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Analytica Chimica Acta 563 (2006) 215–222
ANALYTICA CHIMICA ACTA
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# Behaviour and characterisation of the colour during red wine making and maturation

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Received 15 August 2005; received in revised form 11 November 2005; accepted 14 November 2005
Available online 20 December 2005

**Abstract**

During winemaking and ageing, the colour of red wine evolves from the initial purple-red hues of young red wines towards more red-orange ones. Simultaneously, a modification in the pigment profile takes place. The stability of pigments isolated from red wine has been usually studied in model solutions. However, studies carried out on wines are scarce. The objective of this work was to analyse the changes in composition, colour and stability in relation to pH and $SO_2$ that take place in a red wine during winemaking and maturation. For this purpose, samples of red wine from *Tempranillo* grapes were collected periodically during 18 months and submitted to chromatic analysis using the CIELAB and CIELUV colour spaces and high performance liquid chromatography–diode array detection coupled to a mass spectrometer analysis (HPLC–DAD–MS). The results obtained showed the existence of processes capable of causing quantitative and qualitative changes in the colouring material of the wine. These changes, in spite of the relatively short time considered, are sufficient to cause changes of colour that can be perceived by the human eye and lead to the formation of pigments that are more stable against pH and against bleaching by $SO_2$ than the original anthocyanins.


*Keywords:* Wine; Colour; CIELAB; Anthocyanins; Anthocyanin-derived pigments

## 1. Introduction

The colour of a wine is, generally, the first characteristic perceived and, therefore, conditions its global sensorial analysis. In a young red wine, the main compounds that are responsible for its colour are the anthocyanin pigments, which progressively disappear due to their degradation and transformation into other more stable pigments that would be responsible for the expression of the colour in more evolved wines.

These new pigments constitute a very heterogeneous group of molecules in whose formation several mechanisms are proposed. One of them is the condensation of anthocyanins and flavanols through an ethyl bridge by mediation of acetaldehyde [1–3]. These pigments, whose presence has been demonstrated in wines [4,5], are relatively unstable, although less sensitive than the anthocyanins to the bleaching by sulphur dioxide and by the increase in pH [6].

Another one is the direct condensation between anthocyanins and proanthocyanidins whose formation was hypothesised by Jurd in 1969 [7] and later demonstrated both in model solutions [3,8] and in wine [9,10], where they are found with a different degree of polymerisation [9]. It appears that the behaviour of these pigments would be similar to that of the original anthocyanins [11], however, their chromatic characteristics and those of stability are still not well established and should be studied in depth.

Another family of pigments are the pyranoanthocyanins which result from the nucleophilic addition of vinyl or carbonyl derivatives to the anthocyanins followed by cyclation and oxidation [12,13]. When they are in model solutions, they present greater stability against changes in pH of the medium and are more resistant to bleaching by $SO_2$ than the original anthocyanins [14]. Among them, some of the better studied ones are the A-type vitisins, formed by reaction between the anthocyanins and pyruvic acid [13,15]. Other pyranoanthocyanins,

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doi:10.1016/j.aca.2005.11.044

the adducts with 4-vinylphenol, were first detected in the membranes used for the tangential filtration of red wines [16] and isolated and structurally identified with synthetic samples [12]. The existence of similar products derived from 4-vinylcatechol, 4-vinylguaiacol and 4-vinylsyringol have also been postulated in wines [10,17,18]. The formation of the vinyl derivatives would take place by enzymatic [12] or chemical [19] means from the corresponding hydroxycinnamic acid, which is why the formation of this type of adducts could take place during years of storage.

Acetaldehyde is also involved in the formation of subfamilies of pyranoanthocyanins detected in wine: the B type vitisins [14], the vinyl-flavanols [20] and the vinylpyranoanthocyanidins [21]. In these last two, the instability of the acetaldehyde-mediated condensation products, which leads to the cleavage of the ethyl link [6], would be responsible for their formation. Their characteristics are, at this time, not well established and it is necessary to carry out further research on their chromatic properties and stability.

Colour is a sensation produced by luminous radiation and responds to criteria in which each individual perception intervenes, thus it is a subjective characteristic. With the objective of being able to carry out an analysis of the colour which would be objective and universal, diverse methods have been used that yield quantitative data.

