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Comparison between the tristimulus measurements *Yxy* and *L* a* b** to evaluate the colour of young red wines

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The chromatic characteristics of 10 young red wines elaborated in the region of Murcia (Spain) were determined. The colour measurements obtained using the *Yxy* and CIELAB systems were compared. The calculation of dominant wavelength and its representation in the C.I.E. chromatic diagram revealed almost imperceptible differences in the wines classified, while $L^*a^*b^*$ values achieved a much better differentiation. L^* and a^* gave an accurate definition of the wines. L^* ranged from 37 to 72 while a^* varied between 23 and 54. One wine sample was clearly different from the others, showing the highest degree of lightness (L^*), the lowest redness (a^*) and the lowest saturation (C^*). The graphical representation of metric lightness difference (ΔL^*) against metric chroma difference (ΔC^*) showed the difference in colour between the wines analyzed. Wine number 1 showed the deepest colour followed by wines numbered 9 and 5, while wine number 7 was very pale. The data obtained were correlated by means of the corresponding matrix of Spearman correlation coefficients, which revealed that the highest correlations existed between L^* and colour intensity and between L^* and ionised anthocyanin content.

INTRODUCTION

The colour of red wines is one of the most obvious attributes of their quality, since it is the first characteristic to be noticed. In musts and young wines, the bright red-bluish colour is due to the anthocyanin monomers extracted from the grape skins that rapidly evolve through condensation with other flavonoid compounds.

Individual pigment analysis of different grape cultivars shows important qualitative and quantitative differences (Roggero *et al.*, 1986; Bakker *et al.*, 1986*a*; Hebrero *et al.*, 1988; González-San José *et al.*, 1990), and the colour of musts and wines obtained from them is, moreover, influenced by soil and weather conditions, and in particular by enological practices.

In the physico-chemical analysis of wine colour it is customary to use two different criteria. In the first criterion colour intensity and polymeric forms are evaluated, while the second criterion attempts objective definition of the colour of a wine. For the latter, several numerical expressions based on the tristimulus measurements of the CIE have been established, the most widely used at the present time being the *Yxy* system (O.I.V., 1978) and the CIELAB (C.I.E., 1986). This second system is uniform space of colour and non-lineal transformation of the *Yxy* system (Artigas *et al.*, 1985; Bakker *et al.*, 1993).

To identify and classify the wines elaborated in different wine-producing areas, several criteria have been employed: aromatic composition, acidic composition, anthocyanin composition, etc. In this paper we describe the chromatic characteristics of wines produced in the Region of Murcia (Spain), setting out their differences in colour and comparing their tristimulus *Yxy* and $L^* a^* b^*$ measurements.

MATERIALS AND METHODS

Samples

The 10 red wines used in this investigation were representative of the 1991 vintage in the Region of Murcia (south-east of Spain), and came from different wineries. All the wines were made on skins in the traditional fashion. Samples were taken when wines were 6 months old, prior to being bottled.

Analytical data

The colour measurements were made using a Hitachi U2000 spectrophotometer and glass cells of 2 mm path length. It is of fundamental importance to report the path length of the glass cell because the CIELAB values are directly related with it. The following analytical determinations were carried out on each sample:

—colour intensity [C.I.= $A_{420} + A_{520} + A_{620}$], colour tint [$A_{420}/A_{520}$] and percentage of yellow [100 × A_{420}/C.I.], red [100 × A_{520}/C.I.] and blue [100 × A_{620}/C.I.] pigments (Glories, 1984).

—total anthocyanins, ionised anthocyanins, total phenolic compounds and index of chemical age (Somers & Evans, 1977).

— Yxy coordinates (O.I.V., 1978).

