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Multivariate characterization of aging status in red wines based on chromatic parameters

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The colour of wine is affected by several factors, among the more important being grape variety, pH, temperature, oenological treatments and aging. Chromatic characteristics of young and aged red wines were studied. Several CIE colour spaces and chromatic systems were determined and subsequently submitted to multivariate statistical techniques such as stepwise discriminant analysis in order to predict and classify the aging status of red wines. When the equations obtained were applied to 71 samples of Spanish young and aged red wines, a high percentage of well-classified samples was achieved. © 1997 Elsevier Science Ltd

INTRODUCTION

The red colour of wines is due mainly to both anthocyanins and polymeric pigments and depends on several factors, including the age of the wine (McCloskey & Yengoyan, 1981). Measurement of the age of a wine is an unresolved problem, but the notion of 'chemical age', which relates the composition of a particular wine to the average composition of wines of known age, has been proposed (Archier *et al.*, 1993). The determination of 'chemical age' (Somers & Evans, 1974, 1977; Jackson *et al.*, 1978) is based on spectral measurements related to the anthocyanin equilibria and has been utilized as an indirect parameter to predict the aging status of red wines.

It has been demonstrated that chromatic as well as physicochemical parameters of red wines can be seriously modified during aging (Somers & Evans, 1974; Little, 1977; Bakker & Timberlake, 1986; Heredia & Guzmán, 1988; Bakker *et al.*, 1993; Almela *et al.*, 1995). Chromatic variables, based on direct and objective spectral measurements, have rarely been considered in this context, although they could certainly make a valuable contribution since they follow the real changes in the evolution of colour.

De Gori and Gradi (1955) made a first approach to determining the possible age of wine by selecting 11 different wavelengths ranging from 440 to 540 nm. As the age of the wine increased, a significant hypochromic effect was observed. Other authors, such as Lemperle and Kerner (1968), monitored the evolution of the aging of wines via their spectral behaviour, and found that a hypochromic effect at 515 nm and a simultaneous hyperchromic effect at 420 nm occurred as the aging advanced. These effects were accompanied by a colour change to brownish, mainly due to the enzymic oxidation of anthocyanins and the condensation of their polymeric forms. In Rioja wines aged during periods of 3 or more years, the simplified OIV method (Office International de la Vigne et du Vin, 1969) for colour determination of wines can be employed without significant errors (Negueruela & Echávarri, 1983). However, it has been well demonstrated that the OIV method lacks reliability for strongly coloured young wines (Heredia & Guzmán, 1991). By using chromatic parameters in red and rose Spanish wines, it was possible to follow the structural spoiling of wines over time (Heredia & Guzmán, 1988).

The aim of this study was to determine the utility of objective colour measurement techniques as a valuable tool for the classification and discrimination of young and aged red wines. In a second stage, it could also be employed to determine the most suitable oenological treatment to obtain good-quality wines with standard defined colours. The large amount of information supplied by the chromatic analysis of wines, especially when different defined colour trichromatic spaces and diagrams are considered (Heredia & Guzmán, 1990), makes it necessary to apply multivariate statistical techniques to process and summarize the data.

MATERIALS AND METHODS

Wine samples

A total of 71 samples of Spanish red wines belonging to 12 origin appellations (certified brand of origin) have been considered in this study. Wines were randomly selected following adequate representative criteria, according to their consumption and production. All the wines were bottled commercialized samples supplied by the respective producers. Samples were divided into two groups: 28 samples were declared by the wineries as young wines, less than a year prior to being bottled, without wood contact (set A); 43 samples were declared as aged wines, more than a year prior to being bottled, with at least 6 months in wooden barrels (set B).

Apparatus

Experimental absorbance was measured in a Milton Roy Spectronic 3000 diode array spectrophotometer. Hellma precision glass cells with 1, 2, 5 and 10 mm pathlengths were used.

Experimental

Chemical age, from the analytical scheme for anthocyanin equilibria proposed by Somers and Evans (1974, 1977) and Jackson *et al.* (1978), based on spectrophotometric measurements, was determined as follows:

- Chemical age I ($CA_I = E_{SO_2}/E_{CH_3CHO}$) is the proportion of free pigment colour (once the SO_2 effect has been removed) due to polymeric pigment.
- Chemical age II ($CA_{II} = E_{SO_2}/E_{HCl}$) is the proportion of total pigment colour due to polymeric pigment.
- Chemical age III ($CA_{III} = E_{SO_2}/E_{520}$) is the proportion of wine colour due to polymeric pigment.