Traditionally, the measurement of the colour of wines was carried out using the parameters of Sudraud [22], obtained from the absorbance values at 420 and 520 nm. Later, absorbance at 620 nm was included, characterising the colour of wine by the colouring intensity ($IC = A_{420} + A_{520} + A_{620}$) and the hue ($T = (A_{420}/A_{520}) \times 100$) [23]. These methods are rapid and easy to use in the cellar, but incomplete. In spite of this, they are considered by the "International Organisation of Vine and Wine" (OIV) as the official methods. The OIV also proposes a method of reference in accordance with the "Commission Internationale de L'Eclairage" (CIE) which allows the calculation of tristimulus values from the measurements of absorbance at 445, 495, 550 and 625 nm, defining the colour by the purity and the dominant wavelength [24]. This method is, at present, considered obsolete and new colour spaces have been proposed [25].

The CIE proposed distinct methods of measurement in which, as well as standardising the observer and the light that illuminates the object, the entirety of all the possible colours is considered as a tri-dimensional space, where each colour is defined by three colorimetric coordinates, calculated from the values of transmission of the visible spectrum. Among all the methods proposed the CIELAB colour space is considered the most homogeneous and, therefore, possibly the best model [26–29].

This space defines the colours by the geometrical coordinates $L^*$ (lightness), $a^*$ (red/green) and $b^*$ (yellow/blue). But these parameters are not sufficient to obtain a good characterisation of the colour. For this, it is necessary to bear in mind the psychophysical parameters [30], which correspond with the cylindrical coordinates: hue and chroma ($h_{ab}$ and $C^*_{ab}$). Parameters belonging to other spaces of colour, such as the case of saturation ($s^*_{uv}$), a parameter of CIELUV (CIE, 1976), contributes information on the visual saturation.

In this work the characteristics of colour and stability, in relation to the pH and the bleaching by $SO_2$, of red wine samples taken throughout the process of winemaking are studied.

## 2. Experimental

### 2.1. Samples

The study was made using wines obtained from *Vitis vinifera* cv *Tempranillo* grapes, supplied by Bodegas Roda (D.O. Rioja, Spain). The samples were collected periodically during a period of 18 months. Considering the day of harvest as the starting point of the winemaking process, samples were obtained at 2 weeks (post-fermentative maceration), 18, 36 and 50 weeks (ageing in oak barrels) and 66 weeks (bottled period).

### 2.2. Analysis of pigments

This was carried out by HPLC–DAD–MS, according to Alcalde-Eon et al. [10] in a Hewlett Packard 1100 chromatographic system. The chromatograph allowed the coupling of an LCQ™-Thermoquest (Finnigan) mass spectrometer which was associated to a Pentium Pro 200, mod. Gateway 2000 computer with an X-Calibur™ (Finnigan) programme for data processing.

### 2.3. Assays of pH

To a battery of five samples of each of the wines studied different volumes of 2 M HCl and 1 M NaOH were added with the objective of obtaining samples with pH ranging from 1 to 5. 0.30, 0.20 and 0.10 ml of 2 M HCl were added to reach pH values next to pH's 1, 2 and 3, respectively. To obtain pH's values higher than that of the wine, 1 M NaOH was added: 0.05 ml to reach pH next to 4, and 0.20 ml to pH next to 5. These additions gave rise a perceptible dilution effect, reason why ultrapure water was added to each sample, till a total added volume of 0.30 ml, in order to produce the same dilution effect, and be able to compare each sample to the others. The pH of the samples was measured using a Crison micropH 2000 pHmeter. The spectrum of absorption of the solutions was recorded at room temperature after 3 h of stabilisation.

### 2.4. Assays of addition of $SO_2$

To a battery of six samples of each of the wines, different quantities of $NaHSO_3$ (as powder to avoid a dilution effect) were added with the objective of reaching final concentrations of 10, 25, 45, 70, 100 and 200 mg/ml. The spectrum of absorption of the solutions was recorded at room temperature after 15 min.

### 2.5. Spectrum measurements

Absorption spectra (190–1100 nm) were recorded using a Hewlett Packard UV-vis HP3853 spectrophotometer in a 1 mm pathlength quartz cell.

### 2.6. Analysis of colour

It was made from the visible spectra (380–770 nm) data acquired with 1 mm pathlength quartz cell, with the CIE 1964 standard observer (10° visual field) and the CIE standard illuminant D65, as references. Chromatic analyses were carried out following CIE 1976 ($L^*u^*v^*$) space (CIELUV) and CIE 1976 ($L^*a^*b^*$) space (CIELAB). Calculations were made using the software CromaLab® [31].