—L^*, a^*, b^*, C^* and h^* values (CIE, 1986). To calculate these values the following expressions were used:

$$\begin{aligned}
L^* &= 116\,(Y/Y_n)^{1/3} - 16 && \text{for } Y/Y_n > 0{\cdot}008856\\
L^* &= 903{\cdot}3\,(Y/Y_n) && \text{for } Y/Y_n \leq 0{\cdot}008856\\
a^* &= 500\,[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}]\\
b^* &= 200\,[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}]\\
C^* &= [(a^*)^2 + (b^*)^2]^{1/2}\\
h^* &= \tan^{-1}(a^*/b^*)
\end{aligned}$$

where X_n, Y_n, Z_n are the values of X, Y, Z for illuminant C ($X_n = 98{\cdot}072$, $Y_n = 100{\cdot}00$, $Z_n = 118{\cdot}225$). If any of the ratios X/X_n, Y/Y_n, Z/Z_n is equal to or less than 0·008856 it is replaced by ($77{\cdot}878F + 16$), where F is X/X_n, Y/Y_n, Z/Z_n as the case may be.

Statistical analysis

All the statistical calculations were done using the Systat 4.1 (Systat Inc., USA) and the Instat (Graphpad Inc., USA) packages.

RESULTS AND DISCUSSION

The chromatic characteristics analyzed for each wine are shown in Table 1. In general, all the samples showed a high colour intensity (9·4 to 13·9), with the exception of sample number 7, which only reached 4·6. This can be attributed to the fact that all the samples were young wines in which the colouring matter had not been precipitated to any great extent. Moreover, the principal grape varieties grown in the south-east of Spain have a very high anthocyanin content (Fernández-López *et al.*, 1992). Red wines from other Spanish wine-producing areas usually show slightly lower colour intensities (Heredia & Guzmán, 1990).

The matrix of the Spearman correlation coefficients (Table 2) revealed, with much more accuracy, the relationships between the different colour parameters studied.

Colour intensity showed a high positive correlation (0·865) with the ionised anthocyanin content, while its correlation with total anthocyanin content was lower (0·755). This shows that the colour of young red wines presents a high dependence on the ionised forms of anthocyanins, a conclusion already reached in other investigations (Ribéreau-Gayon *et al.*, 1983; Somers & Evans, 1986).

The chemical age index (I) evaluates the percentage of polymeric pigments at wine pH. In our experiment this parameter generally showed high values (67–76%) although the wines were only 6 months old, indicating a high degree of condensation of the monomeric anthocyanin forms which are not influenced by an excess of SO_2.

The chemical age index (II) related the level of polymeric forms, which are resistant to discoloring by SO_2, with the level of monomers, which at pH < 1·0 move towards the flavylium ion form. Therefore, a low value for chemical age (II) would imply an important residual content of monomeric forms. All the wines analyzed showed chemical age (II) values in the order of 30% or lower.

Table 1. Chromatic data for young red wines analyzed

Wine	C.I.	Tint	Yellow (%)	Red (%)	Blue (%)	T. Ant. (mg/l)	I. Ant. (mg/l)	C.A.(I)	C.A.(II)	Phenol
1	13·9	0·71	35·9	50·9	13·2	256·0	70·4	56·8	22·4	73·2
2	9·4	0·75	37·2	49·4	13·3	170·5	51·3	60·0	23·0	41·0
3	10·1	0·73	36·9	50·5	12·6	233·0	51·3	56·0	20·0	40·8
4	9·4	0·88	41·0	46·4	12·6	100·2	25·0	76·0	33·0	50·1
5	13·5	0·72	36·7	51·6	11·6	233·0	63·4	60·0	24·0	48·7
6	11·4	0·65	34·1	52·6	12·8	176·0	44·0	71·0	28·0	44·1
7	4·6	0·80	40·5	46·9	12·3	58·1	16·4	68·0	30·0	30·2
8	12·9	0·76	36·9	49·9	13·2	225·0	65·4	54·5	23·5	57·2
9	13·5	0·75	36·0	49·1	14·9	210·8	65·4	60·0	26·5	63·2
10	12·8	0·77	35·9	49·9	14·2	210·0	55·4	66·8	33·4	65·2
Mean	11·1	0·75	37·1	49·8	13·1	177·2	50·8	62·9	26·4	51·4
SD	2·9	0·06	2·1	2·1	0·9	63·1	17·9	7·1	4·6	13·2
SEM	0·9	0·02	0·7	0·7	0·3	20·0	5·7	2·2	1·4	4·2

C.I.= colour intensity; Yellow = percentage of yellow pigments; Red = percentage of red pigments; Blue = percentage of blue pigments; T. Ant. = total anthocyanins; I. Ant = ionised anthocyanins; C. A.(I) = index of chemical age (I); C.A.(II) = index of chemical age (II); Phenol = total phenolic content.