In these equations, E_{520} represents the absorbance (520 nm) of the undiluted wine, E_{SO_2} represents the absorbance (520 nm) of the wine containing 2‰ SO_2, E_{CH_3CHO} represents the absorbance (520 nm) of the wine containing 10‰ acetaldehyde, and E_{HCl} represents the absorbance (520 nm) of the wine containing 10‰ HCl (1 M).

Spectra (380–770 nm, $\Delta\lambda = 2$ nm) were registered within 1 h of the bottles being opened in order to avoid the effect on colour stability with time (Heredia & Guzmán, 1988). CIE tristimulus values were obtained by application of the weighted-ordinate method (constant $\Delta\lambda$), to avoid the errors of the OIV method, based on a simplification of the selected-ordinate method (variable $\Delta\lambda$) (Heredia & Guzmán, 1991).

Chromatic parameters were calculated following different recommendations: (1) non-uniform colour space CIE 1931-(x, y), CIEXYZ; (2) uniform colour space CIE 1976-(L^*, a^*, b^*), CIELAB (Wyszecki & Stiles, 1982; CIE, 1986). The colour parameters determined were as follows:

CIEXYZ

- Tristimulus values, X, Y, Z.
- Chromaticity coordinates, x, y, z, obtained by standardizing tristimulus values (X, Y, Z):

$$x = \frac{X}{X+Y+Z} \quad y = \frac{Y}{X+Y+Z} \quad z = \frac{Z}{X+Y+Z}$$

- Dominant wavelength, λ_d (nm), defined as the wavelength of the monochromatic stimulus that, when mixed with some specified achromatic stimulus, matches the given stimulus in colour. It was determined following the method proposed by Heredia and Guzmán (1992).
- Excitation purity, p_e (%), which correlates loosely with saturation of the colour perceived under ordinary observing conditions and indicates how far the chromaticity point is displaced towards the spectrum locus.

CIELAB

- Colour coordinates, L^*, a^*, b^*. L^* represents the perceived lightness, a^* and b^* indicate the change in hue from red to green and from yellow to blue, respectively.
- Chroma, C^*_{ab}, a correlate for saturation.
- Hue angle, h_{ab}, a useful quantity in specifying hue numerically.

Statistics were performed using a CSS software package (Statsoft, Inc., 1991). A ratio of cases/variables of 5.5 was achieved, following general recommendations for multivariate analysis (Tabachnick & Fidell, 1983).

RESULTS AND DISCUSSION

Table 1 shows the basic statistics for the variables included in the study for each set of wines, namely young wines (set A) and aged wines (set B).

An overall multivariate analysis of variance was carried out and significant differences between the two groups of samples were found (Wilks' lambda: 0.3661, P-level ≤ 0.05). Then, taking into account the age status of the wines as an effect, the variables determined are useful altogether to significantly differentiate between the two sets. As can be extracted from the univariate F-values between groups (Table 1), among the chemical age indices, CA_{III} seems *a priori* to be the best for discriminating purposes ($F = 88.682$).

The multivariate study, including both colorimetric information and chemical age indices, was performed in order to improve the differentiation between the two sets of samples.

Samples belonging to sets A and B (a total of 71) were subjected to a cluster analysis. Figures 1 and 2 give the hierarchical tree by the amalgamation rule using single and complete linkage, respectively. No clearly defined structure can be observed by single linkage. By complete linkage, various subclusters according to aging status were obtained, although many samples remained mis-grouped.

The application of stepwise discriminant analysis (SDA) determines which variables discriminate between the two groups. The different number of cases in sets A and B is a reflection of the distribution in the real population since aged red wines are more widely represented in the market than young wines. In this sense, in the SDA, the *a priori* probabilities were set proportional to the sizes of the groups.

Table 2 summarizes the results of SDA, applying forward stepwise analysis and setting F to enter equal to 1.5. The variables included, with a major contribution to the discrimination between sets, were selected in the order: chemical age index (CA_{III}), excitation purity (p_e) and the coordinate a^*.

