JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Changes in the Polyphenolic and Volatile Contents of "Fino" Sherry Wine Exposed to Ultraviolet and Visible Radiation during Storage

PATRICIA BENÍTEZ, REMEDIOS CASTRO,* AND CARMELO GARCÍA BARROSO

Analytical Chemistry Department, Faculty of Sciences, University of Cádiz, Pol. Rio San Pedro s/n, P.O. Box 40, E-11510 Puerto Real, Cádiz, Spain

Experiments of accelerated oxidation of "fino" sherry wines have been conducted at 25 °C and under the influence of UV−visible radiation (a xenon lamp of 1500 W). With the aim of determining the contribution of UV−vis radiation to the browning phenomenon, two types of glass bottles were employed: topaz bottles (with low values of transmittance in the UV−visible range) and transparent bottles. To identify significant differences between the wine before and after being subjected to the influence of the UV−vis radiation, the values of absorbance at 420 nm and the concentrations of various polyphenolic and volatile compounds were submitted to a multivariate variance analysis. Both factors considered (time and type of bottle) had a statistically significant effect on the values of absorbance at 420 nm and on the concentration of most of the polyphenolic compounds, whereas only the "time" factor was significant for volatile compounds. All wines showed losses in several polyphenolic compounds, which were more severe for the wines bottled in transparent glasses. However, these wines exhibited a lower degree of visual browning (abs 420 nm). In the case of volatile compounds, most of these presented increases during storage exposed to the influence of the UV−vis radiation.

KEYWORDS: Sherry wine; oxidation; polyphenol; volatile compound; ultraviolet−visible radiation

INTRODUCTION

The phenomenon known as browning is notable among those that produce undesirable changes in the organoleptic characteristics of white wine. This process, which takes the form, visually, of an evolution in the color toward brown tones and, in sensory terms, of a change in the aroma of the wine, is due to the oxidation of part of the phenolic content of the wine. Some of these phenolic compounds show decreases because they are transformed into quinonic compounds, the presence of which is the direct cause of the visual changes observed (*1*, *2*). Wine oxidation also involves a significant change in wine flavor components (*3*) through the appearance of new odorants and the disappearance of several original odorants.

Because of this deterioration process, wine quality is lost even before the changes in color become apparent, as a consequence of the various oxygen-related off-flavors. Descriptions of aroma, such as "oxidized apple", "woody", and "cement", have been used to describe wine aroma oxidation. It is generally believed that acetaldehyde is the main aroma generated during wine oxidation (*4*, *5*). However, Escudero et al. (*6*) observed that the acetaldehyde content of white wines stored under oxygen did not vary significantly during the oxidation process. There are several aroma compounds related to the effect of oxygen in wines (*7*). Some of these are products of the oxidative degradation of unsaturated fatty acids (*7*), whereas others have a miscellaneous origin.

The "fino" sherry wines, typical of the Jerez-Xérès-Sherry and Manzanilla de Sanlúcar Denomination of Origin region (in southwestern Spain), protected from the action of oxygen thanks to the special system of aging in cask under the "veil of flor" (*8*), along with the other types of white wine, are affected by browning, which occurs after they have been bottled.

There are many factors that intervene in the browning of a bottled white wine, in addition to the main factors of the various phenolic compounds present and oxygen; these include the environmental conditions of conservation (temperature, humidity, illumination, etc.) and the conditions under which the wine has been bottled [type of bottle, type of stopper, introduction of inert gas (*9*, *10*), etc.]. It is known that high temperatures (*11*) and exposure to light accelerate the process of browning of wine. In the case of light, it has not been clear exactly how this factor participates in the process of browning of white wines.

At first, it was thought that oxygen was activated by the light, as a result of the presence of either photosensitizing pigments or metals such as iron and copper. It is now known that the polyphenolic substrates are activated by this agent to produce free radicals of the semiquinone type (*12*).

In the case of the participation of light, the occurrence of an unpleasant taste, variously described as "skunky", "cooked

* Author to whom correspondence should be addressed (telephone +34-56-01-63-63; fax +34-56-01-64-60; e-mail remedios.castro@uca.es).

10.1021/jf030223j CCC: $25.00
Published on Web 09/26/2003

cabbage", and "onion garlic", has been reported in many beverages such as sparkling and white wines. The detrimental effect of light on the aroma fraction of these beverages is connected with different chemical processes, with riboflavin being involved in some of them (*13*, *14*).

Several studies on the influence of temperature on the oxidation of the phenolic content of white wines have been reported. It has been demonstrated that the reactions due to a high temperature are different from those produced during natural browning (*15*). The participation of a high temperature in the phenomenon of browning leads to increased browning, but despite this greater degree of browning, such wines do not experience a dramatic reduction in their polyphenolic content (*15*). This has been explained as being due to hydrolysis reactions of oligomeric derivates, favored by the relatively high temperature.

Scarce literature about the participation of UV−visible radiation and its effect on the polyphenolic and volatile content of white wines is found. Benitez et al. (*16*) studied the degradation of four phenolic acids in water by UV radiation alone and by the advanced oxidation process produced by the combination of ozone and UV radiation. The combination of these two agents led to the highest rate of degradation.

The objective of this study is to determine the degree of participation of this latter agent in the changes in the polyphenolic and volatile compounds of a fino sherry wine and to study whether the use of a particular glass could protect the wine from this phenomenon.

