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Interpretation of Color Variables during the Aging of Red Wines: Relationship with Families of Phenolic Compounds

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The two different methods of color measurement proposed by Glories and Gonzáles were applied to different red wines aged in the wood ("crianza" aging) and in the bottle for 11 months, and the color of variables of the two methods were compared. Brightness could only be measured using the latter method. Relationships between the color variables and certain families of phenolic compounds were established.

Keywords: *Color; wine; aging; oak; phenolic compounds*

INTRODUCTION

Wine is a complex system capable of undergoing many different changes during storage. The series of alterations that takes place goes by the name aging. The sensory parameters altered during aging include color, which tends to lose vividness. Phenolic compounds are the main agents responsible for color changes in wines, in particular anthocyanins in red wines; these compounds undergo different oxidation, condensation, and polymerization reactions usually resulting in changes from bluish tones to orange tones. Such alterations are more intense during oxidative aging (in wood) than during aging in the bottle (a reducing medium). The influence of these alterations on the quality and economic value of wines is undeniable, hence the considerable interest in gaining an understanding of the processes involved.

There is also great interest in achieving exact, specific, and practical measurements of color. Traditionally, the color of wine has been measured using the method of Sudraud (1958) and the tristimulus method of the CIE. In 1984 Glories made certain modifications to the method of Sudraud that provided greater information on the color of wines. Negueruela and Echavarri (1988) put forward a wavelength-based method following the proposals made by Glories in which the tristimulus values are calculated taking into account changes in the illuminant and in the angle of observation. Gonzáles (1990) put forward an automatic data collection and processing technique based on the CIE method that uses 40 spectral measurements, yielding a more precise definition of color than the OIV method, which uses only four. Escolar *et al.* (1992) proposed a method based on a similar number of spectral measurements which was also more precise than the OIV method.

Although automated methods like the two last-mentioned methods using spectrophotometers equipped with data processors have greatly facilitated application of the tristimulus method, on the whole their results are difficult to interpret in practice. Simpler methods are easier to interpret but less exact.

The present study examined color changes in red wines during aging in the wood and in the bottle, employing the color variables of the methods of Glories and Gonzáles and establishing relationships between the variables, and between the variables and changes in the families of phenolic compounds. The two methods can be used to complement each other, not only facilitating the detection of color changes but also helping to establish the relationships between the different color variables and the chemical composition of wine.

MATERIALS AND METHODS

The samples used in the present study were red wines made from *Vitis vinifera* L. cv. Tinto del País from nine wineries participating in the Ribera de Duero Appellation of Origin program. The wines from this region of northwestern Spain are very popular in international markets and are aged for

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Table 1. Correlation Levels between Chromatic Variables of Method A[a]

	%Rd	%Bl	dA%	*I*	To
%Ye	−0.738***	−0.334**	−0.742***	−0.612***	0.698***
%Rd			0.981***		−0.593***
%Bl				0.606***	
dA%					−0.615***

[a] Significance level $p < 0.01$ (**) and $p < 0.001$ (***).

eight months in the American red oak (i.e., "crianza" aging of less than one year) and three months in the bottle.

Samples were taken monthly: six samples were taken at each of the wineries during oxidative aging and two samples during aging in the bottle. The first sample was assigned time zero and was taken when the casks were first filled with the wine. Two replications of each sample were collected at each winery, and two measurements of each variable were likewise taken, yielding a total of four analytical values per variable, sample, and winery.

The variables considered were as follows:

Color Variables of Glories (1984), Method A. A directed measurement of wine absorbance to 420, 520, and 620 nm was carried out in a DU 70 Beckman spectrophotometer, with a 1 mm quartz cell.

The following variables were then calculated: color intensity (*I*), tone (To), proportion of red (%Rd), proportion of blue (%Bl), proportion of yellow (%Ye), and a variable responsible for the proportion of red produced by the flavilium cations of the free and bound anthocyanins (dA%).

Color Variables of Gonzáles (1990), Method B. Spectral wine absorbances between 380−770 nm were measured with 1 mm quartz cell in the spectrophotometer cited above. The data were transfered to a personal computer where they were processed according to Gonzáles automated program.

The following variables were calculated: intensity (IG), tone (ToG), brightness (Br), dominant wavelength (DW), and purity (Pu).