Table 2. Correlation coefficients of the Spearman matrix with the chromatic parameters considered

	C.I.	Tint	Yellow	Red	Blue	T. Ant.	I. Ant	C.A.(I)	C.A.(II)	Phen.	*x*	*y*	*L**	*a**	*b**	*C**	*h**
C.I.	1·000																
Tint	−0·489	1·000															
Yellow	−0·632	0·697	1·000														
Red	0·483	−0·884	−0·740	1·000													
Blue	0·285	0·024	−0·390	−0·150	1·000												
T. Ant.	0·755	−0·628	−0·498	0·652	0·052	1·000											
I. Ant.	0·865	−0·398	−0·503	0·358	0·485	0·810	1·000										
C.A.(I)	−0·444	0·314	0·099	−0·302	−0·191	−0·763	−0·716	1·000									
C.A.(II)	−0·207	0·571	0·024	−0·395	0·018	−0·663	−0·457	0·816	1·000								
Phen.	0·677	−0·061	−0·518	0·103	0·585	0·450	0·750	−0·178	0·115	1·000							
x	0·875	−0·340	−0·657	0·389	0·312	0·674	0·732	−0·230	0·019	0·802	1·000						
y	0·525	−0·407	−0·409	0·407	0·409	0·524	0·525	−0·294	−0·290	0·522	0·557	1·000					
*L**	−0·957	0·553	0·695	−0·501	−0·309	−0·809	−0·939	0·522	0·321	−0·758	−0·853	−0·522	1·000				
*a**	0·994	−0·529	−0·634	0·535	0·256	0·772	0·866	−0·472	−0·248	0·636	0·853	0·522	−0·952	1·000			
*b**	0·671	−0·103	−0·128	0·122	−0·085	0·365	0·433	−0·006	0·103	0·527	0·627	0·522	−0·539	0·636	1·000		
*C**	0·994	−0·529	−0·634	0·535	0·256	0·772	0·866	−0·472	−0·248	0·636	0·853	0·522	−0·952	1·000	0·636	1·000	
*h**	0·098	0·334	0·409	−0·383	−0·433	−0·249	−0·110	0·362	0·370	0·042	0·019	−0·290	0·030	0·067	0·612	0·067	1·000

Abbreviations as in Table 1.

Table 3. Dominant wavelengths (λ_d) calculated by the graphical procedure of the CIE and by the mathematical expression of Heredia and Guzman (1992)

Wine number	CIE				Heredia
	x	*y*	Purity (%)	λ_d (nm)	λ_d (nm)
1	0·677	0·322	98	612	614·0
2	0·675	0·322	98	612	614·2
3	0·676	0·322	98	612	614·1
4	0·676	0·322	98	612	613·8
5	0·677	0·322	98	612	614·3
6	0·676	0·322	98	612	613·5
7	0·620	0·319	84	612	611·0
8	0·676	0·322	98	612	614·3
9	0·677	0·322	98	612	613·8
10	0·677	0·322	98	612	613·7

The correlation of the chemical age (I) and (II) indices with the colour intensity was very weak (−0·444 and −0·207, respectively), which suggests that there is no direct dependence between these two indices and the quantity of colour of a wine. This low correlation could be explained by the fact that they are calculated at 520 nm and are affected by the hipsochromic shift to 420 nm, which is characteristic of polymerization, while the colour intensity (addition of absorbances at 520 and 420 nm) is affected less.

