being introduced into the solera aging system.

the solera aging system, it can be observed from Figure 2 that the losses caused by the forced oxidation are very evident: the wine produced from the oxidized must shows a greatly diminished polyphenolic profile, particularly in the first part of the chromatogram. The compounds most affected were: caftaric, gallic, caffeic, and *cis*- and *trans*-*p*-coutaric acids.

These observations on the effect of the hyperoxidation on the polyphenolic compounds of low molecular weight were corroborated when the chromatographic data were submitted to statistical treatment. The polyphenolic variables considered are those identified from Figure 1.

The results of the analysis of variance applied to the effects of the hyperoxidation treatment on the polyphenolic variables are given in Table 1. From this table it is clear that the main polyphenolic compounds which differ significantly between the two wines over the course of the fermentation period are the esters of cinnamic with tartaric (caftaric and *trans* p-coutaric) together with *p*-OH benzoic, caffeic, and *trans p*-coumaric.

These same analytical data were treated by descriptive techniques for the purpose of identifying those polyphenolic compounds capable of discriminating between the two types of wine during the fermentation period.

Figure 3 shows the differentiation achieved between the samples of hyperoxidized (o) and control (t) must taken during the course of their fermentation, after performing a LDA using only polyphenolic variables. A differentiation of 100% was achieved in respect of caftaric, *cis*- and *trans*- *p*-coutaric.

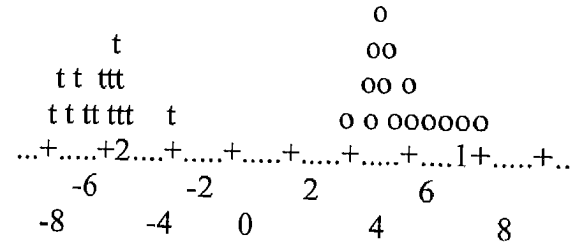
Considering now the evolution of the polyphenolic profile of the two wines during the period of aging in solera, Table 2 shows the results obtained from the analysis of variance made of samples of the two wines corresponding to one, two, and three years of aging.

As can be observed, after the first year of aging, the esters of cinnamic with tartaric continue to be the compounds which differ significantly between the two wines. This situation is repeated after two years, but to a lower degree (lower significance). However, after three years of aging, only one variable, the content of *p*-OH benzaldehyde, differs significantly in the two wines.

These same data were submitted to an LDA study for the purpose of identifying those polyphenolic compounds which would enable the discrimination between the two wines over the course of the biological aging period.

Table 1. Analysis of variance applied to the wines (during fermentation) obtained by the traditional method and by hyperoxidation of the must.

Polyphenolic variable	F value	*p* level
Gallic	8.771	0.007
B	0.065	0.801
C	11.412	0.003
C1	0.418	0.524
Protocatechuic	0.002	0.970
Caftaric	20.618	0.000
cis p-Coutaric	2.679	0.115
Tyrosol	0.967	0.336
trans p-Coutaric	65.034	0.000
p-OH Benzoic	13.818	0.000
p-OH Benzaldehyde	2.190	0.152
Caffeic	13.698	0.001
M	0.000	0.998
Syringic	9.170	0.006
O	0.202	0.657
cis p-Coumaric	0.186	0.670
trans p-Coumaric	16.364	0.001
T	0.564	0.460
Isoferulic	5.357	0.030
Ferulic	3.854	0.062
X	2.774	0.109
AA	3.968	0.058
AD	32.662	0.000
AF	10.956	0.003
AH	3.554	0.072



Standardized canonical discriminant function coefficients

Parameters	Coefficients
Caftaric	+ 0.836
cis p-Coutaric	+ 1.301
trans p-Coutaric	- 2.477

Fig. 3. Grouping analysis for the wines during the course of their fermentation. Percentage of cases correctly classified: 100% (t: control wine; o: experimental wine).