The classification functions (z_A, z_B) obtained were as follows:

$$z_A = 238.42(CA_{III}) + 0.87(p_e) + 1.24(a^*) - 144.44$$
$$z_B = 281.21(CA_{III}) + 0.96(p_e) + 1.16(a^*) - 177.11$$

For the sake of a clearer interpretation of z-values, it should be noted that the very different values for the coefficients are due not only to the discriminating power for the corresponding variable but also to the fact that they are unstandardized, their values being displayed in very different numerical ranges (CA_{III}, 0.4–0.9; p_e, 60–100; a^*, 43–61).

The difference equation ($\Delta z = z_A - z_B$) seems to be a good classification rule:

$$\Delta z = 42.79(CA_{III}) + 0.09(p_e) - 0.08(a^*) - 32.67$$

For $\Delta z < 0$ values, the sample is classified into the young wines group, and for $\Delta z > 0$ values the sample is classified as an aged wine.

The classification functions confirm how CA_{III} remains the most valuable variable for discrimination purposes, as demonstrated by its high coefficient in the equations. In any case, the inclusion of the chromatic variables selected through the SDA (p_e and a^*) clearly enhances the discrimination power.

Table 1. Descriptive statistics for set A (n = 28) and set B (n = 43)

	Set	Range	Mean	SE	SD	*F*-value
Chemical age						
CA_I	A	0.393–0.738	0.576	0.0158	0.0838	72.7946**
	B	0.594–0.867	0.722	0.0108	0.0649	
CA_{II}	A	0.127–0.381	0.268	0.0115	0.0606	35.7806**
	B	0.114–0.581	0.391	0.0178	0.1065	
CA_{III}	A	0.429–0.738	0.613	0.0142	0.0750	88.6818**
	B	0.674–0.867	0.748	0.0069	0.0455	
CIEXYZ						
X	A	3.014–36.226	15.995	1.4140	7.4822	0.0328 NS
	B	0.542–34.274	16.334	1.1955	7.8393	
Y	A	1.169–24.722	8.663	0.9996	5.2891	0.2442 NS
	B	0.200–24.650	9.327	0.8676	5.6890	
Z	A	0.001–10.771	2.103	0.4929	2.6079	0.2231 NS
	B	0.000–11.874	1.806	0.3915	2.5675	
λ_d	A	601.817–642.689	617.772	1.9406	10.2687	4.0903*
	B	596.552–663.188	612.234	1.8114	11.8781	
p_e	A	59.798–99.948	85.062	2.2018	11.6509	1.2190 NS
	B	55.106–100.000	88.060	1.6570	10.8654	
CIELAB						
L^*	A	10.327–56.803	33.179	2.0336	10.7607	0.1374 NS
	B	1.806–56.733	34.194	1.7672	11.5881	
a^*	A	43.152–60.887	53.833	0.9585	5.0718	6.0644*
	B	13.755–59.246	50.007	1.0861	7.1220	
b^*	A	17.794–50.874	38.021	1.3793	7.2987	4.0883*
	B	3.113–56.225	42.363	1.4801	9.7056	
C_{ab}^*	A	46.676–77.018	66.088	1.3895	7.3526	0.0155 NS
	B	14.103–75.840	65.805	1.5924	10.4419	
h_{ab}	A	22.409–43.419	34.903	0.8853	4.6844	10.2527**
	B	12.752–48.866	39.471	0.9950	6.5248	

*$P \leq 0.05$; **$P \leq 0.01$; NS, not significant.