Total phenolic content range from 30 to 73 absorbance units, it being noticeable that wines with the lowest phenolic content also showed the lowest level of ionised anthocyanins and the lowest colour intensity. These observations would suggest that these vinifications had evolved very quickly, developing polymeric forms of high molecular weight which would induce their precipitation. There is a highly positive correlation between phenolic content and ionised anthocyanins (0·750), which might confirm the above hypothesis, as well as suggesting how the wines will evolve.

High levels of phenolic compounds and monomeric anthocyanins indicate a low degree of condensation and precipitation of the colouring matter and, indeed, samples with these characteristics (wines number 1, 5, 9, 8 and 10) showed the highest colour intensities and the highest absorbances at 520 nm (8·2, 7·8, 7·3, 8·1 and 7·4, respectively).

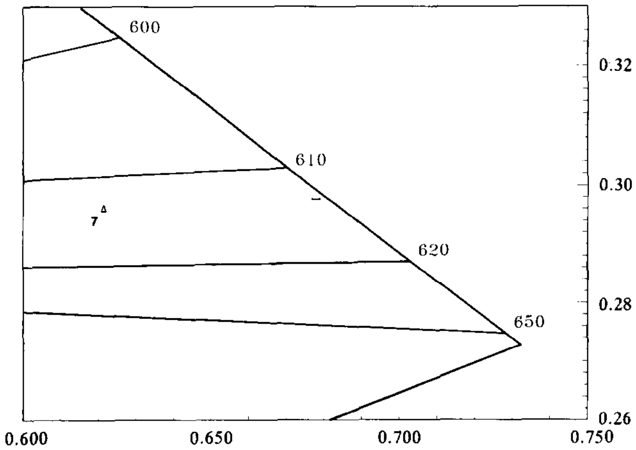

Fig. 1. Representation of dominant wavelengths in the C.I.E. (x,y) chromatic diagram.

Characterization of the colour of the wines was carried out initially by using the coordinates system *Yxy* of the C.I.E., recommended by the O.I.V. The calculation of the dominant wavelength (λ_d) defined by the CIE 1931 (x,y) was performed by the graphical procedure and by using the polynomic quotient expression proposed by Heredia and Guzmán (1992), which optimizes the results obtained with the polynomic equation of Piracci and Spera (1986). Table 3 presents the values of λ_d obtained by both methods. It can be seen that λ_d obtained by the general graphical procedure was 612 nm in all the wines, with a purity of 98%, with the exception of wine number 7 whose purity was 84%. λ_d values calculated by using the mathematical expression of Heredia and Guzmán were slightly different, although these differences were almost imperceptible in the chromaticity diagram of the CIE (Fig. 1).

Chromaticity diagrams show only proportions of tristimulus values, not their magnitudes, and are only strictly applicable to colours having the same luminance (Y) (Hunt, 1987). Hence the need for uniform colour spaces as CIELAB. It is impossible to distinguish, in a bidimensional space, where the luminance differs, as is the case with wine.

For a better characterization of the colour of each sample the CIELAB system was used. L^*, a^* and b^* were calculated using illuminant C as reference. The L^* value is a measure of lightness, from completely opaque (0) to completely transparent (100); a^* is a measure of redness ($-a^*$ greenness) and b^* of yellowness ($-b^*$ blueness). Changes in chroma (C^*) in red wine reflect a bias towards the dominant colour component (a^* or b^*) (Bakker *et al.*, 1986*b*). Hue angle (h^*) is defined as starting as the $+a^*$ axis and is expressed in degrees; 0° would be $+a^*$ (red), 90° would be $+b^*$ (yellow), 180° would be $-a^*$ (green), and 270° would be $-b^*$ (blue).

Wine number 7 reached the highest L^* (Fig. 2), with a very significant difference with respect to the other wines, while wine number 1 was the darkest. When the colour values were compared with the visual appreciation of a panel of expert assessors, in the wine samples

1, 2, 3, 5, 6, 8, 9 and 10 where the a^* value was higher than b^*, a strong predominance of a vivid red colour was noted. Chroma values near or higher than 50 would show the prevalence of vivid colours. Wine number 4 showed a dull colour ($a^* = 37{\cdot}9$), while wine number 7 showed a grayish/weak look.