For this, a study has been conducted about the evolution of the volatile and polyphenolic fractions and the color (abs 420 nm) of this type of wine, bottled in glasses with different transmittances in the UV−vis range and submitted to this type of radiation.

MATERIALS AND METHODS

Wine Samples. A fino sherry wine (ethanol content = 15% v/v) from the Jerez-Xérès-Sherry and Manzanilla de Sanlúcar Denomination of Origin region (southwestern Spain) was bottled into glass bottles of two colors, topaz and transparent. Nine bottles of each type were introduced into a controlled-climate chamber for 45 days, under a constant temperature of 25 °C and the influence of solar-type radiation provided by a xenon lamp of 1500 W (emission of UV and visible radiation). The bottles were initially arranged randomly inside the chamber, and then, each day, the bottles placed furthest from the light source were interchanged with those placed closest, to try to ensure that all bottles received the same degree of illumination. Three bottles of each type were removed after being kept for periods of 10, 30, and 45 days, respectively, in the climate chamber. During the entire period of the trial, the bottles were left without a stopper and covered only with a piece of cotton, to accelerate the process of browning of the wine contained. The volume of wine lost by evaporation (~4% in all cases) was measured to allow correction of the results obtained.

Model Solution of Polyphenolic Compounds. Polyphenolic compounds considered in this study (except those for which commercial standards are not available: caftaric acid, *cis*- and *trans*-*p*-coutaric acids, GRP, and fertaric acid) were added to a solution of Milli-Q water containing ethanol (15% v/v) and adjusted to pH 3.5 with tartaric acid. The concentration employed for each compound was similar to that found in the initial wine. All of these compounds were purchased from Fluka (Buchs, Switzerland) and Eastman Kodak (Rochester, NY). Global solutions of these compounds were introduced into the controlled-climate chamber under the conditions mentioned before.

Determination of the Polyphenolic Compounds. Eighty microliters of fino sherry wine after filtration (0.45 μm pore size) was analyzed by HPLC (Waters Cromatografia, S.A., Barcelona, Spain) in duplicate. The elution phases used were solvent A (95% water, 5% methanol) and solvent B (95% methanol, 5% water) at pH 2.5 (extra pure sulfuric acid). The elution gradient was from 100 to 85% solvent A in 5 min, from 85 to 50% solvent A in 40 min, and isocratic elution for 35 min. The analyses were carried out using a C_{18} column (Lichrospher 100 RP-18, 250 mm × 3 mm, 5 μm particle size) at a flow rate of 0.5 mL/min and detection at 280 and 320 nm.

The various polyphenolic compounds present were identified by comparison with a library of DAD spectra and retention times of standards. Commercial standards of several polyphenols (gallic acid, protocatechuic acid, protocatechualdehyde, *p*-hydroxybenzaldeyde, vanillic acid, catechin, caffeic, epicatechin, ferulic acid, and isoferulic acid) were purchased from Fluka. Other polyphenolic standards (tyrosol, syringic acid, and *p*-coumaric acid) were supplied by Eastman Kodak. Caftaric and coutaric acids were isolated according to the method described by Singleton et al. (*17*). Each compound was quantified by comparison with a calibration curve (absorbances at 320 nm for caftaric acid, *cis*- and *trans*-*p*-coutaric acids, fertaric acid, GRP, caffeic acid, *cis*- and *trans*-*p*-coumaric acids, isoferulic acid, and ferulic acid; absorbances at 280 nm for the rest polyphenols) obtained with the corresponding standard. GRP (2-*S*-glutathionylcaftaric acid) was quantified as caftaric acid and fertaric acid as ferulic acid.

Determination of the Volatile Profile. The volatile profiles were determined by gas chromatography in duplicate, using a prior stage of continuous rotary liquid−liquid extraction (*18*). The extraction was performed on 100 mL of wine diluted to 200 mL with distilled water. The mixture was saturated with NaCl, and 50 μL of the internal standard, 4-methyl-2-pentanol, was added. A mixture (2:1) of diethyl ether/*n*-pentane (total volume = 90 mL) was used as the organic extracting. The extraction time was 150 min (0.8 rpm). The organic phase, after drying for 15 min with anhydrous sodium sulfate, is concentrated in a Turbovap (Zymark, Hopkinton, MA) under a flow of nitrogen at room temperature to a final volume of 2 mL. Subsequently, it was subjected to GC using an HP 5890 series II gas chromatograph with flame ionization detection (FID). The injection volume was 1 μL, splitless, for 0.5 min. The column used was a J&W DB-Wax of 60 m and 0.25 mm internal diameter. Split flow was 30 mL min^{-1}, and purge flow was 1.5 mL min^{-1}. The carrier gas used was helium (column head pressure of 14 psi). The temperature of the detector during the analysis was 250 °C, whereas the injector was held at 200 °C. The temperature gradient used began at 45 °C for 20 min and was raised to 95 °C at a rate of 10 °C min^{-1}. After 1 min, it was increased to 130 °C (2 °C min^{-1}). This temperature was held for 1 min and then increased to 210 °C (1 °C min^{-1}) and held at this temperature for 20 min.