Table 2. Analysis of variance of control and experimental wines during biological aging.

Polyphenolic variable	1st year		2nd year		3rd year	
	F value	p level	F value	p level	F value	p level
Gallic	0.188	0.673	1.020	0.336	0.124	0.731
Protocatechuic	2.109	0.177	1.555	0.241	0.027	0.873
Caftaric	11.758	0.006[A]	8.952	0.013[a]	3.240	0.102
Furfuraldehyde	2.576	0.139	0.531	0.483	1.076	0.324
cis-p-Coutaric	13.072	0.005[A]	6.565	0.028[a]	3.620	0.086
Tyrosol	3.875	0.077	8.047	0.018[a]	1.314	0.278
trans -p-Coutaric	17.755	0.002[A]	6.837	0.026[a]	7.805	0.019[a]
p-OH Benzaldehyde	0.195	0.668	0.916	0.361	13.877	0.004[A]
Vanillic	1.003	0.340	0.806	0.390	0.429	0.527
Caffeic	0.707	0.420	1.720	0.218	0.201	0.663
Syringic	0.505	0.493	0.609	0.453	0.231	0.641
cis- p-Coumaric	1.131	0.312	1.325	0.276	0.056	0.817
trans -p-Coumaric	0.265	0.618	0.341	0.572	0.093	0.767
Isoferulic	1.714	0.220	0.694	0.424	5.846	0.036[a]
Ferulic	3.469	0.092	0.013[a]	0.909	0.001	0.977

A,a: Values are significantly different at $p < 0.01$ (capitals) and $p < 0.05$ (lower case).

Table 3. Percentage of cases correctly classified. Linear discriminant analysis of control and experimental wines during their biological aging.

Phenolic parameters	1st year	2nd year	3rd year
Gallic, Caftaric, *trans-p*-Coutaric *cis-p*-Coutaric, Caffeic, *trans-p*-Coumaric	100	100	83.3
Gallic, Caftaric, *trans-p*-Coutaric, Caffeic	91.6	91.6	66.6
Caftaric, *trans-p*-Coutaric, Caffeic	91.6	83.3	66.6
Gallic, *trans-p*-Coutaric, Caffeic	91.6	91.6	66.6
Caftaric, *trans-p*-Coutaric	91.6	91.6	75
Caftaric, *trans-p*-Coutaric, *cis p*-Coutaric	91.6	91.6	75

From Table 3, it can be observed that, after the first year of aging, the differentiation between the two wines is relatively high in terms of the content in hydroxycinnamic esters and in those polyphenolic compounds with a marked capacity for oxidation, although in line with the increase in the period of aging, the degree of differentiation between the wines, in function of these compounds, decreases.

During the biological aging, losses occur in hydroxycinnamic esters, in favor of their acids, due to phenomena of hydrolysis [4], accompanied by an enrichment in aldehyde-type compounds derived from the degradation of the lignin in the wood of the cask.

It seems, therefore, that the polyphenolic composition of a wine produced from a hyperoxidized must, once it is introduced into the aging system under the flor yeast film, follows a very similar evolution to that of a conventionally treated must. This would explain the decrease in the significant differentiation due to these parameters, between the two wines, during aging.

In addition to the polyphenolic composition, during the period of aging, some of the main parameters of enological interest were studied (pH, acidity, alcohol content), together with the concentration of acetaldehyde, ethyl acetate, methanol, higher alcohols, organic acids, *etc.* The concentrations found for the experimental and control soleras after three years of aging are

Table 4. Results of the analysis of variance applied to the wines during aging. Enological parameters.