Figure 2 shows the cartesian diagrams obtained for a^* vs L^*, b^* vs L^* and a^* vs b^*. The diagrams b^* vs L^* and a^* vs b^* emphasise the fact that there was no close relation between the b^* value and the other two. The evident dispersion is attributed to the variability of the b^* value (blueness–yellowness). Otherwise, the plot of a^* against L^* shows that there was a linear relation between them with a P value $< 0{\cdot}0001$.

Therefore, a^* and L^* values gave an accurate definition of the colour characteristics of the young red wines analyzed. A similar study performed with white wines allowed an analogous relationship between the b^* and L^* values (Chiralt *et al.*, 1987) to be established.

Figure 3 shows the Cartesian diagrams obtained for C^* vs L^*, C^* vs h^* and h^* vs L^*. The diagram C^* vs L^* reveals that there was a linear relation between them with a linear correlation coefficient $r = 0{\cdot}9863$.

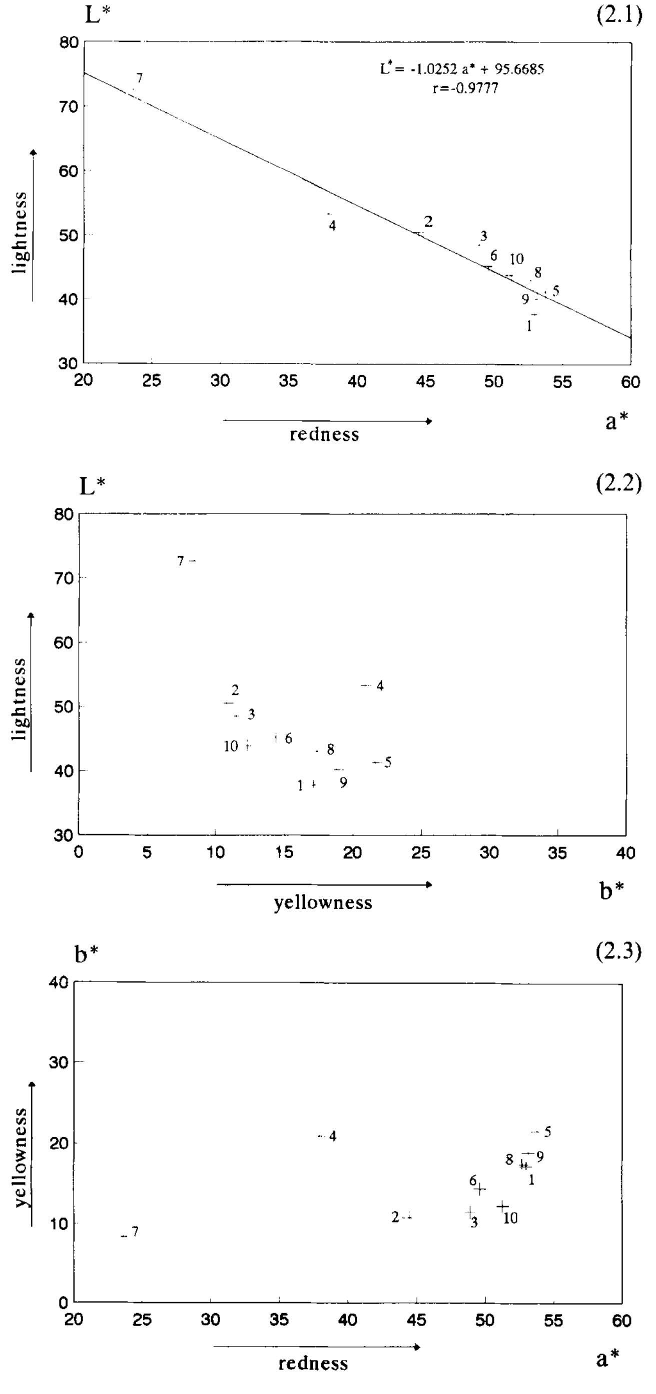

Fig. 2. Relations between a^* and L^* (2.1), b^* and L^* (2.2) and a^* and b^* (2.3) of young red wines analyzed.