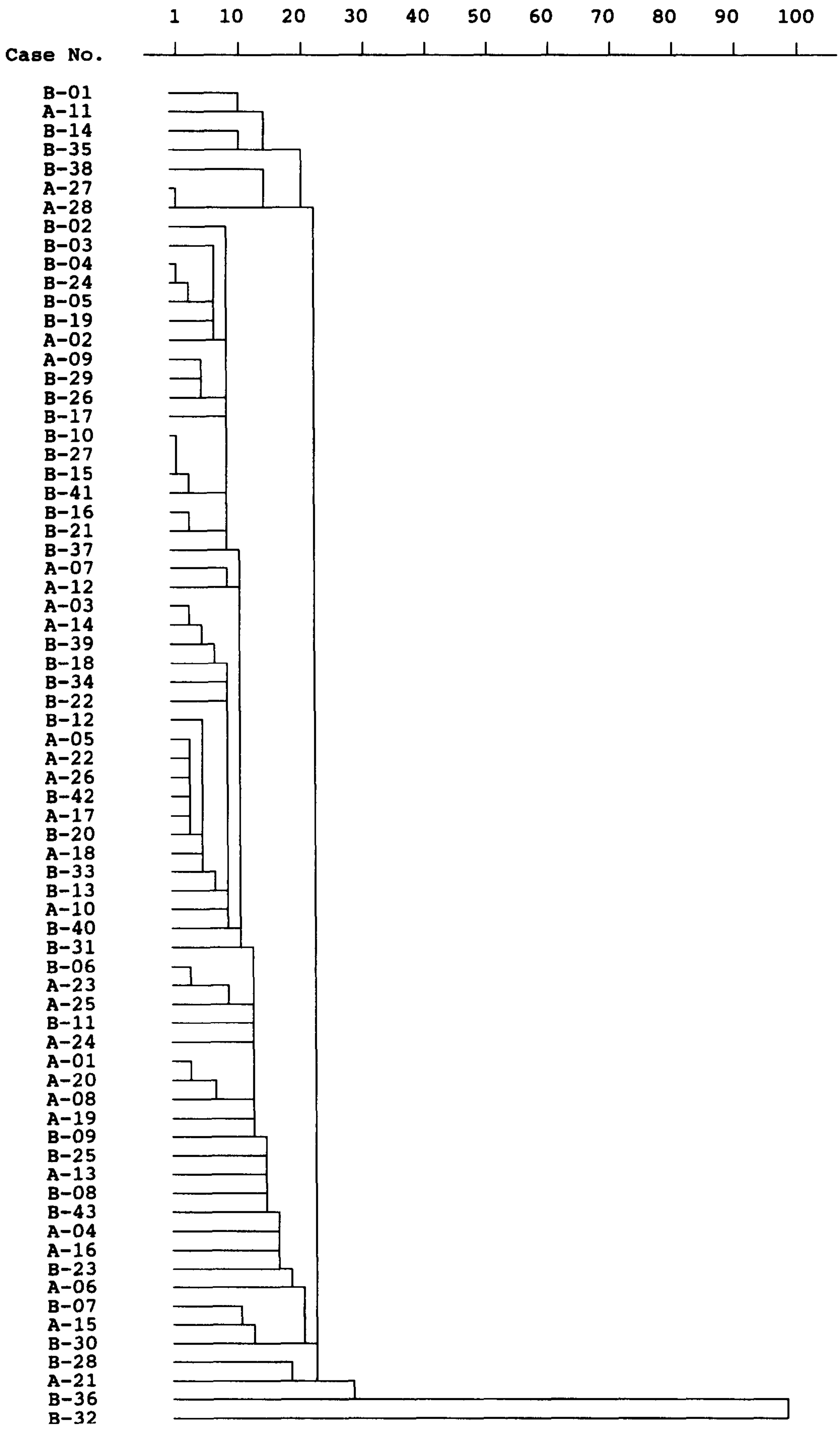

Fig. 1. Hierarchical tree by single linkage.