Parameter	Control Solera			Experimental Solera			Analysis of variance	
	1st row	2nd row	3rd row	1st row	2nd row	3rd row	F value	p level
[9]Al	14.60	14.90	15.00	14.80	14.90	15.00	0.250	0.643
pH	3.15	3.08	3.05	3.14	3.06	3.04	0.098	0.770
Total Acidity	4.00	4.58	5.03	4.12	4.60	4.98	0.006	0.942
Vol. Acidity	0.10	0.20	0.18	0.12	0.20	0.15	0.007	0.935
Tartaric[a] ac.	2.92	2.70	2.57	2.87	2.48	2.43	0.535	0.504
Malic[a] ac.	0.07	0.20	0.31	0.08	0.04	0.08	3.216	0.147
Lactic[a] ac.	0.16	0.47	0.61	0.18	0.56	0.72	0.124	0.742
Acetic[a] ac.	0.19	0.19	0.19	0.18	0.18	0.15	4.000	0.116
Citric[a] ac.	0.03	0.19	0.21	0.02	0.19	0.23	0.001	0.971
Succinic[a] ac.	1.03	1.02	0.98	1.00	0.96	0.99	1.882	0.242
Glycerine[a]	0.94	4.28	5.52	0.91	4.37	5.82	0.004	0.955
Acetaldehyde[b]	78	77	85	68	41	73	3.556	0.132
ethyl acetate[b]	37	44	44	31	34	38	5.628	0.077
Methanol[b]	78	67	57	83	52	50	0.213	0.669
n-Propanol[b]	37	34	30	40	30	32	0.008	0.932
i-Butanol[b]	59	50	39	64	44	40	0.000	1.000
i-Amylic[b]	233	221	213	253	168	175	0.722	0.443

a: g/L; b: mg/L

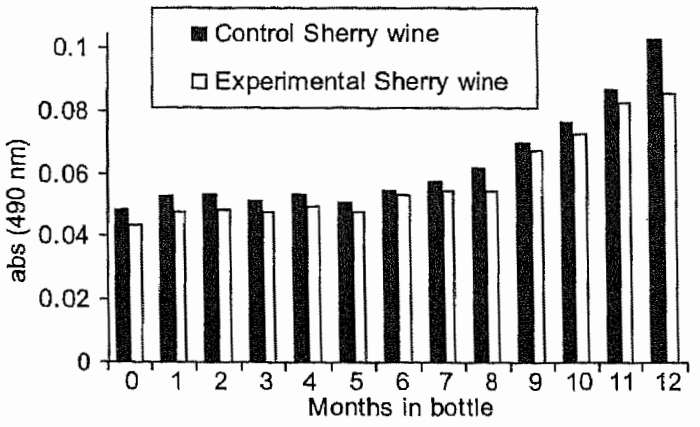


Fig. 4. Comparison of resistance to browning. Wines from the first row (solera) during one year in bottle.

detailed in Table 4. These data were submitted to analysis of variance, but no significant differences were found between the two soleras.

The tastings carried out by the group of experts from Bodegas Osborne & Cía. over the course of the three years demonstrated a poorer organoleptic classification for the third and second row of the experimental solera; however, that assigned to the first or fully aged row showed an improvement towards a classification similar to that of the control solera, after three years of aging.

Figure 4 shows the results of the test of resistance to browning, measured by the evolution of the color (absorbance at 490 nm) of samples taken from the first row of the two soleras over the course of one year in bottle. As can be observed, after the three years of biological aging, the experimental wine not only commenced the year in bottle with a somewhat lower absorbance value than the control, but month by month it maintained a value notably lower than the control wine, thus showing its greater resistance to browning.

It is concluded, therefore, that the hyperoxidation of must of the Palomino Fino grape variety can be employed to obtain a Fino sherry wine whose organoleptic characteristics are similar to those of a "Fino" wine produced conventionally; these characteristics are not altered by the effect of the hyperoxidation, during the wine's aging under the solera system. This is demonstrated by the fact that, in the comparison between the experimental and the control wines, the longer the period of aging, the less the degree of differentiation found in respect of the polyphenolic profile, the better the organoleptic characteristics, and the greater the resistance to browning.