Families of Phenolic Compounds. Total polyphenols (TP), high polymeric polyphenols (HPP), *o*-diphenols (OD), catechins (CAT), and total anthocyanins (TA), were assayed according to the traditional methods set out in Paronetto (1977).

TP were analyzed using Folin−Ciocalteu reagent (Folin and Ciocalteu, 1927); HPP were calculated by difference between TP and low-polymeric polyphenols according to the method of Masquelier *et al.* (1965); OD, by the method of Flanzy and Aubert (1969); CAT, by the method of Swain and Hillis (1959); and TA, by means of color changes according to the pH of the medium, Paronetto (1977).

Phenolic compounds were measured directly in wine without any previous treatment.

Statistical treatment was applied to the analytical results, and correlation matrices were calculated to establish the relationships between the variables considered. Program BMDP4M of the integrated BMDP88 package was employed.

RESULTS

Interpretation of Color Variables and Their Relationships. Table 1 presents the relationships between the color variable values calculated according to method A and shows that the proportion of yellow was inversely related to the proportion of red and dA% (pure red) and directly related to tone, which expressed the increase in the yellow component. The inverse relationship with intensity is not so readily explained, particularly since intensity was positively correlated with the proportion of blue. The proportion of red and pure red were highly correlated and inversely correlated with tone, as would be expected.

Table 2 presents the same information for the color variables calculated according to method B and shows a high inverse correlation between brightness and the rest of the variables, which can be considered normal, except in the case of the intensity.

Table 2. Correlation Levels between Chromatic Variables of Method B[a]

	Pu	DW	IG	TG
Br	−0.846***	−0.806***	−0.887***	−0.609***
Pu		0.784***	0.867***	0.552***
DW			0.924***	0.752***
IG				0.778***

[a] Significance level $p < 0.01$ (**) and $p < 0.001$ (***).

Table 3. Correlation Levels between Chromatic Variables of Methods A and B

	Br	Pu	DW	IG	TG
%Ye	0.555***	−0.486***	−0.755***	−0.657***	−0.902***
%Rd					0.698***
%Bl	−0.711***	0.550***	0.618***	0.584***	
dA%					0.692***
To			−0.414***	−0.360**	−0.635***
I	−0.857***	0.851***	0.909***	0.985***	0.745***

[a] Significance level $p < 0.01$ (**) and $p < 0.001$ (***).

Purity was closely correlated with the dominant wavelength and with intensity and less closely correlated with tone. This suggests that saturation of a color is somehow related to color modifiers as DW, and then purity provides a numeric expression of it.

The dominant wavelength was correlated most closely with intensity and to a lesser extent with tone. Tone was correlated with intensity, which was not the case when method A was employed.

Table 3 gives the correlation values for the variables defined by both methods.

Brightness was positively correlated with the proportion of yellow and negatively correlated with the proportion of blue and intensity, indicating that violet tones increased wine opacity and hence the intensity of the color of the wine (actually, the sum of the absorbances).

Purity, or saturation, was negatively related to the proportion of yellow and positively related to the proportion of blue and intensity, indicating that the higher wavelengths were associated with higher levels of color saturation and thus were closer to the spectral lines for the respective colors.

The dominant wavelength was highly correlated with intensity and exhibited a lower, negative correlation with tone, which itself expresses the change toward the yellow. This is further borne out by the correlation between DW and the proportion of yellow. DW was positively correlated with the proportion of blue, a characteristic hue in these wines. The dominant wavelength displayed no correlation with the proportion of red and pure red, an interesting finding for red wines, which confirms what has already been said above.

The negative relationship between tone in method B and the proportion of yellow and tone in method A can be readily explained by the fact that both these variables reflected changes in the proportions of red and yellow. This was corroborated by the positive relationship of tone with both the proportion of red (%Rd) and pure red (dA%).

Changes in the Color Variables. Figure 1 depicts changes in the color variables defined by Glories for two of the wineries where samples were taken.