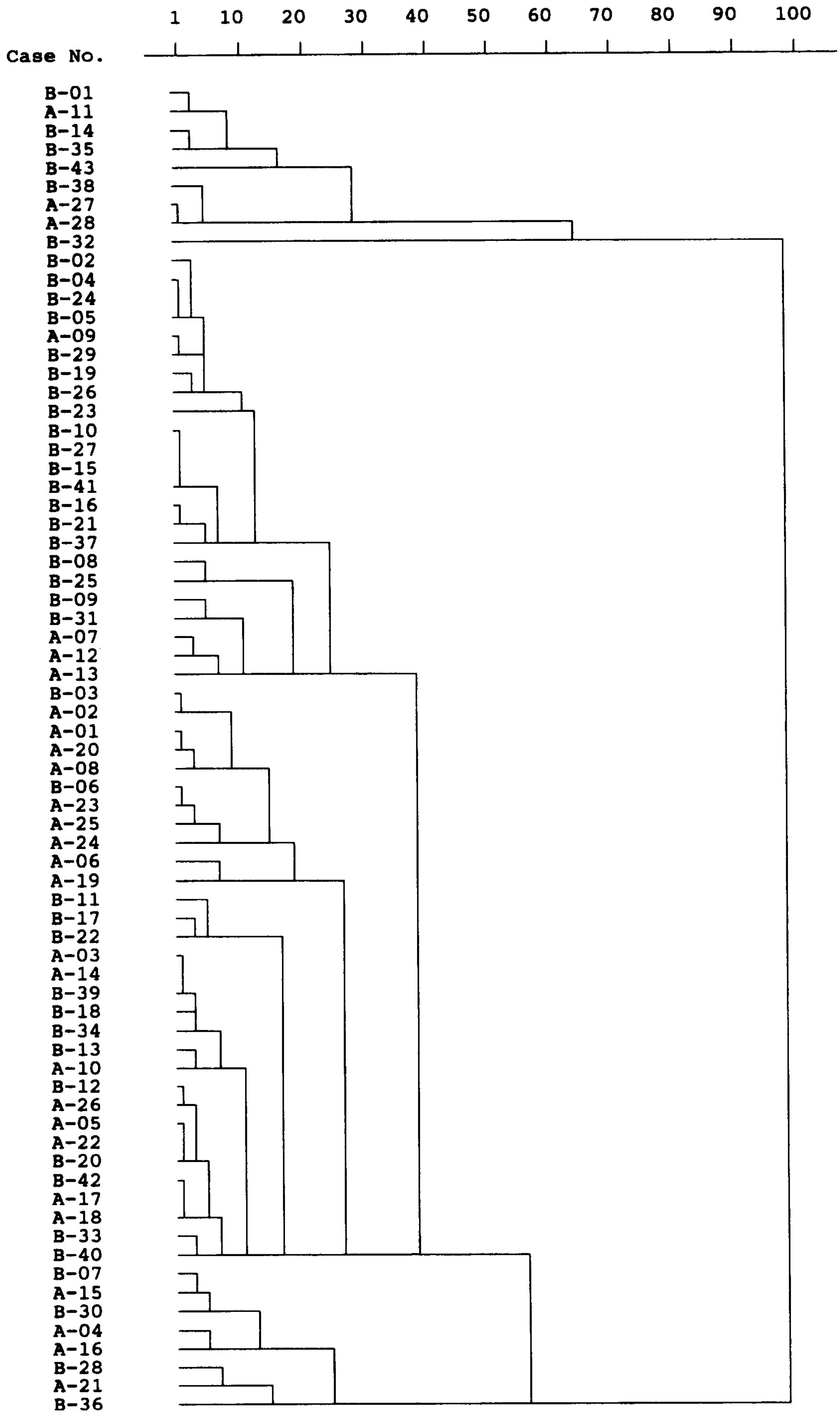

Fig. 2. Hierarchical tree by complete linkage.

Table 2. Summary of stepwise analysis

Step	Variable	F-value
1	Chemical age (CA_{III})	88.682**
2	Excitation purity (p_e)	6.315**
3	CIELAB coordinate (a^*)	1.787 NS

*$P \leq 0.05$; **$P \leq 0.01$; NS, not significant.

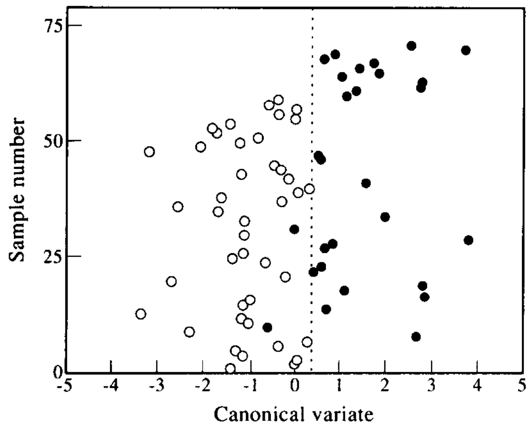

Fig. 3. Scatterplot of the canonical variate obtained by SDA (●, young wines; ○, aged wines).

Table 3. SDA classification matrix

Observed classification	Percentage correct	Predicted classification	
		Young wines (set A)	Aged wines (set B)
Young wines (set A)	92.86	26	2
Aged wines (set B)	100.00	0	43
Total	97.18	26	45

As two sets are considered, only one discriminant function (canonical variate, CV) is obtained by SDA. The scatterplot of this CV (Fig. 3) shows a good separation between the two sets of samples. The percentage of good assignments is very high, as can be seen in Table 3. Only two young wines were misclassified, and all aged wines received the correct assignment.

CONCLUSION

It seems that the chemical age index (CA_{III}) is the variable that contributes most to prediction. Tristimulus colorimetric variables do not readily indicate a certain oenological property, and their inclusion in multivariate statistics presupposes a clear improvement in ascertaining the aging status of red wines.

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