## 3. Results and discussion

In the chromatograms obtained after injection of the wine samples, anthocyanins, pyranoanthocyanins and anthocyanin-flavanol direct condensation compounds were detected. In Fig. 1, as an example, the chromatogram corresponding to the wine sample collected at 2 weeks is presented, in which the location of the principal families of pigments is indicated. In Fig. 2 the evolution of their chromatographic areas is shown. The greatest

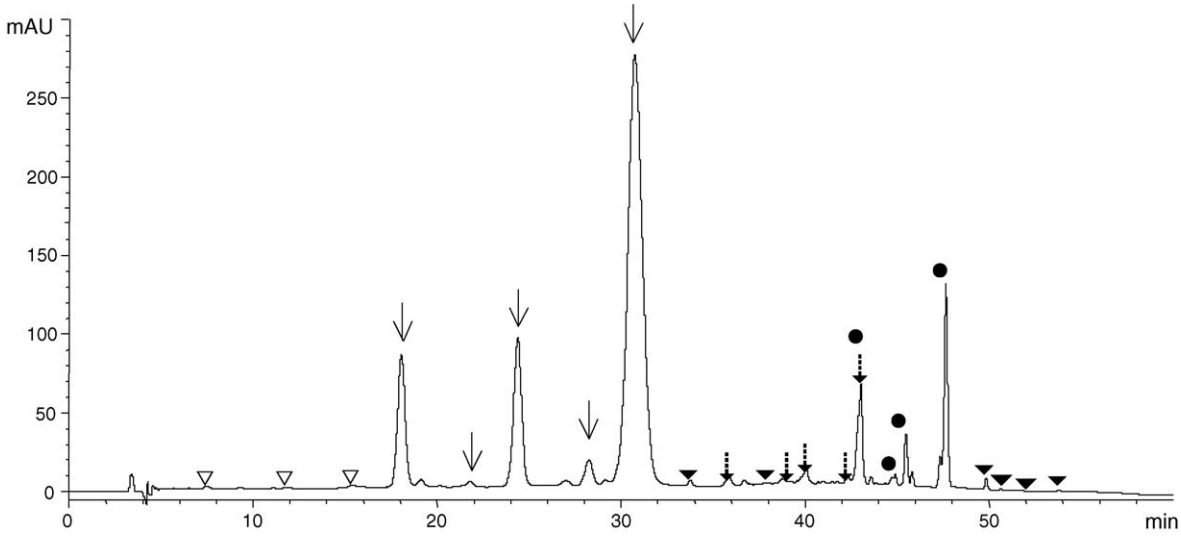


Fig. 1. Chromatogram recorded at 520 nm corresponding to the wine of 2 weeks. The location of the pigments that comprise the principal families of compounds found is indicated. Non-acylated anthocyanins (↓), acetyl derivatives (⇣), coumaroyl derivatives (●), pyranoanthocyanins (▼), anthocyanin-flavanol direct condensation pigments (▽).