A voyager (Thermoquest) gas chromatograph with a mass detector (electronic impact and quadrupole) was used for the identification of the various signals obtained. The signal was recorded and processed with Masslab software supplied with the Wiley 6.0 MS library. Chromatography conditions were as before. Peak identification was carried out by analogy of mass spectra and confirmed by retention indices of standards. All of the volatile standards used in this study were supplied by Merck (Darmstadt, Germany). Quantitative data from the identified compounds were obtained by measuring the relative peak area in relation to that of 4-methyl-2-pentanol, the internal standard.

Spectrophotometric Measurements. A Unicam model PU8730 spectrophotometer was used to determine the absorbances at 420 nm of the wines during the course of the study; this is the wavelength typically used when the degree of browning undergone by a wine is measured. This same instrument was used to obtain the UV−vis absorption spectrum of each of the bottle glasses used in the study; this is the measurement by which we sought to determine the type of radiation that influenced the wine contained in each type of glass. For this latter determination, pieces of glass ~3 cm^2 were used, and measurements were taken between 200 and 1000 nm at 5 nm increments. All measurements were performed in triplicate.

Statistical Treatment. A multifactor analysis of the variance (MANOVA) was carried out on the replicated samples for each compound in relation to time and type of bottle. The compounds with a high dependence ($p < 0.01$) on some of the factors considered were subjected to a principal component analysis (PCA) on the replicated samples. The computer program used was the Statgraphics statistical computer package "Statgraphics Plus 5.0" for Windows 98.

Table 1. Means (Milligrams per Liter ± Standard Deviation) of Polyphenols: Multifactor Analysis of Variance

						p value		
polyphenolic compd	initial	bottle	10 days after	30 days after	45 days after	time	bottle	time–bottle
gallic acid	3.84 ± 0.123	transp	3.13 ± 0.325	nd	nd	0.0000[a]	0.6597	0.8184
		topaz	3.23 ± 0.220	0.81 ± 0.014	nd			
peak 1	0.96 ± 0.004	transp	0.95 ± 0.103	1.19 ± 0.013	1.34 ± 0.049	0.0010[a]	0.0743	0.0112
		topaz	0.97 ± 0.056	1.22 ± 0.107	1.11 ± 0.052			
protocatechuic acid	2.25 ± 0.101	transp	2.52 ± 0.201	1.74 ± 0.172	1.83 ± 0.072	0.0010[a]	0.0000[a]	0.0229
		topaz	2.87 ± 0.020	2.58 ± 0.209	2.67 ± 0.144			
protocatechualdehyde	nd	transp	nd	3.62 ± 0.183	4.45 ± 0.163	0.0000[a]	0.0000[a]	0.0000[a]
		topaz	nd	nd	nd			
tyrosol	34.64 ± 1.544	transp	34.59 ± 1.321	36.61 ± 1.678	36.45 ± 0.885	0.9335	0.1500	0.6262
		topaz	38.68 ± 5.145	37.40 ± 3.76	38.10 ± 2.86			
p-hydroxybenzaldehyde	0.38 ± 0.012	transp	0.75 ± 0.035	2.60 ± 0.073	3.17 ± 0.052	0.0000[a]	0.0000[a]	0.0000[a]
		topaz	0.75 ± 0.075	1.65 ± 0.043	1.67 ± 0.162			
vanillic acid	4.38 ± 0.567	transp	2.18 ± 0.594	nd	nd	0.0000[a]	0.0000[a]	0.2029
		topaz	3.95 ± 0.156	2.24 ± 0.455	2.44 ± 0.097			
syringic acid	0.67 ± 0.032	transp	0.53 ± 0.159	0.72 ± 0.193	0.92 ± 0.132	0.0032[a]	0.2183	0.7809
		topaz	0.67 ± 0.122	0.78 ± 0.077	0.96 ± 0.092			
caftaric acid	27.84 ± 1.672	transp	22.34 ± 1.546	4.26 ± 0.701	2.01 ± 0.224	0.0000[a]	0.0000[a]	0.0000[a]
		topaz	26.56 ± 0.309	20.68 ± 0.946	19.89 ± 2.416			
GRP[b]	4.23 ± 0.677	transp	3.27 ± 0.078	1.93 ± 0.236	1.36 ± 0.113	0.0000[a]	0.0000[a]	0.0048[a]
		topaz	3.80 ± 0.230	2.73 ± 0.346	2.87 ± 0.138			
cis-*p*-coutaric acid	4.42 ± 0.566	transp	3.53 ± 0.029	1.64 ± 0.063	1.30 ± 0.071	0.0000[a]	0.0000[a]	0.0001[a]
		topaz	4.03 ± 0.063	3.74 ± 0.453	3.86 ± 0.541			
trans-*p*-coutaric acid	5.01 ± 0.144	transp	6.30 ± 0.339	2.66 ± 0.15	1.86 ± 0.141	0.0000[a]	0.0000[a]	0.0000[a]
		topaz	6.66 ± 0.120	6.41 ± 0.621	6.57 ± 0.728			
fertaric acid	4.43 ± 0.232	transp	3.52 ± 0.223	0.95 ± 0.270	nd	0.0000[a]	0.0000[a]	0.0000[a]
		topaz	3.97 ± 0.076	4.06 ± 0.082	4.46 ± 0.169			
catechin	5.00 ± 0.033	transp	3.68 ± 0.123	2.67 ± 0.064	0.98 ± 0.023	0.0000[a]	0.0000[a]	0.0004[a]
		topaz	4.25 ± 0.234	3.87 ± 0.078	1.75 ± 0.100			
caffeic acid	2.87 ± 0.233	transp	2.62 ± 0.080	1.64 ± 0.108	1.19 ± 0.028	0.0000[a]	0.0000[a]	0.0024[a]
		topaz	2.84 ± 0.073	2.45 ± 0.252	2.25 ± 0.271			
cis-*p*-coumaric acid	0.94 ± 0.065	transp	0.98 ± 0.014	1.30 ± 0.000	1.28 ± 0.043	0.0000[a]	0.0000[a]	0.0007[a]
		topaz	0.95 ± 0.006	1.06 ± 0.063	1.07 ± 0.035			
trans-*p*-coumaric acid	1.30 ± 0.003	transp	1.40 ± 0.060	1.48 ± 0.039	1.40 ± 0.031	0.0018[a]	0.0004[a]	0.0028[a]
		topaz	1.35 ± 0.014	1.83 ± 0.282	2.06 ± 0.168			
epicatechin	3.78 ± 0.024	transp	2.68 ± 0.056	1.58 ± 0.009	0.35 ± 0.032	0.0000[a]	0.0000[a]	0.0012[a]
		topaz	3.23 ± 0.005	2.70 ± 0.045	1.56 ± 0.017			
isoferulic acid	0.87 ± 0.021	transp	0.90 ± 0.096	0.84 ± 0.036	0.58 ± 0.066	0.1604	0.0000[a]	0.0002[a]
		topaz	0.88 ± 0.073	1.22 ± 0.223	1.41 ± 0.130			
ferulic acid	0.88 ± 0.032	transp	0.83 ± 0.034	0.58 ± 0.024	0.55 ± 0.017	0.2338	0.0001[a]	0.0000[a]
		topaz	0.90 ± 0.018	1.02 ± 0.125	1.15 ± 0.081			
color (abs 420 nm)	0.093 ± 0.0000	transp	0.111 ± 0.0214	0.134 ± 0.0106	0.288 ± 0.0460	0.0000[a]	0.0001[a]	0.0006[a]
		topaz	0.104 ± 0.0035	0.251 ± 0.018	0.655 ± 0.1379			