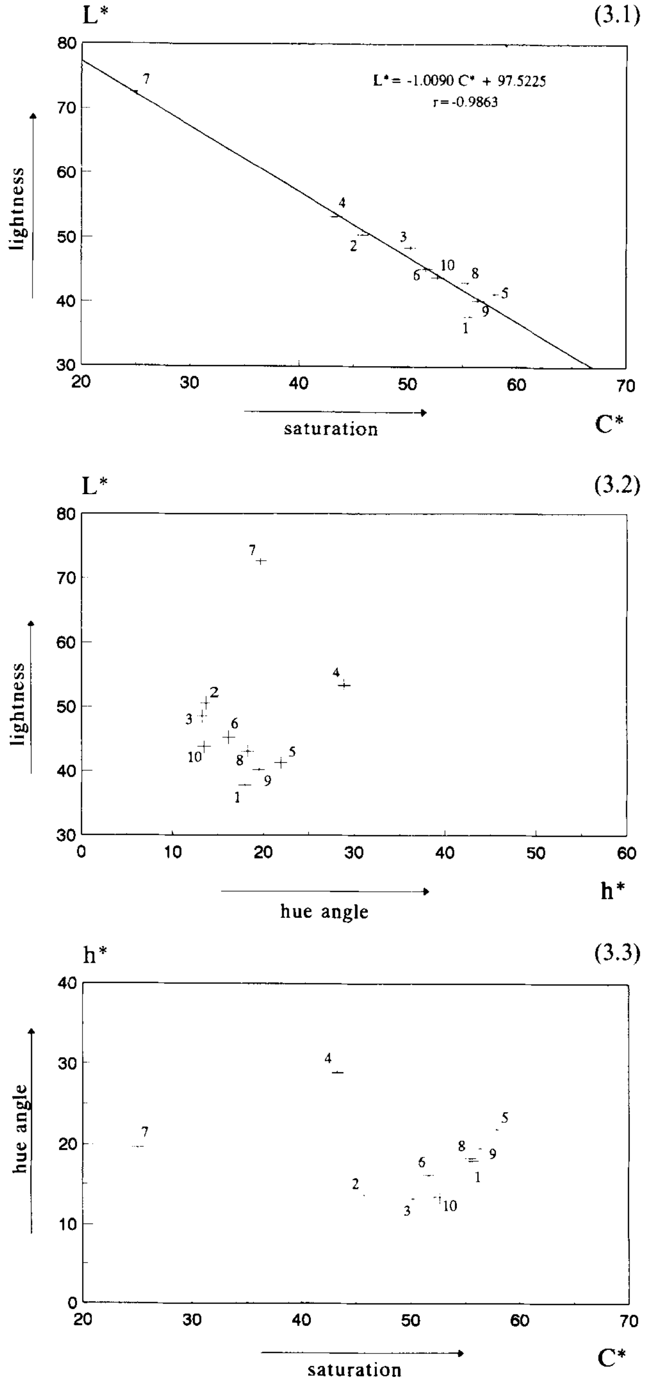

Fig. 3. Relations between C^* and L^* (3.1), h^* and L^* (3.2) and C^* and h^* (3.3) of the wines analyzed.