Literature Cited

1. Barón, R., M. Mayén, *et al.* Effect of two clarification treatments on the evolution of color and phenolic compounds in Sherry-type white wines. Inf. Technol. 9(2):93-99 (1998).

2. Barón, R., M. Mayén, *et al.* Changes in phenolic compounds and color in pale Sherry wines subjected to fining treatments. Z Lebensm Unters Forsch A 205(6):474-478 (1997).

3. Barroso, C. G., M. V. G. Moreno, and J.A. Pérez-Bustamante. Participation of polyphenolic compounds in the diferentation of the different steps of the solera aging system used for the "Fino" Sherry wine. Bull. Liaison Groupe Polyphénols 16:64-68 (1992).

4. Barroso, C. G., R. Cela, and J. A. Pérez-Bustamante. Evolution of phenolic acids and aldehydes during the different production process of Fino Sherry Wine. Z. Lebensm. Unters. Forsch, 182:413-418 (1986).

5. Brú, E. R., C. G. Barroso, *et al.* Development of a rotatory and continuos liquid-liquid extraction technique for phenolic compounds in wine. Analyst 121:297-302 (1996).

6. Casas, J. Descripción resumida de la técnica enológica de los vinos de Jerez. *In:* Proceedings of the University of Cadiz, III Jornadas Universitarias sobre el Jerez. Jimenez-Mena (Ed.). pp 333-361 (1). University of Cadiz Press, Cadiz (1985).

7. Cheynier, V., M. Souquet, and M. Moutounet. Hyperoxidation: influence of various oxygen levels on oxidation kinetics of phenolic compounds and wine quality. Vitis 30:107-115 (1991).

8. Gai, C. Imbottigliamento a bassa dei vini di qualita, Indust. Bevande 18:278-282 (1989).

9. Grandal, M. Viabilidad enológica de la reutilización del vino fino remontado para obtener vino amontillado. Thesis, University of Cádiz (1996).

10. Guerzoni, M., E. R. Zironi, *et al.* Stabilisation of white wine by early hyperoxidation of must. Food Technol. Austral. 33(9):442-446 (1981).

11. Guillén, D.A., C.G. Barroso, and J. A. Pérez-Bustamante. High performance liquid chromatographic analysis of polyphenolic compounds predominanting in Sherry must. J. Chromatogr. A. 655:227-232. (1993).

12. Macheix, J. J., J. C. Sapis, and A. Fleuriet. Phenolic compounds and polyphenoloxidase in relation to browning in grapes and wines. Crit. Rev. Food Sci. Nutr. 30(3):441-486 (1991).

13. Moret, I., and A. Gambaro. Trend analysis in selection of aroma components as variables for chemometric studies of typical wines. Anal. Chim. Acta 86:309-318 (1996).

14. Moret, I., G. Scarponi, and P. Cescon. Chemometric characterization and classification of five venetian white wines. J. Agric. Food Chem. 42(5):1143-1153 (1994).

15. Muller-Spath, H. Le SO_2, l'oxygene et l'etat d'oxydoreduction du vin. Riv. Oenol. 49:7-14 (1988).

16. Nicolini, G. Changes in the sensory profile of Sauvignon blanc wines in connection to the must hyperoxidation. Riv. Vitic. Enol. 4:35-43 (1992).

17. Prass, G., and J. Virgo. Observations on the influence of inert gases on wine quality. Food Technol. Austral. 28:475-477 (1976).

18. Schneider, J. Must hyperoxidation: A review. Am. J. Enol. Vitic. 49:65-73 (1998).

19. Singleton, V. L. Oxygen with phenols and related reactions in musts, wines, and model systems: observations and practical implications. Am. J. Enol. Vitic. 38:69-77 (1987).

20. Zironi, R., E. Celotti, and F. Battistutta. Research for a market of the hyperoxidation treatment of musts for the production of white wines. Am. J. Enol. Vitic. 48:150-156 (1997).