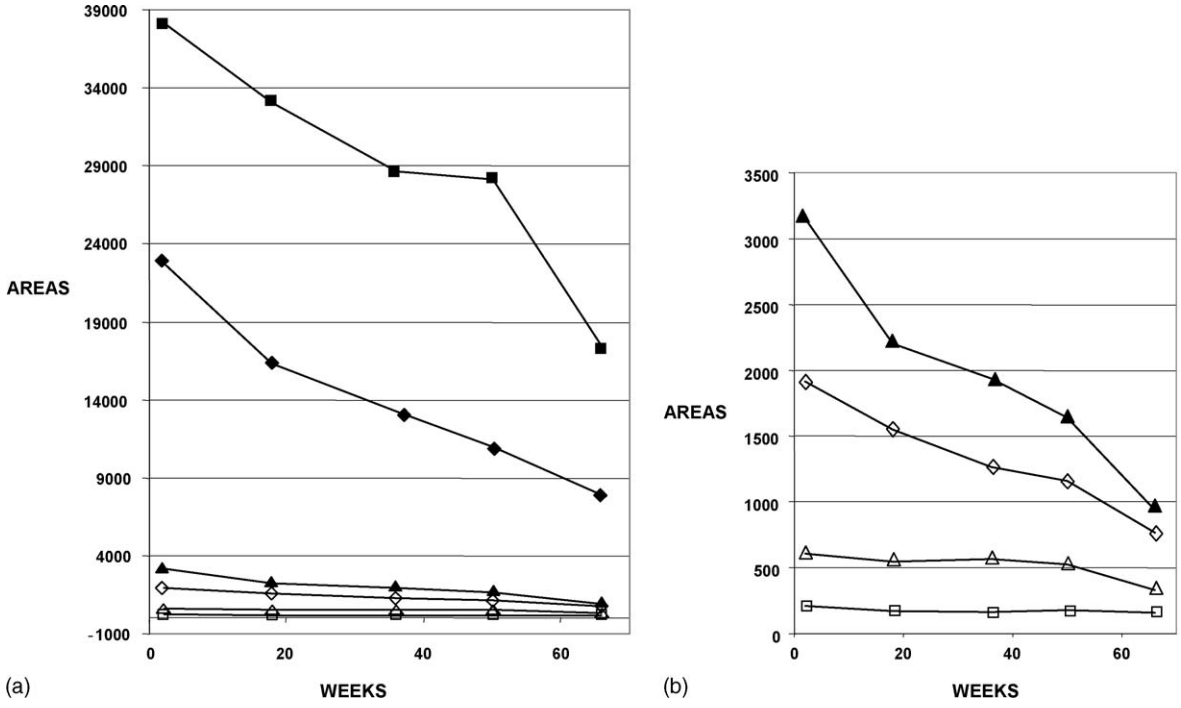


Fig. 2. (a) Evolution through 66 weeks of the concentration of the total pigments (■), anthocyanins (♦), anthocyanins acylated with acetic acid (◊), anthocyanins acylated with *p*-coumaric acid (▲), pyranoanthocyanins (△) and direct condensed anthocyanin-flavanol pigments (□), observed in the chromatograms registered at 520 nm. (b) Zoom showing the evolution of acylated compounds, pyranoanthocyanins and condensation products.

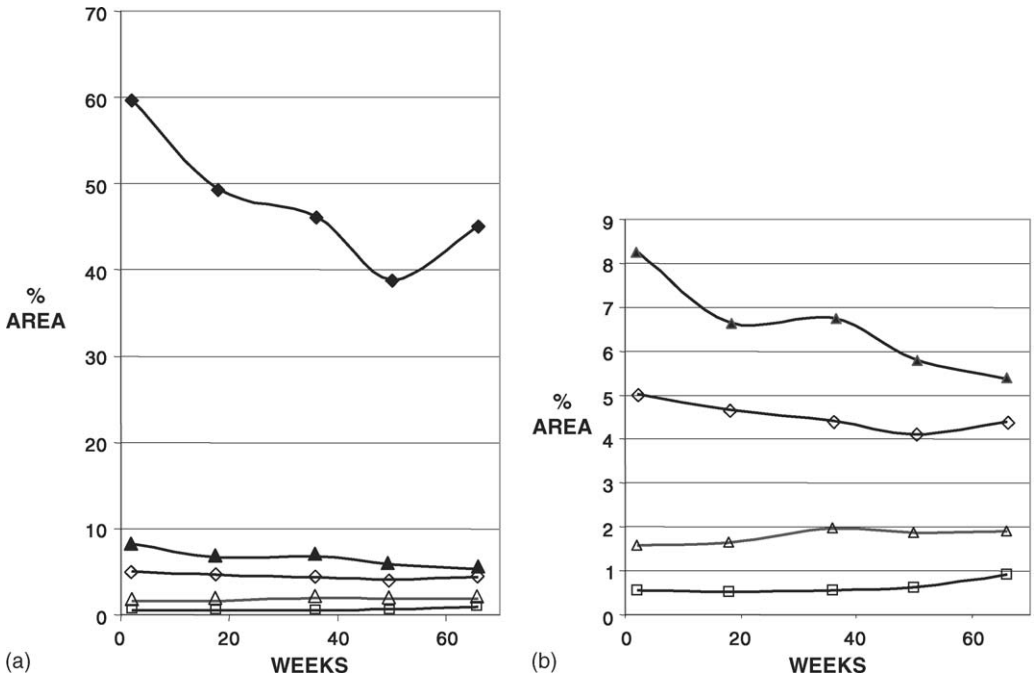


Fig. 3. (a) Relative percentage in relation to the total of pigments present in the chromatograms of anthocyanins (♦), anthocyanins acylated with acetic acid (◊), anthocyanins acylated with *p*-coumaric acid (▲), pyranoanthocyanins (△) and direct condensed anthocyanin-flavanol pigments (□), observed in the chromatograms registered at 520 nm. (b) Zoom showing the evolution of relative percentage of acylated compounds, pyranoanthocyanins and condensation products.

concentration of pigments present in the chromatograms corresponds to the non-esterified anthocyanin monoglucosides, which undergo an important decrease (65%) during the period of the study.

The pigments formed from the anthocyanins are present in the chromatograms from the first sample and thus are of very early formation. Among them, the pyranoanthocyanins seem to be formed rapidly, initiating a slow decrease from 36 weeks, which is more appreciable from week 50. The concentration of the direct condensation pigments increases slowly up to 50 weeks, from that time onwards it decreases. The greater stability of the pyranoanthocyanins than the anthocyanin monoglucosides is well known, as well as the fact that they have a maximum of absorbance at lower wavelength than the anthocyanins and higher values of absorbance at 420 nm region, which is why they show more orange hues [13,14]. Regarding the chromatic characteristics and stability of the direct condensation pigments, it has been postulated [11] that they could be similar to those of the original anthocyanins, though they are still not well established.