[a] Values are significant at $p < 0.01$. [b] GRP = 2-*S*-glutathionylcaftaric acid.

RESULTS AND DISCUSSION

This paper focuses on the chemical changes that take place in the composition of polyphenolic and volatile compounds in a fino sherry wine during oxidative storage under UV−vis radiation, to establish the general pattern of changes and to study if the use of a particular glass (with low values of transmittance in the UV−visible range) could protect the wine from this phenomenon.

With a view to finding significant differences between the initial wine and that subjected to various periods of influence of UV−vis radiation, the values of absorbance at 420 nm and the concentrations of the various polyphenolic and volatile compounds studied were submitted to variance analysis. In this case, the factors considered were time and type of bottle used, so a two-way variance analysis was carried out. Results are given in **Tables 1** and **2**.

Evolution of the Color. In relation to the evolution of the color (absorbances at 420 nm), both factors had a significant influence on this, with a greater increase for the wine contained in topaz bottles in line with the increasing time. This fact cannot be explained, taking into account that this wine presented a lower loss in its polyphenolic content (**Table 1**).

With the aim of trying to establish a certain relationship between the incidence of radiation on the wine contained in bottles and the degree of browning suffered, the next step was to determine the transmittance in the UV−visible range presented by the two types of glass. The results obtained are shown in **Figure 1**.

A much lower transmittance value in the UV−visible range was observed for the topaz than for the transparent glass. The greatest differences between the two glasses were located in the UV range (**Figure 1**). Despite this fact, the wine contained in topaz bottles suffered lower decreases in polyphenolic content but a more marked evolution in the color (abs 420 nm).

Polyphenolic Compounds. It can be observed that both factors (time and type of bottle) have a statistically significant effect on most polyphenolic compounds (**Table 1**).

It is observed that there was an increase of one compound that could not be identified (marked as peak 1) and that presented a maximum UV−vis absorption at 285 nm. This increase was generally in proportion to the length of time the bottled wine was kept under the UV−vis radiation. Mayén et al. (*15*) found an increase in a certain compound with similar analytical characteristics in white wines subjected to an accelerated process of browning (temperature of 50 °C for 3 months). Basing our reasoning on the fact that the content of this compound increased in line with the increasing browning,

Table 2. Means (Relative Peak Area ± Standard Deviation) of Volatile Compounds: Multifactor Analysis of Variance