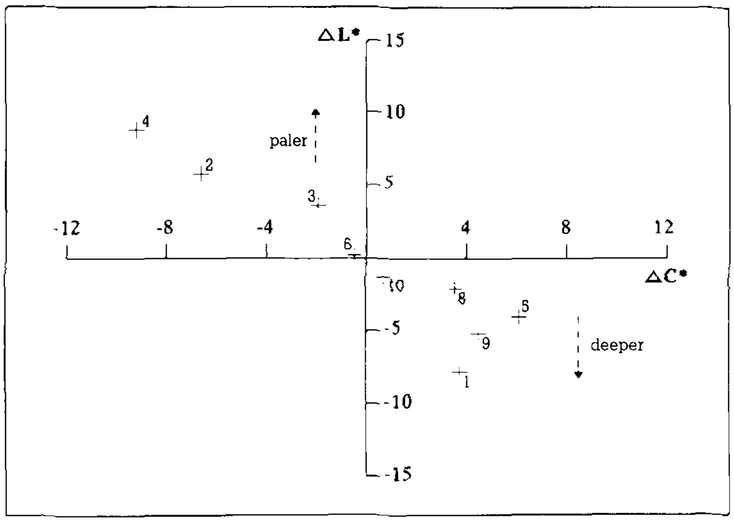

Fig. 4. Plot of metric lightness difference (ΔL^*) vs metric chroma difference (ΔC^*) for differentiating the wine samples considered.

There were high correlations between the CIELAB values and some of the chromatic parameters recommended by the O.I.V. Colour intensity showed a very high correlation with L^* (−0·957), a^* (0·994) and C (0·994) (Table 2). A negative correlation with L^* would indicate that an increase in colour intensity leads to a darker colour in the wine (lower L^*); the positive correlations with a^* and C indicate that an increase in colour intensity corresponds with very saturated reddish colours. With respect to the *Yxy* system, it can be seen that there was a quite high positive correlation between colour intensity and x, suggesting a displacement towards pure reddish tints in the C.I.E. chromatic diagram.

L^* showed a good correlation with ionised anthocyanins (−0·939), while the correlations with total anthocyanins and phenolic content were a bit lower (−0·809 and −0·758, respectively). a^* and C^* also showed high correlations with total and ionised anthocyanins.

To differentiate the colour of the samples analyzed more precisely, we calculated the colour difference values, ΔL^* (metric lightness differences), ΔC^* (metric chroma difference) and ΔE (total colour difference), defined as:

$$\Delta L^* = L^*_i - L^*_o$$
$$\Delta C^* = C^*_i - C^*_o = [(a^*_i)^2 + (b^*_i)^2]^{1/2} - [(a^*_o)^2 + (b^*_o)^2]^{1/2}$$
$$\Delta E = [(L^*_i - L^*_o)^2 + (a^*_i - a^*_o)^2 + (b^*_i - b^*_o)^2]^{1/2}$$

Table 4. Colour difference values of the wines analyzed

Wine	ΔL^*	ΔC^*	ΔE
1	−7·10	3·71	8·01
2	5·63	−6·20	9·16
3	3·62	−1·72	5·87
4	8·47	−8·66	15·08
5	−3·57	5·98	7·88
6	0·37	−0·31	1·78
7	27·7	−26·89	38·63
8	−1·77	3·50	3·92
9	−4·66	4·42	8·86
10	−1·00	0·76	4·34

where L^*_o, a^*_o and b^*_o are the values of the target colour and L^*_i, a^*_i and b^*_i the measured values of the specimen. As target colour we chose the mean value of all the wines analyzed, excluding sample number 7 which showed markedly different chromatic characteristics from those of the young red wines of this area. Table 4 presents these colour difference values.

The plot of ΔL^* against ΔC^* (Fig. 4) revealed the colour differences of the wines studied. With this representation the CIELAB parameters can be reduced to a two dimensional colour space. It can be seen that samples 1, 9, 5 and 8 showed a deeper colour than the wine of reference, while samples 4, 2 and 3 were paler than the mean. Wine number 7 presented an extremely pale colour and it is out of range.

CONCLUSIONS

The ionised anthocyanin content and, to a lesser extent, the total anthocyanin content are a good measure of the colour intensity of 'quantity of colour' of a wine. As an objective evaluation of wine colour, the *Yxy* system did not differentiate sufficiently between similar colours, while the CIELAB parameters showed much more accuracy. In the young red wines analyzed, the L^* and a^* values permitted the precise differentiation of their colour. The representation of ΔL^* against ΔC^* revealed the colour differences between the different wines.

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