In spite of the steady decline observed in the anthocyanin pigments during winemaking and maturation of the wine, between weeks 36 and 50 a stabilisation of the total pigment contents is produced, which suggests that in this period of time the loss of the anthocyanins is due more to their transformation into derived pigments than to degradation. In the chromatic profile corresponding to the sample of 50 weeks an increase is produced in the base line which was more evident towards the end of the chromatogram. It can be expected that the pigments responsible for this increase in absorbance are formed from the pigments present in earlier samplings, probably from anthocyanins, or, even, the pyranoanthocyanins, since the decline of these latter coincides with their appearance. The fact that in the chromatogram corresponding to the wine of 66 weeks a decrease in the base line is appreciated leads to the supposition that the previously indicated pigments are unstable and tend to degrade rapidly or precipitate. They could be polymers or compounds with complex structures of diffuse elution which are not seen in the chromatograms as well-defined peaks. The decrease of these pigments in the chromatograms could be the cause of the relative increase that the anthocyanin monoglucosides undergo at the end of the study (Fig. 3). Anthocyanin monoglucosides at 66 weeks represent 45% of the pigments recorded in the chromatogram, a similar percentage to that found at 36 weeks (46%). It should be emphasised that the sample of 66 weeks corresponds to wine that has been bottled and in spite of the fact that no filtration was carried out, some pigments could have been retained in the barrel.

An observation which supports that the possible polymer pigments present in the sample of 50 weeks could be compounds derived from the anthocyanins is the fact that the $A_{420}/A_{520}$ ratio tends to increase throughout the study period (Table 1). This

Table 1
Values corresponding to percentage of red (d$A$%) and contribution of the yellow ($A_{420}/A_{520}$) [23], calculated from the absorbance obtained on measuring in the spectrophotometer at wavelengths 420, 520 and 620 nm, the samples of wine collected at 2, 18, 36, 50 and 66 weeks

| | 420 nm | 520 nm | 620 nm | IC | d$A$% | $A_{420}/A_{520}$ |
|---|---|---|---|---|---|---|
| 2 weeks | 0.426 | 0.699 | 0.161 | 1.286 | 58.011 | 0.609 |
| 18 weeks | 0.404 | 0.567 | 0.154 | 1.125 | 50.794 | 0.713 |
| 36 weeks | 0.406 | 0.553 | 0.148 | 1.107 | 49.910 | 0.734 |
| 50 weeks | 0.395 | 0.548 | 0.137 | 1.080 | 51.460 | 0.721 |
| 66 weeks | 0.404 | 0.541 | 0.144 | 1.089 | 49.353 | 0.747 |

is due, probably, to the decrease in the anthocyanin pigments and the increase of the contribution of the pyranoanthocyanins. Despite this, in the sample taken at 50 weeks, in which the appearance in the chromatograms of these pigment complexes is produced, a decrease of $A_{420}/A_{520}$ is observed. Moreover, the percentage of red (d$A$%) tends to diminish through the study, except at week 50 when it increases. Hayasaka and Kennedy [9] detected, by direct injection of a wine in the mass spectrometer, the presence of direct condensation compounds with a degree of polymerisation in the range of dimers to octomers. It can be supposed that the most polymerised are not observed in the chromatograms as defined peaks and therefore that could be the nature of the compounds that appear in our chromatograms as an elevation of the baseline. Nevertheless, this aspect remains to be confirmed, since in our study they could not be identified.

In the analysis of colour made by the study of the CIELAB parameters (Table 2), it is observed an increase in the hue value ($h_{ab}$), which undergoes a displacement from purple hues, which are characteristic of the monoglucosides of the anthocyanins when they are at moderately acid pH [32], towards more red hues. These changes seem to be more noticeable between 2 and 18 weeks, the period that coincides with an important loss of anthocyanins (approximately 25%). As a result of this loss of pigments, the quantitative component of the colour, the Chroma ($C^*_{ab}$), diminishes. In spite of the fact that the anthocyanin monoglucosides are the majority chemical species, at the pH of the wine the equilibrium between the different structural forms is displaced towards the formation of colourless hydrated bases. Thus the pyranoanthocyanins, more resistant to nucleophilic attack of the water, contribute significantly to the colour despite they are in lower proportion (approximately 19% at the end of the study). As it has been previously indicated, the pyranoanthocyanins show a more orange hue, which justifies that the value of $h_{ab}$ of the sample increases. In earlier paragraphs it has been remarked that between weeks 36 and 50 a stabilisation of the total quantity of pigments was observed, in spite of a decrease in the relative amount of anthocyanins. The values obtained for $C^*_{ab}$ in this same period hardly undergo modifica-