						p value		
aroma compd	initial	bottle	10 days after	30 days after	45 days after	time	bottle	time–bottle
acids and esters								
ethyl lactate	0.02 ± 0.005	transp	0.04 ± 0.021	0.07 ± 0.006	0.08 ± 0.018	0.0006[a]	0.0008[a]	0.0219
		topaz	0.03 ± 0.012	0.04 ± 0.014	0.03 ± 0.007			
ethyl octanoate	1.88 ± 0.392	transp	1.97 ± 0.681	2.90 ± 0.309	3.33 ± 0.622	0.0235	0.7440	0.0825
		topaz	2.86 ± 0.532	2.55 ± 1.150	2.97 ± 0.292			
ethyl succinate	0.30 ± 0.043	transp	0.28 ± 0.074	0.40 ± 0.048	0.39 ± 0.044	0.0251	0.5925	0.0483
		topaz	0.40 ± 0.070	0.42 ± 0.082	0.38 ± 0.038			
phenylethyl acetate	0.23 ± 0.034	transp	0.19 ± 0.049	0.22 ± 0.031	0.19 ± 0.029	0.2404	0.1832	0.2263
		topaz	0.26 ± 0.051	0.26 ± 0.050	0.22 ± 0.024			
isovaleric acid	0.07 ± 0.001	transp	0.12 ± 0.027	0.14 ± 0.024	0.16 ± 0.029	0.0055[a]	0.8239	0.5860
		topaz	0.14 ± 0.036	0.14 ± 0.027	0.15 ± 0.022			
acetic acid	1.52 ± 0.224	transp	2.24 ± 1.377	2.04 ± 0.304	1.50 ± 0.187	0.0450	0.6406	0.9865
		topaz	2.11 ± 0.410	2.04 ± 0.429	1.44 ± 0.162			
hexanoic acid	0.29 ± 0.051	transp	0.31 ± 0.054	0.35 ± 0.056	0.28 ± 0.042	0.0022[a]	0.7896	0.0673
		topaz	0.41 ± 0.085	0.36 ± 0.075	0.26 ± 0.023			
octanoic acid	0.11 ± 0.085	transp	0.06 ± 0.028	0.22 ± 0.040	0.11 ± 0.062	0.0000[a]	0.9405	0.0089[a]
		topaz	0.04 ± 0.022	0.26 ± 0.038	0.19 ± 0.029			
decanoic acid	0.05 ± 0.009	transp	0.04 ± 0.021	0.12 ± 0.021	0.11 ± 0.021	0.0000[a]	0.0517	0.6985
		topaz	0.07 ± 0.015	0.13 ± 0.027	0.12 ± 0.008			
alcohols								
n-propanol	0.78 ± 0.177	transp	1.39 ± 0.131	0.98 ± 0.125	0.83 ± 0.205	0.0000[a]	0.9427	0.4092
		topaz	1.59 ± 0.31	1.03 ± 0.183	0.85 ± 0.129			
2-methyl-1-propanol	4.38 ± 0.596	transp	5.58 ± 0.790	4.02 ± 0.180	3.19 ± 0.340	0.0000[a]	0.8111	0.2904
		topaz	6.13 ± 0.811	4.06 ± 0.329	3.23 ± 0.252			
butanol	0.23 ± 0.025	transp	0.27 ± 0.058	0.23 ± 0.010	0.20 ± 0.021	0.0000[a]	0.6870	0.3880
		topaz	0.29 ± 0.045	0.23 ± 0.023	0.19 ± 0.015			
2-methyl-1-butanol	45.11 ± 4.875	transp	45.68 ± 5.002	34.44 ± 16.383	24.42 ± 10.381	0.0000[a]	0.9412	0.8796
		topaz	50.42 ± 5.915	36.69 ± 3.025	25.59 ± 11.306			
isoamyl alcohol	0.31 ± 0.044	transp	0.21 ± 0.166	0.29 ± 0.028	0.35 ± 0.027	0.0025[a]	0.0017[a]	0.0009[a]
		topaz	0.34 ± 0.038	0.24 ± 0.038	0.24 ± 0.013			
n-hexanol	0.32 ± 0.020	transp	0.34 ± 0.11	0.23 ± 0.013	0.19 ± 0.014	0.0000[a]	0.5819	0.8579
		topaz	0.32 ± 0.04	0.23 ± 0.020	0.19 ± 0.011			
2,3-butanediol	0.23 ± 0.030	transp	0.68 ± 0.257	0.84 ± 0.089	0.83 ± 0.132	0.0001[a]	0.9451	0.7742
		topaz	0.74 ± 0.137	0.86 ± 0.153	0.76 ± 0.054			
3,4-dimethylpentanol	0.31 ± 0.034	transp	0.28 ± 0.10	0.61 ± 0.082	0.77 ± 0.093	0.0000[a]	0.5596	0.2325
		topaz	0.35 ± 0.061	0.59 ± 0.125	0.69 ± 0.040			
benzyl alcohol	0.36 ± 0.067	transp	0.32 ± 0.067	0.49 ± 0.069	0.52 ± 0.063	0.0001[a]	0.9000	0.2122
		topaz	0.41 ± 0.074	0.53 ± 0.108	0.50 ± 0.030			
phenylethanol	12.61 ± 8.200	transp	14.08 ± 2.628	22.64 ± 3.352	23.50 ± 2.858	0.0000[a]	0.3500	0.0228
		topaz	18.72 ± 3.55	24.41 ± 5.204	23.16 ± 1.456			
4-ethylguaiacol	0.03 ± 0.010	transp	0.02 ± 0.009	0.05 ± 0.005	0.04 ± 0.006	0.0000[a]	0.8100	0.2281
		topaz	0.03 ± 0.004	0.05 ± 0.008	0.05 ± 0.002			
4-ethylphenol	0.06 ± 0.027	transp	0.03 ± 0.018	0.09 ± 0.023	0.09 ± 0.022	0.0000[a]	0.6217	0.1653
		topaz	0.06 ± 0.011	0.11 ± 0.023	0.10 ± 0.007			
aldehydes and ketones								
acetoin	0.05 ± 0.008	transp	0.04 ± 0.020	0.05 ± 0.005	0.05 ± 0.005	0.9484	0.2422	0.2700
		topaz	0.05 ± 0.008	0.05 ± 0.007	0.04 ± 0.003			
furancarboxaldehyde	0.04 ± 0.001	transp	0.06 ± 0.032	0.10 ± 0.018	0.14 ± 0.016	0.0000[a]	0.0008[a]	0.0021[a]
		topaz	0.06 ± 0.020	0.06 ± 0.010	0.07 ± 0.015			
benzaldehyde	0.77 ± 0.156	transp	2.03 ± 0.898	2.65 ± 0.269	1.95 ± 0.505	0.0001[a]	0.4952	0.5471
		topaz	2.60 ± 0.499	2.92 ± 0.472	1.96 ± 0.209			