The behavior of the sets of variables considered was quite similar at all the wineries, and for that reason the results for only two wineries, 1 and 3, have been presented for each method, to reduce the number of

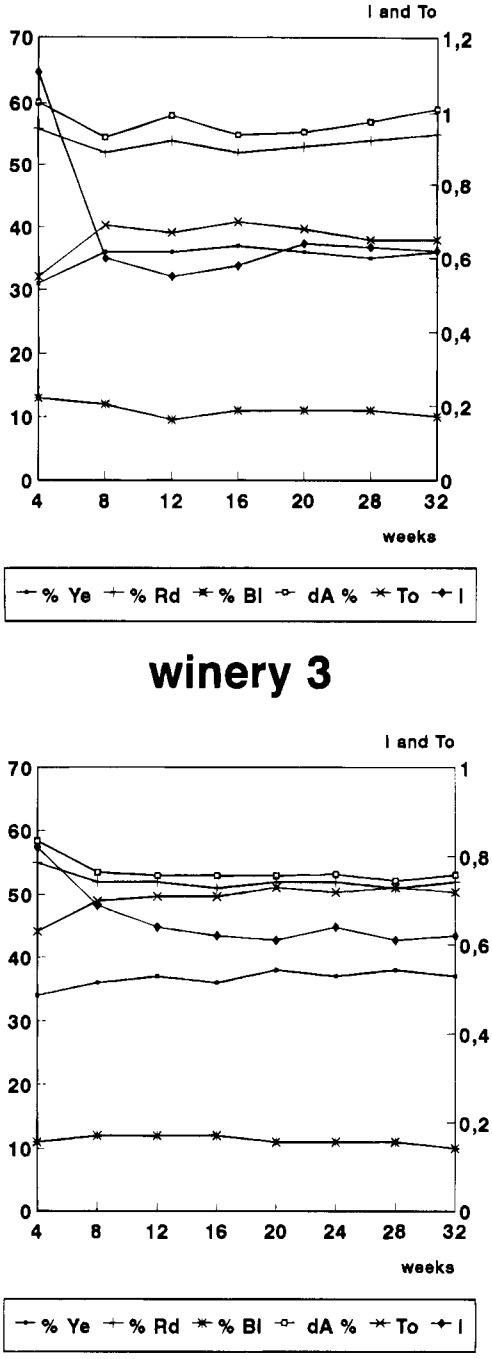

Figure 1. Changes in the color variables defined by method A (Glories, 1984) for wineries 1 and 3, during aging of wine: Percentage of yellow (%Ye), red (%Rd) and blue (%Bl); *I*, color intensity; To, tone; dA%.

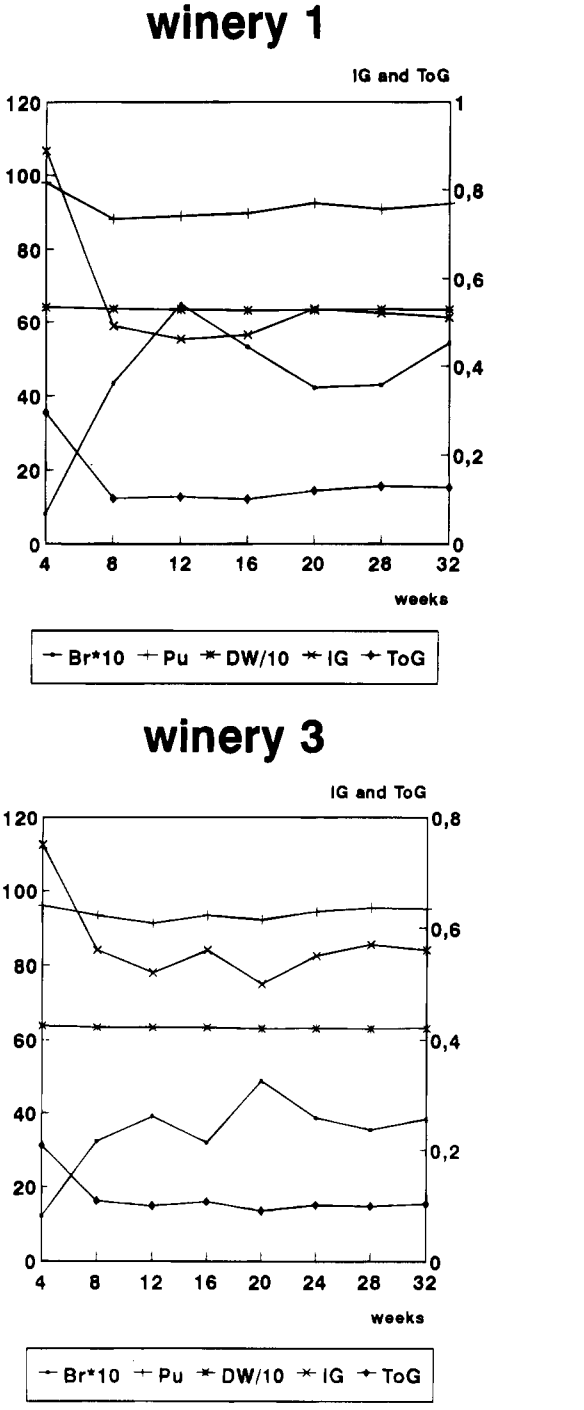

Figure 2. Changes in the color variables defined by method B (Gonzáles, 1990) for wineries 1 and 3, during aging of wines: Br, brightness values multiplied by 10, Pu, purity; DW, dominant wavelength values divided by 10; IG, color intensity; ToG, tone.