Table 2
Values obtained for $L^*$, $C^*_{ab}$, $h_{ab}$, $\Delta E^*_{ab}$ and $s^*_{uv}$ in the samples corresponding to 2, 18, 36, 50 and 66 weeks

| | $L^*$ | $C^*_{ab}$ | $h_{ab}$ | $\Delta E^*_{ab}$ | $s^*_{uv}$ |
|---|---|---|---|---|---|
| 2 weeks | 65.861 | 36.196 | −1.795 | | 0.051 |
| 18 weeks | 68.992 | 29.602 | 2.113 | 7.631 | 0.032 |
| 36 weeks | 69.754 | 29.112 | 4.424 | 8.815 | 0.031 |
| 50 weeks | 70.416 | 28.832 | 6.472 | 9.828 | 0.031 |
| 66 weeks | 70.207 | 28.197 | 7.727 | 10.533 | 0.030 |

The values corresponding to $\Delta E^*_{ab}$ were obtained taking as a reference the first point of sampling (2 weeks).

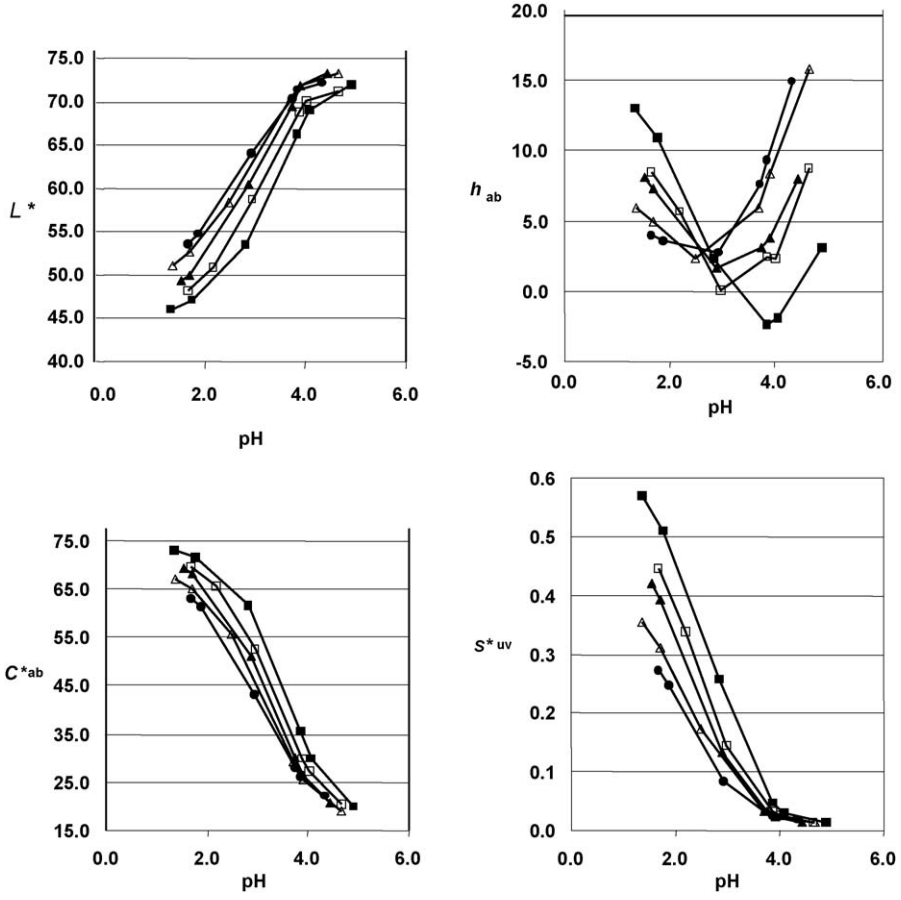


Fig. 4. $L^*$, $h_{ab}$, $C^*_{ab}$ and $s^*_{uv}$ values of wine samples in the range of pH from 1 to 5. Two weeks (■), 18 weeks (□), 36 weeks (▲), 50 weeks (△), 66 weeks (●).

tions, indicating that the global quantity of pigments remained stable.