[a] Values are significant at $p < 0.01$

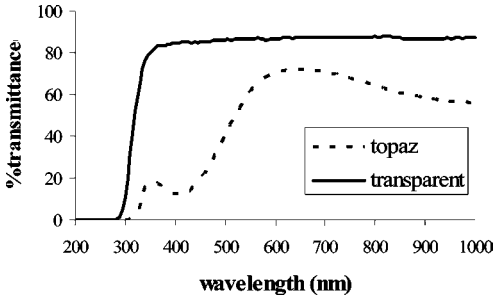

Figure 1. UV–visible spectra of glasses used in this study.

we could assumed that this is a compound produced by the oxidation, possibly a hydroquinone.

All wines showed losses in several polyphenolic compounds (gallic acid, vanillic acid, caftaric acid, GRP, *cis*- and *trans*-*p*-coutaric acids, catechin, fertaric acid, epicatechin, caffeic acid, etc.), which were more severe for the wines bottled in transparent glasses. For these samples, significant increases in protocatechualdehyde and *p*-hydroxybenzaldehyde have been obtained.

This finding is in agreement with the evolution observed for the standard solutions of these polyphenolic compounds contained in transparent and topaz glass bottles that were kept under the same environmental conditions (25 °C and UV−vis radiation) and sampled after 10, 30, and 45 days. In this case, again, larger decreases were clearly observed for the solutions contained in transparent bottles. In these, certain polyphenolic compounds such as caffeic acid, *p*-coumaric acid, ferulic acid, isoferulic acid, catechin, and epicatechin disappeared after 10 days under the climatic conditions considered. An important

increase in the *p*-hydroxybenzaldehyde content was also observed for this type of glass bottle.

Most of the compounds cited have been previously shown to present a marked tendency toward oxidation (*1*, *12*).

With respect to the time−glass type interaction, this also appears to produce significant effects on the color of the wines and several phenolic compounds, with larger decreases for the wine contained in transparent bottles as the time factor increases.

This could be evidence that, in order for UV−vis radiation to act as effective catalyzer of the oxidation of the polyphenolic content, a certain period of time is needed.

The increases observed for various polyphenolic compounds could be explained on the basis of oxidation reactions facilitated by the UV−vis radiation, taking into account that these increases were higher for wine contained in transparent bottles.

It could be deduced from these results that, under the influence of an excess of UV−vis radiation, polyphenolic compounds take part in reactions that compete with the polymerization and condensation reactions that characterize the process of the visual browning. Fabios et al. (*19*) found that the oxidative disappearance of catechin in a model solution containing flor yeasts resulted in an increase of compounds that absorbed in the UV region and did not darken the solution. Their explanation for this fact was that the catechin degradation pathway could be altered by the presence of flor yeasts. Other findings, such as the reduced production of CO_2 per unit of O_2 consumed in oxidation reactions occurring in the presence of light (*12*), suggest that under the influence of this agent, these reactions compete with others also stimulated by the incidence of this one. Further research in this direction is needed for a safe assertion.

On the other hand, from the results obtained, it can be seen that the glass with protection against UV−vis radiation employed in this study (topaz glass) was not able to impede the visual browning of the wine.

Volatile Compounds. Table 2 shows the relative areas (compound area/internal standard area) found for the volatile compounds studied and the statistical significance of each factor on them.

The data obtained clearly reveal that the great majority of compounds were affected by the time factor, whereas only a few compounds were affected by the type of glass.

Esters and Acids. In the case of the esters present, all increase during storage under the influence of UV−vis radiation. These results are not surprising and can be explained on the basis of their hydrolysis−esterification equilibria. Other authors have reported these increases in wines stored under oxygen (*7*, *20*).

Isovaleric acid, octanoic acid, and decanoic acid showed a tendency to increase. It is generally accepted that fatty acids increase during the maturation of alcoholic beverages (*21*, *22*).

Acetic acid and hexanoic acid did not change significantly during the experiment. This fact had already been observed by other authors in wines stored in darkness and under the influence of oxygen (*7*).

Alcohols. All of these compounds were strongly affected by the time factor. In general, a tendency to increase is observed, with the exception of 2-methyl-1-butanol, hexanol, and 2-methyl-1-propanol. Ethylphenols (4-ethylphenol and 4-ethylguaiacol) are responsible for animal and smoky odors (*23*). In our case, these compounds appear in concentrations below their sensory thresholds.