figures needed to provide plots of all the measurements collected (9 wineries × 3 sets of variables = 27 figures).

Color intensity fell rapidly during the first stage of aging and then leveled off. In contrast, tone increased along with the proportion of yellow. These results were concomitant with a decrease in the red component, a drop in absorbance at 520 nm that resulted in an increase in the value for tone, which is the quotient for absorbance at 420 nm/520 nm. These results would have been as expected and consistent with normal results, in view of the oxidative aging in the wood, except for the fact that the values for tone leveled off after the first months and for the constant value of the blue component throughout the study period.

Figure 2 depicts the changes in the color variables defined by Gonzáles for the same two wineries.

The two methods of measuring color provide very similar information with respect to certain variables. The changes in color intensity were entirely comparable in both cases and displayed a distinct drop in values during the first stage of aging. The results for tone would, on cursory examination, appear to be converse, depending upon the method used, with tone expressing the increase in yellow in method A and the loss of red in method B, and hence, although the plots follow opposing trends, they in fact furnish the same information.

Purity, underwent a slight decline during the first stage of aging, associated with the loss in color intensity. Together purity and the dominant wavelength, with

which it exhibited good correlation, defined the chromaticity of the sample.

The dominant wavelength remained constant over the study period, attaining values of between 630 and 640 nm, characteristic for young wines. This variable provided information similar to that furnished by the proportion of blue in method A, with which it was closely correlated. Together these variables were highly characteristic and distinctive for the wines considered. The constant values for both these variables were an objective indication of the constant presence of purple and/or violet tones in these wines despite the aging process.

Brightness, a parameter that is undefined in method A, representing the wine transparency, followed an increasing trend over the aging period. Initially there was a marked rise which varied in duration according to the winery concerned but which in no case exceeded four months. Following the rise values stabilized, with minor fluctuations.

Brightness provides information on the clarity and appearance of wines, and for that reason monitoring this variable is essential, since it has a direct influence on the quality and acceptability of the final product.

Changes in the Families of Phenolic Compounds. On the whole the levels of all the families were similar in all the wineries sampled, and behavior patterns were also nearly the same.

Figure 3 plots the trends in the families of phenolic compounds during aging. The figure shows that the anthocyanins decreased slightly over aging. Thus, these compounds took part in condensation and polymerization reactions, yet no sizeable variations in overall levels were observed, and this family of compounds did not lose its ability to impart the characteristic color to the medium.

The concentrations of catechins and *o*-diphenols also declined. The decline was much more pronounced in the case of the *o*-diphenols, particularly in the early stages of aging. These compounds are ideal substrates for oxidation and condensation reactions, giving rise to the appearance of brown polymers. The *o*-diphenols and the highly polymerized polyphenols were the families that underwent the greatest variations among wineries.

The trends in the total polyphenols, which remained more or less constant, and in the highly polymerized polyphenols showed that condensation reactions took place slowly and that high molecular weight polymers did not form during the aging period studied, since precipitation of such polymers would have led to a decrease in the total polyphenol values.

Correlations between Color Variables and Families of Phenolic Compounds. Table 4 gives the significant correlations established between the color variables and the families of phenolic compounds.

The correlation matrix showed that catechins were positively correlated with the yellow component (%Ye) and negatively correlated with violet tone (DW) and purity.

The associations between anthocyanins and the parameters listed in the table confirm that the anthocyanins retained their coloring ability, i.e., that they were not condensed or were condensed to such a low extent that they retained their copigmentation ability and the violet tones characteristic of monomers.