The value of lightness ($L^*$) of the samples also increases through the 66 weeks, demonstrating that at the end of the study the samples are less dark. In model wine solution, an increase in $L^*$ is observed when either the hydrated forms of anthocyanin increases [32] or the dilution of the samples is produced [33]. In our samples the progressive loss of pigments observed would be responsible for the increase in lightness.

Saturation is a parameter ($s^*_{uv}$) only defined in CIELUV space which gives an idea of the purity of the colour. The value of this parameter diminishes through the study, showing the increase of the contribution of other pigments different from the anthocyanins as the age of the wine increases.

With regard to the values found in the calculation of the colour difference between each sample and the 2 weeks sample ($\Delta E^*_{ab}$), they are higher than three units, indicating that those colour differences can be visually discriminated. The changes of chemical composition that have taken place during 66 weeks are, therefore, sufficiently relevant to produce variations in colour which can be perceived by the human eye.

### 3.1. Influence of the pH on the colour of the samples of wine

In all the samples analysed, as the pH increases, a notable decrease in $C^*_{ab}$ (Fig. 4) is produced, which is due to the loss of the coloured forms of the anthocyanins as a consequence of the displacement of the equilibria of their structural forms towards the formation of colourless hydrated pseudobases. Studies previously carried out in our laboratory with isolated anthocyanins [32] showed that $C^*_{ab}$ underwent a linear decrease as pH increases, reaching values close to 0 at pH 5, which means that the colour approaches the grey line. Nevertheless, in wines, at pH 5 the value of $C^*_{ab}$ is close to 20, a value that the samples of isolated anthocyanins reached at values of pH around 3.5. Moreover, the decrease of $C^*_{ab}$ is less pronounced in more evolved samples showing the presence of more stable pigments in them, or the existence of mechanisms, such as copigmen-