Alcohols were not affected by their oxidation to aldehydes. Ferreira et al. (*7*) explained the increases in the concentrations of some alcohols in wines stored under oxygen on the basis of the degradation of some precursors present in the wine, following a process similar to that of oxidative aging in wood.

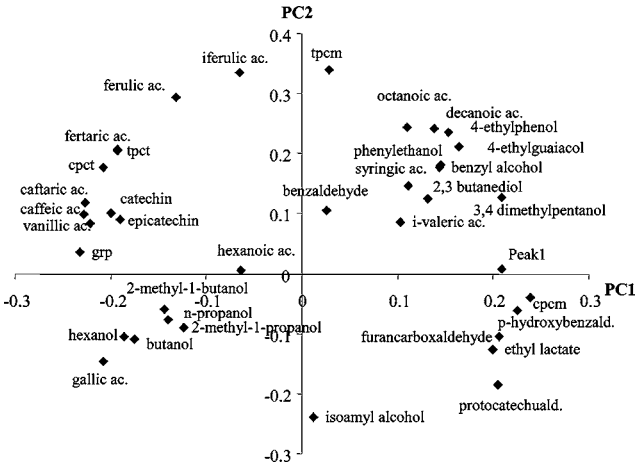

Figure 2. Projection of polyphenols and volatile compounds on the first and second principal components.

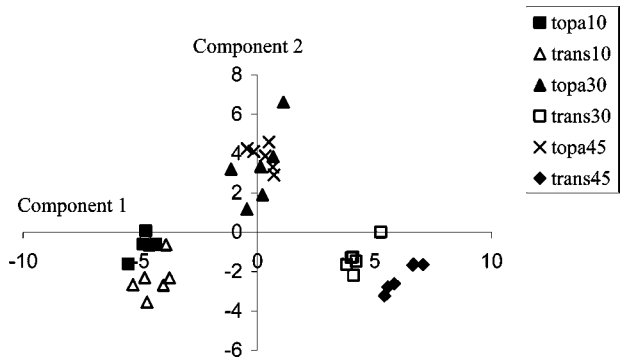

Figure 3. Score plot of the studied samples on the first and second principal components.

Aldehydes and Ketones. The furancarboxaldehyde and benzaldehyde concentrations increased during the oxidation process. Furfural is derived from carbohydrate dehydration followed by cyclation in Maillard-type systems (*24*), whereas the formation of benzaldehyde is attributed to phenylalanine oxidation (*25*).

The concentration of acetoin was not affected during the oxidation process.

Principal Component Analysis (PCA). To observe more clearly the main contribution of the various volatile and polyphenolic compounds during the experiment, the compounds that depended on some of the two experimental variables (time and type of bottle) at $p < 0.01$ were subjected to PCA.

When the data matrix was subjected to PCA, five significant PCs arose according to Kraiser's criterion (eingenvalues > 1). With these factors, 91.44% of total variance is explained. The first PC, PC1, which explains 48.97% of total variance, mainly contains caftaric acid, GRP, caffeic acid, vanillic acid, *cis*-*p*-coumaric acid, *cis*- and *trans*-*p*-coutaric acids, gallic acid, catechin, epicatechin, peak 1, *p*-hydroxybenzaldehyde, ethyl lactate, *n*-hexanol, furancarboxaldehyde, and 3,4-dimethylpentanol (**Figure 2**). Most of these compounds are influenced by the process of oxidation (*1*, *6*, *7*, *15*, *19*, *20*). The second PC, PC2, which explains 20.31% of total variance, was preferentially constituted by *trans*-*p*-coumaric acid, isoamyl alcohol, isoferulic acid, octanoic acid, decanoic acid, and 4-ethylphenol (**Figure 2**).

Figure 3 shows the score plot for the wines considered in this study obtained by selecting the first two PCs as axes. As

can be seen, the first component (PC1) separates the samples into three groups: wines contained in transparent bottles after 30 and 45 days under the influence of UV−vis radiation (trans30 and trans45); wines contained in topaz bottles after 30 and 45 days under the influence of UV−vis radiation (topa30 and topa45); and wines contained in transparent and topaz bottles after 10 days under the fixed climatic conditions. PC2 does not show any structure relationship.

This distribution would corroborate the conclusion that, for short periods of time, the type of glass employed does not determine the changes in the polyphenolic and volatile content of the wine.

From the results obtained, it can be seen that fino sherry wine oxidation facilitated by UV−visible radiation involves significant changes in its volatile and polyphenolic content. An excess of UV−vis radiation, that is, in transparent glass bottles, provokes greater decreases in several polyphenolic compounds, but these do not produce a higher visual browning (abs 420 nm). Regarding volatile compounds, significant changes in wine volatile compounds have been observed during this study, but for these compounds, the type of glass employed does not have a statistically significant effect on them.

ABBREVIATIONS USED

UV, ultraviolet; vis, visible; DAD, diode array detector; GRP, 2-*S*-glutathionylcaftaric acid; MANOVA, multivariate analysis of variance; PCA, principal component analysis; PC, principal component; GC, gas chromatography.

LITERATURE CITED

(1) Macheix, J. J.; Sapis, J. C.; Fleuriet, A. Phenolic compounds and polyphenol oxidase in relation to browning in grapes and wines. *Crit. Rev. Food Sci. Nutr.* **1991**, *30*, 441−486.