The positive correlation of the highly polymerized polyphenols with the blue component and the dominant wavelength and the negative correlation with the yellow component substantiated the special color of these

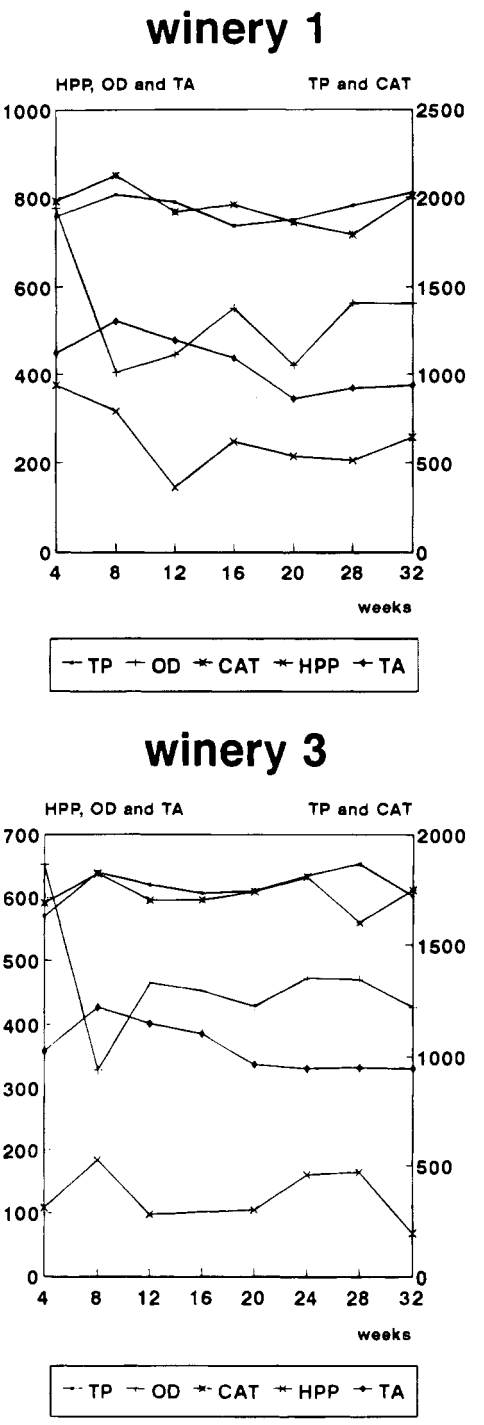

Figure 3. Changes in the families of phenolic compounds during aging for wineries 1 and 3: HPP, high polymeric polyphenols and, TP, total polyphenols, as mg of gallic acid/L; OD, *o*-diphenols and, CAT, catechins, as mg of D-catechin/L; TA, total anthocyanins as chloride of malvidin-3 glucoside, mg/L.

Table 4. Correlation Levels between Chromatic Variables and Values of Phenolic Families

	CAT	AT	HPP
TG		0.556***	
%Ye	0.372**	−0.470***	−0.389**
%Rd		0.496***	
%Bl			0.404**
DW	−0.394**	0.354**	0.440***
Pu	−0.365**		0.330**

[a] Significance level $p < 0.01$ (**) and $p < 0.001$ (***).

wines. Ordinarily, these condensed molecules are associated with the orange tones characteristic of aged

wines. They are formed chiefly through condensation of anthocyanins with tannins, thereby resulting in the formation of high molecular weight compounds in which the chromatic properties have been altered by shifting the absorbance peak from 545 to 400 nm. However, in the wines produced in the Ribera del Duero Appellation of Origin region, the main reactive groups of the polymers formed would appear to be the same as those of the free anthocyanins, either because an equilibrium between the flavilium (red) and quinone (violet) forms is maintained or because the compounds formed by condensation with the tannins are only slightly oxidized, thus preventing the formation of orange pigments and hence hardly altering the chromatic properties of the molecules, whereby the purple tones of the young wine are not lost.

CONCLUSIONS

The color variables defined by the two methods employed were closely related and taken together enhanced the definition of wine color and facilitated practical interpretation.

Brightness, purity, and the dominant wavelength were not correlated with the red color component but rather with the blue and yellow component (modifiers of principal color).

The catechins, anthocyanins, and highly polymerized polyphenols were the families of phenolic compounds most closely correlated with the color variables, although only the highly polymerized polyphenols showed close correlation with the blue component.

Color intensity fell rapidly during first stage of aging, while tone increased alone with the proportion of yellow.

The constant values of the blue component and the dominant wavelength during aged of wines, are the most significant results and provided characteristic and distinctive properties for them.

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