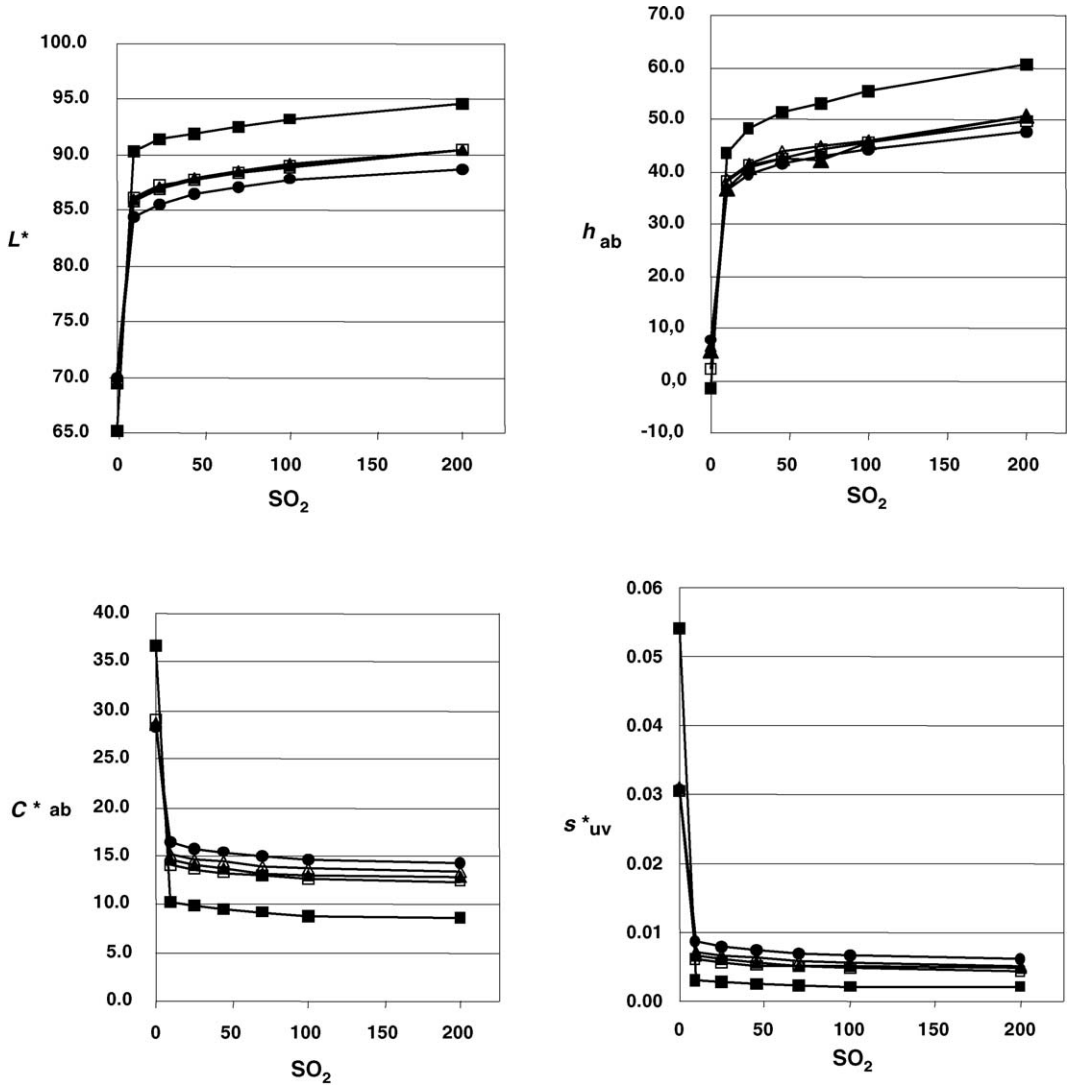


Fig. 5. $L^*$, $h_{ab}$, $C^*_{ab}$ and $s^*_{uv}$ values of wine samples with addition of increasing concentrations of $SO_2$ (mg/ml). Two weeks (■), 18 weeks (□), 36 weeks (▲), 50 weeks (△), 66 weeks (●).

tation, that counteract the effect of the increase in pH. As was already observed in the analysis by HPLC–DAD, with time there is a smaller quantity of pigments in the wines, since at the most acid pH (pH 1), at which it is to be expected that all the coloured forms are expressed, the value which is obtained for $C^*_{ab}$ is progressively lower. In the same way, $s^*_{uv}$, descends on increasing the pH (Fig. 4), obtaining lower values as the age of the collected samples increases.

The trend observed for the hue angle ($h_{ab}$) was similar to that observed with isolated anthocyanins [32]. Thus, as the pH increases, a decrease towards the blue hues is produced, followed by a sharp increase of it. This increase is notably more acute in the more evolved samples of wine though they lead to reddish hues whereas in the isolated anthocyanins the evolution of the hue takes place towards green-yellow zones. There are, therefore, in the more evolved samples, coloured forms resistant to hydration that express reddish hues at values of pH at which it is to be expected that the anthocyanins are in colourless form. These forms must chiefly be found in the samples of 50 and 66 weeks, in which the highest values of $h_{ab}$ are obtained.

In relation to the evolution of $L^*$ versus pH, as pH increased, higher $L^*$ values were obtained as a consequence of the progressive formation of the colourless hydrated bases. The value of $L^*$ at pH 1 increases with the age of the samples, in agreement with the decrease in the content of anthocyanins produced with time. In spite of that, the value of $L^*$ reached at pH 5 is similar in all of them (close to 72). Thus it seems that the pigments, that in the more evolved samples lead to the changes of hue and chroma observed and mentioned previously, do not undergo discoloration.

### 3.2. Bleaching by $SO_2$

The effect of the addition of $SO_2$ on the chromatic parameters of the wines is shown in Fig. 5. A considerable increase in $L^*$ is observed in all the samples due to the bleaching produced in them when adding the $SO_2$. This increase is of greater magnitude in the sample of wine collected at 2 weeks than in the rest of the wines, as a consequence of the greater proportion of easily decolourable anthocyanins in it.

The quantity of $NaHSO_3$ added to the samples was sufficiently high to bleach the anthocyanins present. So that, chromatic characteristics such as hue and colourfulness must be attributed, basically, to pigments more resistant to the bleaching. Thus, on increasing the concentration of $SO_2$ in the sample taken at 2 weeks, the values of hue obtained were situated in the yellow zone (around 60°) and that could be attributed to products of oxidation of flavanols. In this sample, with very high concentrations of $SO_2$, it seems that the total discoloration of pigments, whose structure is related to the anthocyanins, is achieved. Nonetheless, the rest of the samples evolve towards more orange hues (approximately 50 units), in which pyranoanthocyanin structures probably participate.

A considerable decrease in the values of $C^*_{ab}$ is produced in all the samples as a consequence of the bleaching by $SO_2$. The decrease is less pronounced as the samples are older. This indicates the presence of resistant pigments in them which have a significant influence on colour.

## Acknowledgements

Financial support received from CICYT (Grant ref. AGL2002-00167) is greatly acknowledged. The authors also thank the MECD (Ministerio de Educación, Cultura y Deporte, Spain) for an F.P.U. predoctoral scholarship to E. García-Puente. Thanks are also due to Bodegas RODA (Haro, La Rioja, Spain) for supplying the wine samples and Mr. G.H. Jenkins for helping with the English version of the manuscript.

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