(2) Nicolas, J.; Cheynier, V.; Fleuriet, A.; Rouet-Mayer, M. A. Polyphenols and enzymatic browning. *Polyphenolic Phenomena*; Scarlbert, A., Ed.; INRA: Paris, France, 1993.

(3) Escudero, A.; Cacho, J.; Ferreira, V. Isolation and identification of odorants generated in wine during its oxidation: a gas chromatography−olfatometric study. *Eur. Food Res. Technol.* **2000**, *211*, 105−110.

(4) Baro, A. L. J.; Quirós, J. A. Les conditions de formation des aldéhydes dans les vins. Relation et importance en rapport avec les phénomenes d'oxydation et les caractéristiques organoleptiques. *Bull. OIV* **1977**, *50*, 253−267.

(5) Meirland, S.; Pernot, N. *Les Phénomènes d'Oxydation et de Réduction en Vinification*; Comité Interprofessional du Vin de Champagne: Epernay, France, 1992.

(6) Escudero, A.; Asensio, E.; Cacho, J.; Ferreira, V. Sensory and chemical changes of young white wines stored under oxygen. An assessment of the role played by aldehydes and some other important odorants. *Food Chem.* **2002**, *77*, 325−331.

(7) Ferreira, V.; Escudero, A.; Fernández, P.; Cacho, J. F. Changes in the profile of volatile compounds in wines stored under oxygen, and their relationship with the browning process. *Z. Lebensm. Unters. Forsch. A* **1997**, *205*, 392−396.

(8) 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.; University of Cadiz Press: Cadiz, Spain, 1985; pp 333−361 (1).

(9) Gai, C. Imbottigliamento a bassa dei vini di qualita. *Ind. Bevande* **1989**, *18*, 278−282.

(10) Prass, G.; Virgo, J. Observations on the influence of inert gases on wine quality. *Food Technol. Aust.* **1976**, *28*, 475−477.

(11) Berg, H. W.; Akiyoghi, M. Some factors involved in browning of white wines. *Am. J. Enol. Vitic.* **1956**, *7*, 1−7.

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

(13) Mattivi, F.; Monetti, A.; Vrhovsek, U.; Andrés-Lacueva, C. High-performance liquid chromatographic determination of the riboflavin concentration in white wines for predicting their resistance to light. *J. Chromatogr. A* **2000**, *888*, 121−127.

(14) Andrés-Lacueva, C.; Mattivi, F.; Tonon, D. Determination of riboflavin, flavin mononucleotide and flavin-adenine dinucleotide in wine and other beverages by high-performance liquid chromatography with fluorescence detection. *J. Chromatogr. A* **1998**, *823*, 355−363.

(15) Mayén, M.; Barón, R.; Mérida, J.; Medina, M. Changes in phenolic compounds during accelerated browning in white wines from *cv.* Pedro Ximenez and *cv.* Baladi grapes. *Food Chem.* **1997**, *58*, 89−95.

(16) Benitez F. J.; Beltran-Heredia, J.; Acero, J. L.; Pinilla, M. L. Simultaneous photodegradation and ozonation plus UV radiation of phenolic acids-major pollutants in agro-industrial wastewaters. *J. Chem. Technol. Biotechnol.* **1997**, *70*, 253−260.

(17) Singleton, V. L.; Timberlake, C. F.; Lea, A. G. H. The phenolic cinnamates of white grapes and wine. *J. Sci. Food Agric.* **1978**, *29*, 403−410.

(18) Bru, E.; Barroso, C. G.; Cela, R.; Pérez-Bustamente, J. A. Development of a rotatory and continuous liquid−liquid extraction technique for phenolic compounds in wine. *Analyst* **1996**, *121*, 297−302.

(19) Fabios, M.; Lopez-Toledano, A.; Mayen, M.; Merida, J.; Medina, M. Phenolic compounds and browning in sherry wines subjected to oxidative and biological aging. *J. Agric. Food Chem.* **2000**, *48*, 2155−2159.

(20) Ramey, D. D.; Ough, C. S. Volatile ester hydrolysis or formation during storage of model solutions and wines. *J. Agric. Food Chem.* **1980**, *28*, 928−934.

(21) Nykanen, L. Formation and occurrence of flavor compounds in wine and distilled alcoholic beverages. *Am. J. Enol. Vitic.* **1986**, *37*, 84−96.

(22) Puech, J. L.; Leauté, R.; Clot, G.; Nomdedeu, L.; Mondiés, H. Evolution of volatile and phenolic constituents of cognac during aging. *Sci. Aliments* **1984**, *4*, 65−80.

(23) Chatonnet, P.; Boidron, J. N.; Pons, M. Maturation of red wines on oak barrels−evolution of some volatile compounds and their aromatic impact. *Sci. Aliments* **1990**, *10*, 565−587.

(24) Boidron, J. N.; Chatonnet, P.; Pons, M. Influence du bois sur certaines substances odorants des vins. *Connaiss. Vigne Vin* **1988**, *22*, 275−294.

(25) Loyaux, D.; Roger, S.; Adda, J. The evolution of champagne volatiles during aging. *J. Sci. Food Agric.* **1981**, *32*, 1254−1258.

Received for review March 26, 2003. Revised manuscript received July 31, 2003. Accepted August 3, 2003.

JF030223J